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### **Contributors**

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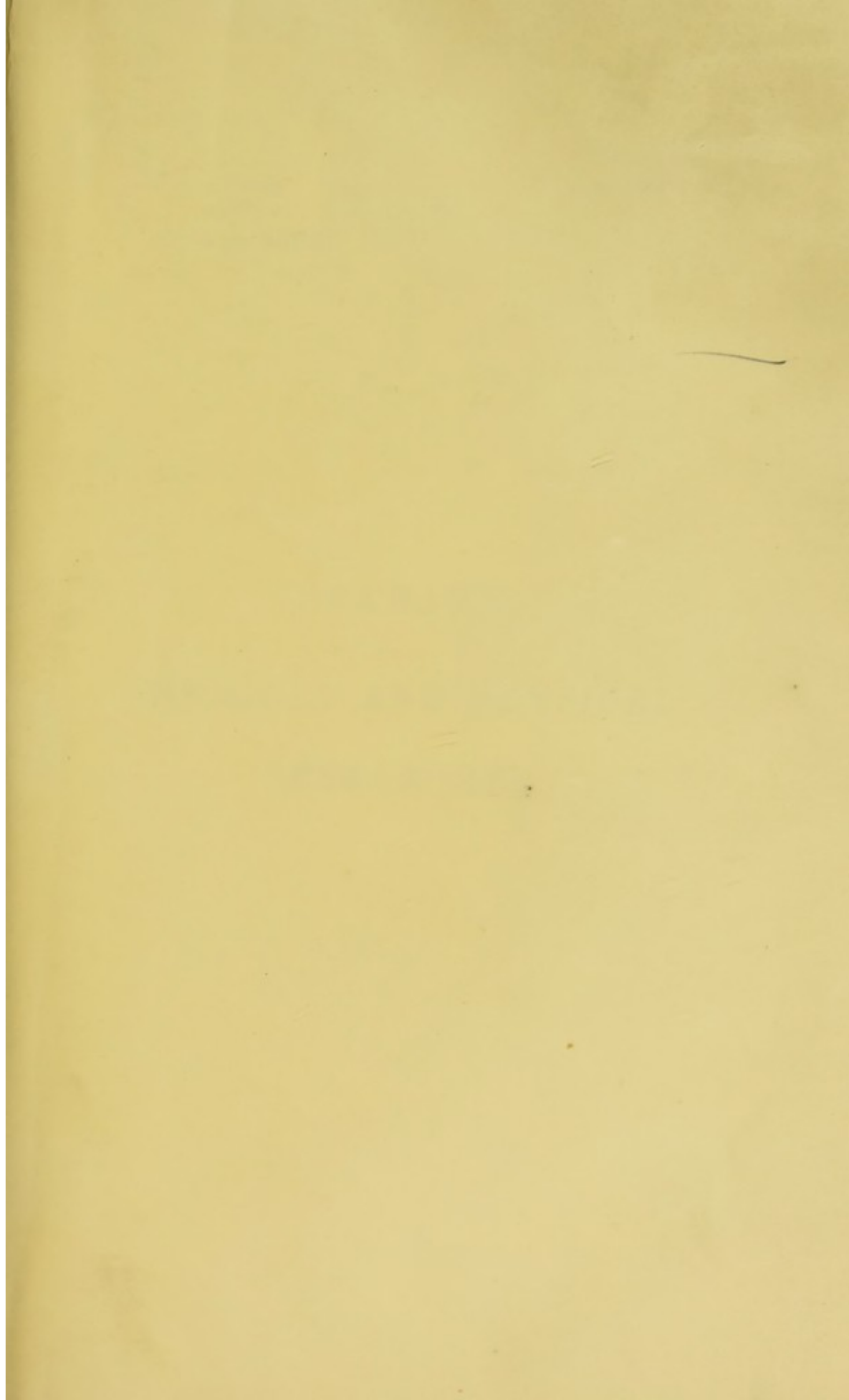




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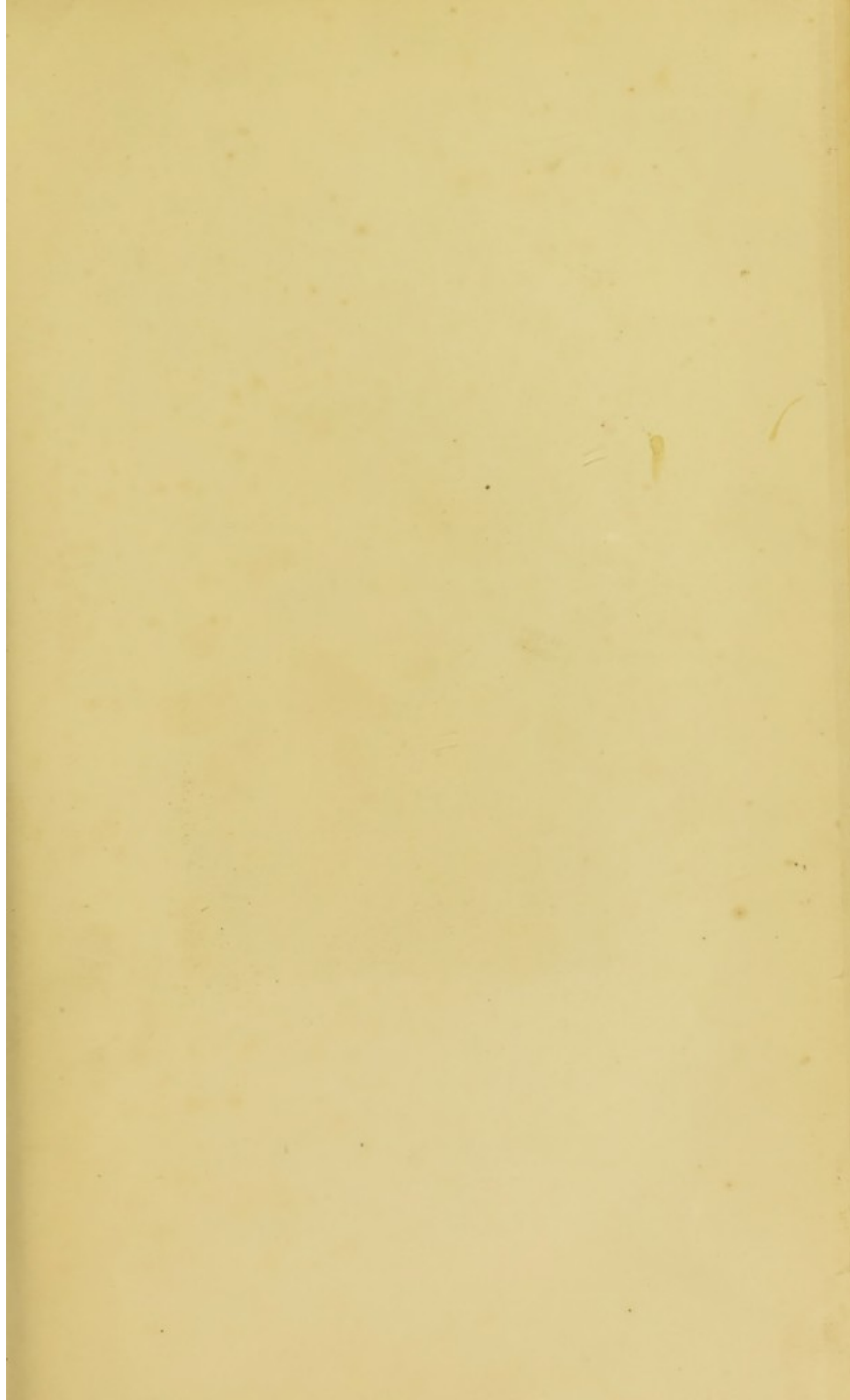
*From*

*James Young*  
*and*  
*R. Angus Smith* } *F.R.S., &c.*

*DAVID STEWART,*  
WOODSIDE,  
WEMYSS BAY, N.B.

GRAHAM'S  
CHEMICAL AND PHYSICAL  
RESEARCHES.







Ever truly Yours  
Thos. Graham



CHEMICAL  
AND  
PHYSICAL RESEARCHES

BY  
THOMAS GRAHAM,

D.C.L., F.R.S.,

CORRESPONDING MEMBER OF THE INSTITUTE OF FRANCE, ETC. ETC.

*COLLECTED AND PRINTED FOR PRESENTATION ONLY.*

PREFACE AND ANALYTICAL CONTENTS

BY  
DR. R. ANGUS SMITH.

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## PREFACE.



### GRAHAM AND OTHER ATOMISTS.

ATOMS and eternal motion are amongst the first known scientific ideas. We find them discussed with full keenness of insight by the earliest Greeks of whom we have received definite accounts. If the opinions did not spring from Hellenic soil they certainly found themselves in a land well fitted for their development; but so many of the thoughts of men have come from the East that it is natural to suppose that both had their origin there. India has had several atomic systems and acute discussions on atoms and matter. I shall leave it to others to decide at what time the earliest known were written, but it is at least clear that the subject was thought out in a peculiar method, with occasional logic of the keenest known, moving forward into regions where reasoning is difficult and mysticism reigns. There we may find thoughts, the same apparently as led to the centres of force of Boscovich and original fluid or universal ether, as well as the various atoms of the Greeks, or the clearest ideas of moderns, too clear at times to be sufficiently comprehensive. It is said that Leucippus obtained his opinions from a Phœnician called Moschus (and Mochus), and it is pleasant to think of this earlier name of an atomist to whom it seems unnatural to deny existence, even if he be little known. And although Zeller<sup>1</sup> tells us that the roots of the ideas lay in the earlier Greek mode of thought, this scarcely is sufficient for separating the

<sup>1</sup> In *Die Philosophie der Griechen*, p. 688.



East and the West, since tradition in very remote times led to the belief in frequent and interesting communication. Such names are not forged, and when characters are invented we find them rarely to be men of science. Still, the accounts are vague, and Indian literature waits arrangement. Although Kapila as a philosopher is almost lost as a personality, his system<sup>1</sup> shows a long train of successfully cultivated thought. How and when did Cánáde's notion arise that an atom was the sixth part of a mote in a sunbeam? If, however, we turn to the second idea, namely, "eternal motion," we must claim for it decidedly an Eastern origin, and perhaps it is still to be found among the remnants where Chaldæans or Accadians may have recorded their thoughts, when their astronomers and astrologers sought wisdom out of the heavens. Science seems to have begun amongst the heavenly bodies, and even amongst the Greeks Anaximander brought forward his mystic idea of the immeasurable, before the smaller movements in matter were considered. To follow a late writer,<sup>2</sup> even the idea of eternal motion, as held by that early Greek speculator, referred only to the motion of the stars and the unceasing changes of the sun and moon. When Leucippus gave his mind to the study of atoms he saw there also the need of movement, and the restlessness of all creation in detail was thus early expressed by him. It was the result of a process of reasoning, begun by observing objects that strike all men unceasingly, and ending amongst those too small to be visible; it began with what to us is infinitely great, and ended with what to our senses is infinitely small. Leucippus seems to have concluded, as so many thinkers have since done, that arguments concerning the infinite divisibility of matter must end in empty words, or in thoughts of awe regarding the unlimited, which

<sup>1</sup> Colebrooke's *Essays on the Religion and Philosophy of the Hindus*.

<sup>2</sup> Gustav Teichmüller, *Studien der Geschichte der Begriffe*. Berlin, 1874.



we cannot comprehend. To assume an actual end of division was to take a basis of thought; without such a foundation where would he stand to observe the building up of the world? The assumption, if it be one, formed the atom of science, and its study, although without a distinct advance for ages, has richly rewarded the student of the present century, giving us the basis of a rational view of matter, as the atoms are the basis of the matter itself. In the mind of this early Greek, first or not, the action of the atom, as one substance taking various forms by combinations unlimited, was enough to account for all the phenomena of the world. By separation and union, with constant motion, all things could be done.

These great thoughts, the oneness of matter and the power of motion and combination, were given to gifted men of the early days, and, like some other great thoughts, they have been misunderstood or neglected to a very late time. It is because Graham took a similar view, and advanced the idea of atomic motion with unity of material to that which might be fairly called its utmost limit, that he is brought forward here with Leucippus. The Greek told us that all was in motion. Graham conceived the idea that the diversity in the motion was the only basis of the diversity of the material, or, in other words, that an atom constituted an element of a special kind, according to rate or peculiarity of its movements. To the study of the motion of atoms, or at least of molecules, the practical atom of our chemistry, or that which although in a sense divisible is not known to be divided, Graham gave all the leisure of a thoughtful life. When he came to the subject it had advanced far beyond the early stage, notably by the thoughts of Dalton and the chemists of the earlier part of this century. To pass over more than two thousand years in a bound is apparently to forget the effect these thoughts had on mankind; but it cannot be denied that no important results followed for the human race, and only a few men seemed seri-



ously to think on the subject until very modern times. A glance at a few of the more striking halting-places will help us to see better the relative position of Graham as an atomist and a philosopher, words which suit his character better than chemist, although chemistry was his profession and the source of all his speculations and reasoning.

Leucippus was soon almost forgotten, until a time came when men gladly treasured the little that was remembered of him ; but his successor was better known, and Democritus has obtained much of the honour of the acute thoughts that taught us atomic motion. It is said that Xerxes himself stayed, when at Abdera, with the father of Democritus, who was very wealthy, and that the magi in the great king's train taught the theory of atoms to the young man. It may be true, for the East ever appears at the beginning of things, and the fresh minds caught up the richest crops as they showed themselves on the face of the creation, expanding before men's eyes. A few words, quoted from Lange,<sup>1</sup> give the position of Democritus so far as we are here concerned :—

“ The difference of substances arises from the difference in the number, size, shape, and arrangement of the atoms. The atoms have no internal conditions ; they act by pressure and percussion only.”

These words express the early theory with great beauty and precision. We do not say here with Aristotle, “ Matter cannot move itself,” and so inquire further into the subject ; for us it is enough to remember the physical theory. So far as is apparent, Democritus left the pure physical theory of oneness of atom, and he makes many varieties, so that at last it is said that “ the soul consists of round atoms, fine and smooth like those of fire, and by their motion, which penetrates the whole body, the whole phenomena of life are produced.” But although this theory leaves the oneness of atoms, it keeps

<sup>1</sup> F. A. Lange, *Geschichte des materialismus*. 1873.



closely to the idea of motion as the only one phenomenon conceivable for matter or mind, and it is without much doubt the origin of the saying that life is motion, the great thought of Heraclitus. All life consists of this constant moving, nothing is but as a movement. If we care to view the subject very strictly, we may say that the simplicity of the atom is gone even at this early stage; but if the simplicity of the atom is gone, the age of the molecule commences, a body composed of bodies not to be separated; and although the atom of Democritus is spoken of as one in quality, its diversity of size gives it a composite character, and one might even choose to find in him the germ of an opposition to the theory showing itself during the very building.<sup>1</sup> The peculiar soul-atoms<sup>2</sup> destroy even the supposed qualitative uniformity of atoms; but Leucippus is said to have had the same opinion. At best this early atom is a practical one, like that of Newton's, not an intelligible one, an idea that has still to be imagined in a reasonable manner. This difficulty produces the non-atomists, but the atomist may see it quite as clearly, and leave the reasoning for a stage, since he cannot proceed with any firmness of step. A consistent atomist of the Dalton type may be a thorough non-atomist when he breaks up in his mind the present elements.

We do not find that anything fitting our present purpose was added to the theory of atoms until the time of Lucretius, if indeed he can be said to have added anything. He, however, as the only full expositor of the doctrine among the ancients, must be viewed with attention. As a philosophic poet, Lucretius is interesting, it ought rather to be said interesting for the time in which he lived, but he contradicts himself more than the early Greeks in his theories, and his explanations, that are so satisfactory to himself, seem to many men to explain little. Nevertheless he deserves a full share of honour.

<sup>1</sup> Zeller, vol. i. 699; Aristotle quoted in the note.

<sup>2</sup> P. 729.



If it is attempted to give by quotations from Lucretius a good idea of his system, we get rather into confusion. The reason probably is, that he had not thought out the details clearly in his own mind, and indeed every man who has attempted consistency in this department has failed; but it may be said that his atoms are solid and eternal, with some unalterable motion, and a tendency downwards as well as to the side, easily agitated also by many forces. They are made of parts, which parts cannot exist by themselves, the atoms are partly like our molecules, but the parts seem hypothetical existences, conceived apparently in order to bridge over the distance between nothing and something, a difficulty frequently attempted by those who reason outside the atomic idea. Motion is to him everything that can be found in life and thought, which are only the clashing of atoms, light or heavy, round or smooth, made by more or fewer of the combinations of small points that do not exist by themselves. This theory allows of any shape of molecules, even hooked ones, which are spoken of as explaining combination both in Lucretius and more modern writers, and to which the name of atom is applicable only with suitable explanation.

In reality, Lucretius sometimes loses the clear meaning of the atom he admires; as he loses also and objects to the idea of centres in the universe, preferring up and down as fundamental ideas. After the first great thoughts are uttered, the rudest ideas come into play, and the carpenter and hammer seem to be set to do the whole work as was done by his predecessors, and which his successors continue to admire.

The alchemists got rid of this, but lost also the idea of atoms. They retained, however, the one fundamental matter of which they were composed; with a loss of clearness they gained in breadth. Roger Bacon, so much superior to the most, may be looked on as an ideal one. He says logically:



“The elements are made of *ylé*.<sup>1</sup> Barley is a horse by possibility, that is occult nature, and wheat is a possible man, and man is possible wheat.”—*De Arte Chymicæ*.

If, however, we come to the atom which has done most good work in modern chemistry, we are after all obliged to turn back to one of the descriptions of it by Lucretius in one of his best moments, and after it has been modified by the powerful hand of Newton, and freed from connecting obscurities. Lucretius says, book i. line 603, “Primordial bodies are solid in their simplicity, and consist of the smallest parts closely united, not combined by a union of others, but rather endowed with eternal simplicity: from them nature allows nothing to be taken away or to be diminished, reserving them as seeds for bodies.”<sup>2</sup>

Newton’s well-known words may be quoted, since they form an era in the theory of atoms, not so much by new ideas as by distinctness, and the elimination of much confusion:—  
“It seems probable to me that God in the beginning framed matter in solid, massy, hard, impenetrable, moveable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced to the end for which He formed them; and that these primitive particles being solid, are incomparably harder than any porous bodies compounded of them; even so very hard as never to wear or break in pieces; no ordinary power being able to divide what God himself made one in the first creation. While these particles continue entire, they may compose bodies of one and the same texture in all ages; but should they wear away, or break in pieces, the nature of things depending on them would

<sup>1</sup> Or the one original matter.

<sup>2</sup> “Sunt igitur Solida Primordia simplicitate,  
Quæ minimis stipata coherent partibus arcte;  
Non ex ullorum conventu conciliata,  
Sed magis æterna pollentia Simplicitate:  
Unde neque avelli quicquam, neque diminui jam  
Concedit natura, reservans semina rebus.”



be changed. Water and earth composed of old worn particles would not be of the same nature and texture now with water and earth composed of entire particles in the beginning. And, therefore, that nature may be lasting, the changes of corporeal things are to be placed only in the various separations and new associations and motions of these permanent particles; compound bodies being apt to break, not in the midst of solid particles, but where those particles are laid together, and only touch on a few points."

Here, then, is the real atom of the chemist—explaining a mode of combination which Bergman, Wenzel, and Richter laboriously tried to understand, which Higgins reached but did not see with vigour—the atom with which Dalton made his fertile discovery—the atom which has built up the modern science of chemistry, and from which our most precise ideas of the constitution of matter have been acquired, one which must remain probably without fundamental alteration until a new mode of analysis is found, and one which probably is in principle true even at stages considerably below that which contains our unaltered elements. This atom, however, is by no means of necessity indivisible in every sense; it is only indivisible by us, although some chemists may have different views. It may be in a strict sense a molecule, but it is much better to keep that word for a combination of atoms of known bodies rather than of hypothetical existences, a double atom of hydrogen or other element being our simplest molecule.

When we arrive at this point we pass to the next important stage, namely, the motion of gaseous molecules, if not of atoms, and the beginning of the attempt to define it precisely. The first definite ideas are by D. Bernoulli. They are explained in his *Hydrodynamics*,<sup>1</sup> which, although published in Strasburg

<sup>1</sup> Danielis Bernoulli, Joh. Fil., Med. Prof. Basil. *Hydrodynamica, sive de viribus et motibus fluidorum Commentarii* (Argentorati, 1738), p. 200. Sectio decima:—

"Fluida nunc elastica consideraturis licebit nobis talem iis affingere constitutionem,



in 1738, were previously worked at when he was Professor in St. Petersburg.

D. Bernoulli says,—“The chief peculiarities of fluids are these: 1st, they are heavy; 2d, they expand in all directions unless they are confined; and 3d, they allow themselves to be compressed more and more, according to the increased force applied.”<sup>1</sup> Speaking of a vessel of air with a weighted cover, and which he illustrates with a diagram, he says, “So the minute bodies, whilst they impinge on the cover EF, keep it up by their continually repeated strokes, and form an elastic fluid, which expands itself when the weight is removed or diminished.”<sup>2</sup> “We shall consider the corpuscles enclosed in the hollow of the cylinder as infinite in number, and when they occupy the space ECDF we shall say that they constitute the natural air.”<sup>3</sup>

Davy and Count Rumford entered the field when this theory of gaseous motion was forgotten, and inaugurated a new theory of heat founded on molecular activity. That heat is immaterial was no rare opinion last century, or since Lord Bacon spoke of it as *motus et nihil aliud*. However, atomic motion ceased from the time of Rumford to be a vague idea. Davy<sup>4</sup> spoke definitely when, without calling in the aid of forces, he supposed that in solids the particles are in a vibratory motion, the particles of the hottest bodies moving with greatest velocity and through the greatest space; that in

quæ cum omnibus adhuc cognitis conveniat affectionibus, ut sic ad reliquas etiam nondum satis exploratas detur aditus.”

<sup>1</sup> “Fluidorum autem elasticorum præcipuæ affectiones in eo positæ sunt: 1°, ut sint gravia; 2°, ut se in omnes plagas explicent, nisi contineantur, et 3°, ut se continue magis magisque comprimantur crescentibus potentiis compressionis: ita comparatus est aër, ad quem potissimum presentes nostræ pertinent cogitationes.”

<sup>2</sup> “—— Sic corpuscula dum impingunt in operculum EF idemque suis sustinent impetibus continue repetitis fluidum componunt elasticum quod remoto aut diminuto pondere P sese expandit ——”

<sup>3</sup> “Corpuscula cavitati cylindri inclusa considerabimus tanquam numero infinita, et cum spatium ECDF occupant, tunc aërem illa dicemus formare naturalem.”

<sup>4</sup> *Collected Works*, vol. iv. p. 67.



fluids and elastic fluids, besides the vibratory motion, which must be considered greatest in the last, the particles have a motion round their own axes with different velocities, the particles of elastic fluids moving with the greatest quickness; and that in ethereal substances the particles move round their own axes and separate from each other, penetrating in right lines through space. Temperature may be conceived to depend on the velocity of the vibrations, increase of capacity on the motion being performed in greater space, etc.

This is evidently the work of Rumford and Bernoulli, with additions after passing later through an original and powerful mind.

We may take the next step to Herapath.<sup>1</sup> At p. 15, vol. i., he says:—

*“Theory of Gases.*—From these considerations it follows that if a number of small bodies be inclosed in any hollow body, and be continually impinging on one another, and on the sides of the inclosing body; and if the motions of the bodies be conserved by an equivalent action in the sides of the containing body, then will these small bodies compose a medium, whose elastic force will be like that of air and other gaseous bodies; for if the bodies be exceedingly small, the medium might, like any aeriform body, be compressed into a very small space; and yet if it had no other tendency than what would arise from the internal collision of its atoms, it would, if left to itself, extend to the occupation of a space of almost indefinite greatness. And its temperature remaining the same, its elasticity would also be greater when occupying a less, and less when occupying a greater space; for in a compressed state the number of atoms striking against a given portion of the containing vessel must be augmented, and the space in which the atoms have to move being less, their

<sup>1</sup> *Mathematical Physics, etc.*, by John Herapath. 2 vols. 8vo, 1847.



motions or periods must be shorter, and the number of them in a given time consequently greater; on both of which accounts the elasticity is greater the greater the compression. Besides, when other things are the same, the elastic force augments with an augmentation of temperature and diminishes with a diminution; for an increase of temperature, according to our theory, must necessarily be attended with an increase of velocity, and therefore with an increase in the number of collisions."

Joule took up the subject immediately after Herapath, and says: "Since the hypothesis of Herapath, in which it is assumed that the particles of a gas are constantly flying about in every direction with great velocity, the pressure of the gas being owing to the impact of the particles against any surface presented to them, is somewhat simpler, I shall employ it in the following remarks on the constitution of elastic fluids," etc.<sup>1</sup> Dr. Joule continued the subject, and introduced it into the region of experiment and observation, or, in other words, to the science of modern times.<sup>2</sup> Joule might have added that the view he adopted is not only in accordance with the known laws of the elasticity of gases, but conforms to the ratio of the specific heats of gases. The mathematical development continued to make progress in the hands of Clausius, Clerk Maxwell, Holtzmann, and others, taking us to new fields, and outside the region of Graham's activity.

Graham is as strict an atomist as perhaps can be found. We have seen how difficult it has been to hold the doctrine pure, how even Democritus looked on the atoms as containing parts, and to get rid of the difficulty, Lucretius makes the parts incapable of existence *per se*,—thus introducing the inconceivable; even, with Newton, and decidedly with

<sup>1</sup> *Memoirs of Lit. and Phil. Soc. of Manchester*, vol. iv. 1851, p. 111. Read in 1848.

<sup>2</sup> See *Math. Physics*, vol. i. p. 264.



Dalton, hitherto the greatest of atomists, because his system has had the most substantial results, the atoms are either compounded of matter, besides many properties which for want of a better name we might call metaphysical, or are surrounded with forces which act very independently, and attach themselves to the atoms doing apparently most of the work.

It was a true movement in the direction of atomism, when Davy gave his ideas; and one may almost say that it was the object of Graham's life to find what the movement of an atom was. Davy does not define his vibratory motion, which could scarcely be imagined in an unconfined space unless the body had parts; for fluids he gives a motion of rotation making thereby a definite boundary; but we do not see in his opinions what an atom, say of iron, would do when alone. He would probably in such a case give it the same revolving motion as he gives the parts of gas. Graham avoids picturing the most primitive motion in all its character, but he seems to indicate one of revolution as he brings in the similarity to the orbit of a planet, and in this way with Davy connects in an interesting manner the very first speculations on the eternal motion of the heavens with those movements the smallest conceivable of atoms.

He has, however, advanced further, when he adopts the theory of one kind of matter, each atom being distinguished by the extent of its motion, one primordial impulse for each kind. This movement is an unalterable one, unaffected even by heat. These atoms do not come to us free, but are believed to be congregate, forming the compound atom or molecule, whose movements have of late been more carefully studied, and which form, in fact, the elements as the chemist finds them. And then, in his cautious manner, he adds that they have a singular relation connected with equality of volume. Equal volumes can coalesce and form a new atomic



group, retaining the whole or the half, or some simple proportion, of the original movement and consequent volume. This is chemical combination.

It is therefore clear that Graham was a true descendant of the early Greeks, his mind altered, of course, by intervening thinkers ; but in one point he differs from most, if not all, known to us, in that he devoted his whole life to the study of this subject.

In all his work we find him steadily thinking on the ultimate composition of bodies ; he searches after it in following the molecules of gases when diffusing ; these he watches as they flow into a vacuum or into other gases, and observes carefully as they pass through tubes, noting the effect of weight and of composition upon them in transpiration. He follows them as they enter into liquids and pass out, and as they are absorbed or dissolved by colloid bodies, such as caoutchouc, he attentively inquires if they are absorbed by metals in a similar manner, and finds the remotest analogies, which, by their boldness, compel one to stop reading and to think if they be really possible. He follows gases at last into metallic combination, and the lightest of them all he makes into a compound with one of the heavier metals, chasing it finally through various lurking-places until he brings it into an alloy and the form of a medal, and puts upon it the stamp of the Mint. Indeed, he is scarcely satisfied even with this, and he finds in bodies from stellar spaces—in meteoric iron—this same metallic hydrogenium, which he draws out from its long prison in the form of a gas.

It was a wonderful, and one may say romantic, ending to a series of inquiries, to the eyes of most men the most uninteresting. His works are full of care, but not of joy. He slowly collected figure after figure, never idle with his theories, but never venturing without a reason.



If we examine his work on Salts and on Solutions we have a similar train of thought. One might have slighted the importance which he attached to the water of salts and the temperature at which it was reduced, but in his hands it was a revelation of some of the most mysterious internal phenomena of these bodies. Although the inquiry was made without reference to the new position which hydrogen takes in acids, it was entirely on a track of preliminary necessary thought; the modern view he received favourably at an early period in his system of chemistry. Other advanced ideas were stimulated by him in the 1st vol. of the publications of the Cavendish Society,—a Society established mainly by his influence.

A chemist must take great pleasure in following Graham when he seeks the laws of the diffusion of liquids, and traces their connections, especially when they lead to such results as he has expressed by dialysis, a process founded on a new classification of substances, and promising still the most valuable truths. We see in the inquiry how carefully Graham thought on the internal constitution of bodies, by examining the motion of the parts, and from the most unpromising and hopeless masses under the chemist's hands—amorphous precipitates of alumina or of albumen—brought out analogies which connected them with the most interesting phenomena of organic life. Never has a less brilliant-looking series of experiments been made by a chemist, whilst few have been so brilliant in their results or promise more to the inquirer who follows into the wide region opened.

It is easy to see that, however various the subject on the surface of his writings, Graham's inquiries all led to one end, namely, the condition and motion of the molecule or atom. In using the word *atom* chemists seem to think that they bind themselves to a theory of indivisibility. This is a mistake. The word atom means *that which is not divided*, as easily



as it may mean *that which cannot be divided*, and indeed the former is the preferable meaning. Even when Lucretius speaks of primordial bodies that cannot be divided, he does not deny that they have parts, although these, as we have seen, cannot exist by themselves, and Graham, as well as other atomists, give a similar opinion, that is, that the original atom may be far down. Graham speaks of this in more than one place. There comes to us a something indivisible by us, and it is consistent to call it an atom, as it is consistent to call the smallest particle of alum, with its twenty-four equivalents of water, an atom, simply because it is the smallest possible portion of alum, which to divide would be to destroy.

Some have preferred to leave the atom without believing in infinite divisibility, and it is strange that when we come to the point of deciding on the existence of atoms the mind insists on going further and finding of what the atom is composed. By doing this the atomist often ends by being a non-atomist, and probably this is the necessary double conclusion: we believe in atoms because Nature seems to use them, and we break them up continuously because we know not when to stop. There are various methods of spanning the distance from nothing to something. Boscovich, by his centre of force, forms an atom, but it differs in nowise from Newton's but in name. Newton and Dalton, and all others, would allow all the forces that Boscovich can desire. Sir W. Thomson has made a vortex atom in the perfect fluid described by Helmholtz, and some such fluid is much required for the explanation of many phenomena.

In 1868 Graham acknowledged the possibility of the vortex atom when he said, "We may imagine the same result from atoms and from a fluid medium to a position of which a special rate of pulsation is imparted, enlivening that portion of matter into an individual existence and constituting it a distinct substance or element."



Davy's revolving atom has been more fully considered by Czirnianski, but our real success is confined to the fuller development of the idea of motion in gases and in solutions.

We see, then, that Graham advances the idea of atomic motion, and teaches us also how to observe it. The accuracy of his method, as well as of his work, is proved by the results; and it is not without reason that he is placed in that chain of eminent thinkers which has been represented by such as Leucippus, Lucretius, Newton, Higgins, and Dalton.

In Graham's lifetime chemistry had been enriched with inquiries into atomic volumes, the volumes of compound molecules, and the specific heat of the atom, or the relation of heat to the atomic weight. The relations in which the atoms of a compound stand to each other have been viewed very differently by chemists, and given rise to a certain change in the names, whilst the idea of atomicity has been developed more fully. To some of these Graham contributed his part in his inquiries on Salts, but to the mechanics and statics of the molecule, so to speak, he gave his special attention; and although new names have already arisen of men who have carried the subject in directions not followed by Graham, it is still true that his own mode of thought is peculiar, and he has left no one who can be called a successor.

His *Elements of Chemistry* form two admirable volumes, where the kernels of thought could be obtained free from shell, and where the student was led up to the newest opinions. As a text-book, however, time has removed much of its value.

It is not intended to give here any account of Graham's life. That, if done well, cannot fail to be an interesting picture of a mind devoted to the study of nature, and entirely free from display. It may be interesting, however, to note down the date of his birth and of his death, and the chief periods

which affected his outer life. He was born in Glasgow on December 21st, 1805—studied Chemistry with Dr. Hope in Edinburgh—was made Lecturer in the Andersonian Institution in Glasgow in 1830—was made Professor of Chemistry at the London University (now University College) in 1837—and succeeded Sir John Herschel as Master of the Mint in 1855. He died in London on the 16th September 1869.

R. ANGUS SMITH,

Ph.D. : F.R.S.

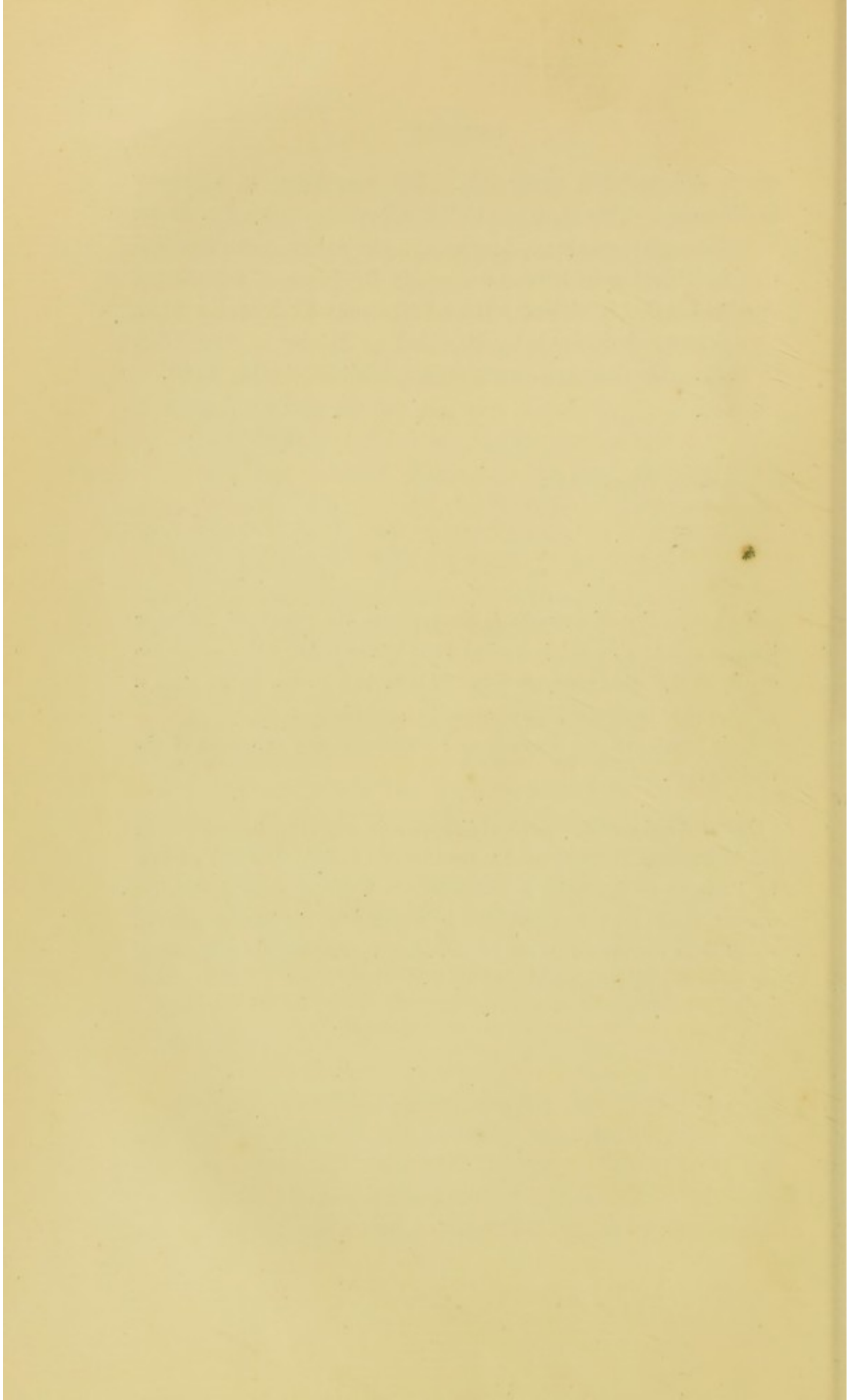
MANCHESTER, *November 1875.*

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THIS collection of Memoirs is presented to the friends of Professor Graham and to chemists in various parts of the world. The works are exactly of that class which are most liable to be forgotten by the general public, and to become difficult of access to men of science.

It is hoped that the Analysis of the Contents may save some of the reader's time.

Eloquent and careful accounts of Graham's life and works have appeared ; one by Professor Hofmann, read to the Chemical Society of Berlin ; another by Professor Odling, being a lecture delivered at the Royal Institution. Shorter notices have been published by Professor Williamson and others ; one of these was written for the Royal Society by the writer of this preface, but there is room for something fuller.





# GRAHAM'S CHEMICAL AND PHYSICAL RESEARCHES.

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# GRAHAM'S CHEMICAL AND PHYSICAL RESEARCHES.

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# G A S E S.

## I.

### ON THE ABSORPTION OF GASES BY LIQUIDS.

From *Annals of Philosophy*, xii. 1826, pp. 69-74.

1. LIQUIDS are in general miscible with one another, in all proportions as water and alcohol, or in a limited degree as ether and water; ether agitated with water taking up one-tenth of its weight of that liquid.

2. Frequently the mixing of liquids exhibits the closeness of chemical union, among other points, in the manner in which the *volatility* of the compound liquid is affected. Thus the vapour from pure alcohol at  $170^{\circ}$  Fahr. supports a column of mercury of 30 inches, but by mixing the alcohol with a quantity of water, we impair the volatility of the alcohol; and we may form mixtures which require a temperature of upwards of  $200^{\circ}$  to produce vapour capable of supporting such a column. In the same way portions of water are retained with so great force by sulphuric acid as to require, in order to drive them off, a degree of heat greatly higher than the boiling point of water. From these, and other instances of this affinity, we learn that, in a mixture of a volatile and more fixed liquid, the tendency of the more volatile ingredient to pass into vapour may be checked in a considerable degree by its connexion with the other liquid.

That many reputed gases, at a low temperature, or under great pressure, assume the liquid form, has been demonstrated by Mr. Faraday.<sup>1</sup> The researches of that ingenious chemist on gaseous liquefaction strongly impress the doctrine, that in the physical states of gas, liquid and solid, there is nothing of absolute permanency, and that any body may assume consecutively all these forms. Hence it follows that those bodies which, at the temperature of the atmosphere, we experience to be gases, may be considered without impropriety as volatilized liquids; and we may predicate of such bodies the common properties of liquids. Of

<sup>1</sup> *Philosophical Transactions*, 1823.



these properties, two have been mentioned, which alone will be applied to the elucidation of the phenomena of absorption.

It is then assumed that the gases, if liquefied (by pressure or any other means), would in general mix in some proportion or other with such ordinary and reputed liquids as we had it in our power to present to them; and that they would be retained in part by these liquids, through the agency of the mutual attraction evinced in liquid mixture, even although the pressure under which the union took place were considerably reduced, and the temperature raised. In this way there might result a mixture of a liquefied gas and a common liquid in reduced proportions, at the ordinary atmospheric pressure and temperature.

But it is not necessary to suppose that the gaseous bodies, whose absorption by liquids it is attempted to explain, be presented in a liquefied state. Analogy will lead us to expect that the mere injection into our absorbing liquids of such gases, in their elastic state, will occasion their liquefaction, and consequently bring into play the affinities of liquids, and the concomitant diminution of volatility, on which the explanation is founded.

Thus sulphuric acid, concentrated as much as it can be, boils at about  $620^{\circ}$ . Let a quantity of sulphuric acid so concentrated be heated to  $600^{\circ}$ , and kept at that temperature, and let the steam of water previously raised to the same temperature be conducted into it, we would predict, without the least hesitation, as the result, the detention and absorption of the steam, notwithstanding its high elasticity, until the boiling point of the acid was reduced by the dilution to  $600^{\circ}$ . Here then we have an instance of the absorption of a gaseous body (steam at  $600^{\circ}$ ), by a liquid at the same temperature; yet, in order to liquefy the gaseous body absorbed, in the ordinary way, it would be necessary to cool it down through the long space of nearly  $400^{\circ}$ , or to  $212^{\circ}$  Fahr. Such a reduction below the degree of temperature at which the absorption took place would be productive, in all probability, of liquefaction in the case of the most refractory of the gases. Now a composition of sulphuric acid and water, the same in every respect, might be obtained more directly by simply mixing together the ingredients, both being in the liquid state. This case of the absorption of a gaseous body by a liquid is, therefore, dependent upon the affinity which occasions the miscibility of liquids, and is, in fact, an instance of the mixture of two liquids. Many similar illustrations might be adduced if required.

We are, therefore, authorized in concluding that gases may owe their absorption by liquids,—to their capability of being liquefied, and to the affinities of liquids (apparent in their miscibility), to which they become in this way exposed. These properties may, therefore, be considered as



the proximate or immediate causes of the absorbability of the gases. Upon this supposition, solutions of gases in liquids are mixtures of a more volatile with a less volatile liquid; and to them may be extended the laws which hold in such mixtures.

Several circumstances are favourable to this view of the absorption of gases.

1. The cause assigned is one which we know to exist, and to be in operation. It is no supposititious cause of the existence of which we can adduce no other evidence than its conveniency in explaining certain phenomena. We possess evidence that almost all the gases may be condensed into liquids. They are, therefore, necessarily under the influence of those causes which we have supposed to occasion gaseous absorbability. Thus Mr. Faraday condensed sulphurous acid gas into a liquid, and found that its vapour possessed an elasticity which was balanced by the weight of about two atmospheres at  $45^{\circ}$  Fahr. Here then is a liquid which, from the frequency of the intermiscibility of liquids, might be expected to possess the property of mixing so intimately with certain of our reputed liquids as to admit of being detained by them in considerable quantity at the ordinary pressure and temperature. And, accordingly, sulphurous acid is absorbed and detained in large proportions by sulphuric acid and by alcohol, and in a considerable measure by water.

2. It is a coincidence which appears more than accidental, that the gases which yielded to Mr. Faraday are, generally speaking, of easy absorbability. This will appear from the following table of the gases which were liquefied by that experimenter, of the pressure of their vapours in atmospheres, and of the amount of their absorption by water and alcohol at  $60^{\circ}$ , according to the experiments of Thomson, Henry, Dalton, and Saussure:—

Gases Liquefied.	Pressure of vapours in atmospheres.	1 vol. water absorbs in vols. at $60^{\circ}$ .	1 vol. alcohol absorbs in vols. at $60^{\circ}$ .
Ammoniacal, . . . .	6.5 at $50^{\circ}$	780	...
Sulphurous acid, . . .	2 at 45	43.78	115.77
Muriatic acid, . . . .	40 at 50	516	...
Cyanogen, . . . .	3.7 at 45	4.5	23
Chlorine, . . . .	4 at 60	2	...
Sulphuretted hydrogen,	17 at 50	1	6.06
Carbonic acid, . . . .	36 at 32	1	1.86
Nitrous oxide, . . . .	50 at 45	1	1.53
Euchlorine, . . . .	...	8	...

With the exception of fluosilicic and fluoboric gases, all the gases absorbed in considerable quantity by water are contained in the fore-



going table. While the other gases, such as oxygen, hydrogen, etc., which are condensed into liquids with great difficulty, are absorbed by water in very minute quantities indeed. This, however, is more than the theory requires.

3. Mr. Faraday was enabled to give approximations to the specific gravities of some of the liquids into which the gases were reduced. Now it would be an objection to the hypothesis, if there were an excessive discordance between the specific gravities obtained by Mr. Faraday, and the specific gravities which these liquids maintain in mixture, or when in solution with water, etc. For although the specific weight of a mixture of two liquids is rarely the mean of the weights of the liquids, yet in general the variation from the mean is not excessive. There exists, however, no such discordance. Indeed, a comparison of these specific weights, which I have made, remarkably confirms the theory.

In addition to these facts, this hypothesis has in its favour all those circumstances which are thought to recommend the chemical theory of the absorption of gases, so ably illustrated by Berthollet, Thomson, and Saussure. Indeed, the account here given may be considered as a development of that theory.

By the latent heat which becomes sensible in the condensation of vapours, and also by the heat which is frequently evolved in the mixing of liquids, that increase of temperature, which always marks the absorption of gaseous bodies, is explained. The same liquid absorbs different quantities of different gases, and different liquids absorb unequal quantities of the same gas, from the attraction between the absorbing liquids and the gases when liquefied being variable, as is the case among ordinary liquids. Diminution of pressure or increase of temperature uniformly lessens the quantity of a gaseous body retained by a liquid, because the absorbed gas is itself then in a liquid state; and the volatility of all liquids, whether by themselves or mixed with others, is dependent upon pressure and temperature. The law, however, which Dr. Henry deduced from his experiments upon carbonic acid, viz., that the quantity of a gas which water absorbs is *directly* proportional to the pressure, is at variance with this theory. It is not likely that Dr. Henry would have come to the same conclusion had he experimented upon the more absorbable gases. In the case of muriatic acid gas, for instance, it is unlikely that he would have succeeded in impregnating water with a double portion by doubling the pressure. There may, nevertheless, be an approximation to such a law when the quantity of gas absorbed is inconsiderable, as it is the case of carbonic acid gas; our knowledge of the laws by which a volatile is retained by a more fixed liquid being too superficial to enable us at present to decide the point in question. The existence, however, of a general mechanical law



of that description is incompatible with any chemical theory which can be given. Supposing such a law to hold, it is remarked by Dr. Thomson, that "the proportion of the ingredients in this case is entirely regulated by the bulk, whereas in chemical combinations it is regulated by the weight." Dr. Thomson, notwithstanding this admission, attempts ingeniously to reconcile such a law to his modification of the chemical theory.<sup>1</sup>

The same objections are applicable to the analogous mechanical law, that the quantity of a gas absorbed, estimated by the bulk, is unaffected by variations in temperature. Such a law would be agreeable to the theory illustrated, if it were true that the pressure of vapours from liquids is exactly proportional to the temperature. But we know that the elasticity of vapours, over their liquids, increases in a much higher ratio than the temperature. Hence we are led to propose a different law, viz., that by increasing the temperature of a liquid we diminish its capacity to absorb any gas, not in the same but in a much greater proportion.

Dr. Henry and Mr. Dalton have proved that the amount of any gas, absorbed by a quantity of water in a vessel, depends greatly upon the gaseous residue. This fact is deducible from the supposition that the gases are liquefied when absorbed. For all liquids continue to evaporate until they are pressed upon by an atmosphere of their own vapour, equal in elasticity to that which they are capable of evolving at the temperature of the experiment. In a solution of carbonic acid in water, we ought, therefore, to expect carbonic acid to be given out or to evaporate till an atmosphere of that gas be formed of elasticity sufficient to counteract the tendency to assume the gaseous form of the remaining liquid carbonic acid. If the solution be freely exposed to the air, the whole of the carbonic acid will in a short time assume the gaseous form, from the impossibility of forming such an atmosphere. But if the solution be exposed to a limited quantity of any foreign gas, the carbonic acid will cease to evaporate, when the elasticity of the gaseous portion can counteract the volatility of the liquefied part. The greater the quantity of the foreign gas with which the solution is in free communication, the less carbonic acid will be detained, or would be taken up, were the absorption but commencing. Hence the influence of the gaseous residue, as it is called.

To the partial displacement of one gas absorbed by a liquid by another gas, parallel cases may be adduced from the mixture of liquids. Thus, if alcohol, holding a volatile oil in solution, be poured into water, the greatest part of the oil separates, while the alcohol unites with the water.—The simultaneous absorption of several gases by a liquid be-

<sup>1</sup> *System of Chem.*, vol. ii. p. 61.



longs to this class of appearances. From Mr. Dalton's theory it follows that two gases absorbed into a liquid should really occupy always the same room as they would occupy, if each of them had been absorbed singly, at the degree of density which it has in the mixture. This law is inconsistent with the explanation given here; but it has been fully disproved by the subsequent experiments of Saussure.

It may be stated, in conclusion, that all that is insisted upon in the foregoing sketch is, that when gases appear to be absorbed by liquids, they are simply reduced into that liquid inelastic form, which otherwise (by cold or pressure) they might be compelled to assume. That their detention in the absorbing liquid is owing to that mutual affinity between liquids, which is so common. An affinity which occasions the miscibility of liquids affects the bulk or density of the mixture, and frequently impairs the volatility of the more easily vaporized liquid in the mixture. In this way the phenomena of the absorption of gases are brought into the same class as those of the miscibility of liquids.

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## II.

### ON THE FINITE EXTENT OF THE ATMOSPHERE.

From *Philosophical Magazine and Annals of Philosophy*, i. 1827, pp. 107-109.

Edinburgh, December 14, 1826.

To Dr. Wollaston we owe a satisfactory reason for a limit to the atmosphere, even upon mechanical principles. The idea that the mere weight of the matter of gaseous substances might afford, at a certain degree of rarefaction, a balancing resistance to further expansion is certainly beautiful,—a conception worthy of that sagacious philosopher. Mr. Faraday, with his usual felicity in experimental research, has endeavoured to adduce instances of this equilibrium between the expansive power of gaseous matter and its clogging gravity—to give an experimental demonstration of the hypothesis.

Admitting, as we do without hesitation, that the cause assigned would be fully adequate to produce the effect, the question still remains,—but is it really the cause which does produce the effect? The atmosphere may possess some well-known property which necessarily renders it limited, and the proposal of any supposititious cause may be therefore unnecessary.

Such a property we believe the atmosphere does possess, although



we are not aware of its having been noticed with this view previously. The law of the expansion of gaseous bodies by heat and their contraction by cold involves a curious consequence, which has attracted the attention of several philosophers. Bodies cannot exist in that state below a certain temperature. Let us direct our attention to a volume of air at  $32^{\circ}$  Fahr. It is a well-established law, that for every degree Fahrenheit which the volume of air is heated above that temperature, it increases 1-480th part; and also for every degree which it is cooled below  $32^{\circ}$ , it is reduced 1-480th part of what it was at that temperature. Hence if it should be cooled down  $480^{\circ}$ , and reduced by so many parts, it would be reduced into a volume infinitely small:—it would really be annihilated. To avoid this absurdity, we are constrained to believe that all gases would be reduced into the liquid or solid state by a fall of temperature which does not amount to  $480^{\circ}$  below the freezing point of water. The proposition, therefore, that the earth's atmosphere cannot exist in the gaseous state at a temperature below  $-480^{\circ} + 32^{\circ} = -448^{\circ}$  Fahr. is susceptible of demonstration *ad absurdum*.

Now meteorologists have discovered a law in the atmospheric temperature which makes this fact available in elucidation of our subject. It has been found that the temperature of the atmosphere decreases as we ascend, and that with considerable regularity. The observations which we possess upon this subject indicate a decrease of 1 degree for every elevation of about 300 feet. This brings us rapidly to a limit to the height of the atmosphere. Supposing the temperature of the surface of the earth  $32^{\circ}$ , the air would lose its elastic state at a height which would be less than 480 times 300 feet, or under 27.27 miles. However, without questioning the continuance of this decrease of temperature at great elevations, it is probable that in the higher regions of the atmosphere it is by no means so rapid as in the lower regions, where the law has been verified by observation. For the great source of the heat of the atmosphere is its contact with the surface of the earth, and not in the calorific rays of the sun which it arrests in their progress. Hence the lower strata of the atmosphere will possess a comparatively high and extraordinary temperature, and the fall of temperature as we ascend will appear for some time rapid. But at a certain elevation, the effect of this adventitious supply of heat will be greatly diminished.

The increase of capacity for heat in gases, attendant upon increase of bulk, accounts in a satisfactory manner for reduction of temperature in a mass of air as it is elevated and less compressed. The superior stratum of the atmosphere we may suppose to expand from its unrestrained elasticity: its temperature is thereby lowered, till at last it



arrives at that point which involves the loss of its elastic state. As the liquid state is a physical state of bodies, which implies pressure and a power to maintain the evolution of vapour (certainly in all non-metallic bodies), the cooled and uncompressed superior air will be at once reduced from the gaseous to the solid state. In this way may temperature occasion a limit to the diffusion of the atmosphere.

From the length of time during which the sun's rays continue to be reflected back upon the earth by the superior parts of the atmosphere, after he has sunk beneath the horizon, there is reason to believe that the atmosphere extends in a state of great tenuity to a very considerable height above the surface of the earth, and therefore that the theatre of this condensation is considerably removed. Let us suppose that it is so, and inquire whether its existence would be indicated by any notable effect.

We know well that in ordinary cases the reduction of a body from the gaseous to the liquid or solid state is attended with a considerable extrication of heat. Light, too, has been observed in condensation following sublimation, particularly in the case of benzoic acid. Now, the superior and condensing strata of the atmosphere are of a tenuity incomparably greater than that of the vapours whose condensation we generally witness. But this tenuity has been arrived at at the expense of the previous absorption of much more heat; or, in other words, the latent heat of vapours, which is emitted upon their condensation, is in proportion to their tenuity. Hence it is probable that the condensation of the elastic air into solid particles would be attended with the emission of accumulated stores of light and heat. Would not air, too, it might be asked, emit light upon its complete condensation and loss of physical state, while it may be made to do so by mere mechanical compression? Here, perhaps, we have the cause of that degree of luminosity which is generally associated with the upper regions of the atmosphere, and which has induced Professor Leslie, with that daring originality which frequently characterizes his beautiful speculations, to attribute to them a phosphorescent property.

These luminous appearances will be more frequent and striking at the polar regions, from the temperature there approaching more closely to the condensing point of the gaseous substances constituting the atmosphere. Their proper sites will be the thermal poles, or points on the earth's surface of lowest temperature. From late observations, the thermal poles of the earth appear to coincide with its magnetic poles. Let us suppose a determination to condensation to take place in the superior regions of the atmosphere at the thermal pole, the surrounding elastic air would rush in, and expand, to fill the vacuity occasioned by the condensation. But this rarefaction, with its attendant fall in tem-



perature, would frequently be productive of condensation and deposition in these masses of air themselves. In this way the tendency to condensation, originating perhaps at the thermal pole, would be widely and rapidly propagated, and the attending streams of light would appear to shoot from that point. Here we recognise the brilliant phenomena of the aurora borealis.

It evidently follows from this theory that the atmosphere will be of different altitudes over different parts of the earth, according to their temperature. Within the tropics it will be higher than over the polar regions. Hence the higher parts of the equatorial atmosphere will tend to fall back upon the poles,—a disposition which will co-operate with the inferior current in an opposite direction, to produce a grand circulation of the atmosphere, and to impress a general character upon winds.

### III.

#### AN ACCOUNT OF M. LONGCHAMP'S THEORY OF NITRIFICATION, WITH AN EXTENSION OF IT.

From *Philosophical Magazine and Annals of Philosophy*, i. 1827, pp. 172-180.

M. LONGCHAMP, in a memoir read some time ago before the Academy of Sciences, and published lately in the *Annales de Chimie et de Physique* (t. xxxiii. p. 1), has developed a theory of the natural production of nitre in various soils, and superficially upon certain rocks. This theory, in its full detail, is, perhaps, not altogether new; for several of the opinions of which it consists have been advocated, or at least broached, by preceding chemists. But M. Longchamp has certainly the merit of confidently displaying these opinions in their full force, and of methodizing them into a consistent system. Of this theory we propose to give an account, as nearly as possible in the words of the author, and to subjoin certain speculations with the view of supplying a material deficiency in the theory of M. Longchamp.

It may be premised that M. Longchamp confines himself to the production of the acid of the native nitrous salts, and very properly avoids any supposition of the production of their base previously existing, as fact and reason point out that it must be, and, unlike the nitric acid of these salts, incapable of a synthetic formation.

There is reason to doubt the original proposition of Glauber, and which, as far as regards the nitric acid, has been the prevailing theory



to the present day, that "saltpetre is formed by the decomposition of animal and vegetable substances;" for nitrates form and are found in materials and in places which contain no vegetable or animal matter, and which have never been exposed to the emanations of animals.

Persons engaged in the production of nitre know well that earths taken from caves furnish nitrates by lixiviation, and that earths, replaced in the same circumstances, yield again, after eight or ten years, new quantities of saltpetre. This fact cannot be denied; but some have attempted to weaken its force by the reflection that, in general, the nitrous materials are not completely deprived of their salts by the washing to which they are subjected; while these materials, exposed again to the air, become dry, and as the water does not evaporate except at their surfaces, it deposits there all the nitre which it held in solution. This objection would be of weight, if it were true that only a small quantity of nitre could be obtained from materials which had been replaced; but it is well known that if earth from a cave has given, by the first lixiviation, 100 parts of nitric acid, saturated with the different bases, the whole mass, being returned to the same place, will yield again, after eight or ten years, the nitrates which represent the same quantity of acid. It is not, therefore, only the nitre which the materials have retained which is obtained by the second lixiviation; but besides, and for the greater part, what is formed anew upon replacing the earth in the circumstances which had induced its first nitrification. Moreover, the same materials twice lixiviated, returned again to the same cave, will yield, after eight or ten years, the same quantity of nitre which they furnished at each of the two former lixiviations; and the nitrification is perpetuated without a limit, provided that the returned earth possess a sufficient portion of the base, which commonly solicits the formation of the nitric acid, and absorbs that acid as it is produced.

Lavoisier took from the quarry a great number of specimens of chalk, at Roche Guyon and Mousseaux, and all when washed yielded a small quantity of nitrate of potash, mixed with much nitrate of lime. These specimens were frequently taken at a distance of many hundred toises from any habitation, and from parts of the rock exposed to the rain and all vicissitudes of weather; and he has drawn this consequence from the facts related in his memoir: "the nitric acid does not pre-exist in the chalk of Roche Guyon, but is formed by the action of the air."<sup>1</sup> It is remarkable that this chalk was often richer in nitre than the best nitrous soils. The quantity of nitre which any specimen contained was found to depend most upon its vicinity to the surface. As the organic remains of these rocks do not retain their animal matter,

<sup>1</sup> *Mémoires Etrangères de l'Académie des Sciences*, xi. P. II. p. 565.



no influence can be attributed here to the decomposition and putrefaction of animal substances in contact with the air.

But nitric acid forms in the open air, and in materials which contain no vestige of animal or vegetable matter. An experiment is related by one of the competitors for the French prize,<sup>1</sup> in which a quantity of earth from the fields, washed with great care, dried by exposure to the sun, and afterwards kept moist by occasional watering for a year, afforded by lixiviation a saline solution, in one case of one degree of the areometer, and in another of half a degree. Thouvenel, too, who has produced nitric acid by exposing chalk to the gases evolved from the putrefaction of animal or vegetable substances, mixed with common air, likewise obtained this acid when the chalk was in contact with nothing but atmospheric air.<sup>2</sup> It is true that in the experiment which he relates, the materials exposed to the atmospheric air, loaded with putrid gases, yielded fifteen parts of nitrate of lime; while those which were in contact with pure atmospheric air afforded no more than six parts of the salt. Thouvenel concludes, "It is demonstrated by our experiments that atmospheric air possesses all that is necessary to serve for nitrification, as well as the air which emanates from putrescent bodies, provided it finds matter capable of absorbing the materials."<sup>3</sup>

M. Longchamp having thus shown how ill-founded the proposition is, that the materials proper for nitrifying *never* nitrify in the air, without the concurrence of animal matter, attempts, in the next place, to prove that the nitric acid is formed exclusively from the elements of the atmosphere.

It is admitted, he observes, that the animal matters do not require to be in contact with the earths, but that their emanations are sufficient for the production of nitre. Could it be through the instrumentality of azote, which animal matter might disengage during putrefaction? But chemists know that the products of this putrefaction are ammonia, carbonic acid, carburetted hydrogen, and perhaps some carbonic oxide and water, but no azote; and even if this gas were produced, how would it combine with the carbonate of lime? There are instances of extraordinary combinations of gases in the nascent state, but the azote is not presented in that state in the case referred to, since the putrescent blood was at the distance of two feet from the carbonate of lime, which it is pretended that it nitrified.<sup>4</sup>

<sup>1</sup> *Mémoires Etrangères de l'Académie des Sciences*, xi. P. I. p. 160.

<sup>2</sup> *Ibid.* P. II. p. 124.

<sup>3</sup> *Ibid.* p. 89.

<sup>4</sup> The commissioners of the Academy, among whom was Lavoisier, took a quantity of the carbonate of lime, which they carefully washed in boiling water to extract all the salts; they placed the washed carbonate of lime in baskets, which were hung at the distance of two feet from a quantity of blood in a state of putrefaction.—*Mém. Etrang. de l'Acad.*, xi. P. I. p. 126.



Might it arise from some combination of azote, which these emanations bore along with them? But it is known that in the putrefactions of blood, urine, and similar matter, all the azote goes to form ammonia: admitting, however, that a part of the azote escapes the hydrogen, and enters into some combination hitherto unobserved; why, it may be asked, does it exhibit no nitrifying power without the co-operation of carbonate of lime? For if directed against caustic lime, magnesia, alumina, etc., no nitric acid is formed, or at least a scarcely sensible quantity, and only after a long lapse of time; while if potash, caustic or carbonated, be presented, not an atom of nitre is formed.<sup>1</sup>

Might it be through a reaction of the putrid emanations upon the atmosphere? But, besides that this reaction is difficult to conceive, and that otherwise it would be the azote of the air which formed the nitric acid, and not that of the animal matters, it may still be asked, Why is the carbonate of lime the only body which solicits this reaction?

Considering it as proved, that animal substances do not nitrify by means of their *emanations*, M. Longchamp believes that insuperable difficulties attend the supposition, that putrescent bodies, *in contact* with carbonate of lime, contribute in any measure to the production of nitric acid. For there is no chemical fact which entitles us to suppose, that urine or blood would yield by their putrefaction, other products when they are mixed with calcareous earths, than when they putrefy without the admixture. Provided, too, that the animal matters remained in the solid state, their action upon the solid calcareous matter would be very much circumscribed, extending only to the particles in immediate contact with their surfaces. Even supposing that the animal matter was liquid, and would thereby become diffused more generally through the mass, still its action would be limited, to a great degree, by the total insolubility of the carbonate of lime. From a review of these circumstances, Mons. L. considers himself entitled to conclude, that animal matters, whether solid or liquid, do not concur by their azote to the formation of the nitric acid. He then proceeds to the development of his own theory, or to show how atmospheric air, without the concurrence of any vegetable or animal matter, may form nitric acid.

It is universally admitted that nitric acid is not formed in sheltered situations, unless a certain degree of humidity prevails, and the air circulates through all the parts; for in places where the air cannot be renewed, there is no formation of acid. Thus, Lavoisier observed at Roche Guyon that in the caverns or pits, which were very deep and had but one issue, nitric acid did not appear in the deep parts, but only at the entrance. The same observation was made by that celebrated

<sup>1</sup> Thouvenel, *Mém. Etrang. de l'Acad.*, xi. P. II. p. 119.



philosopher in the tufa quarries of Touraine. The nitric acid is formed only in places which contain porous rocks or light soils, possessing carbonate of lime, moisture, and a constant circulation of air.

Tufa, light earths and chalk, act chiefly as absorbents. Chevrard met with compact chalks, which did not nitrify. Hence we never find marble, whether in the quarry exposed to the atmosphere, or in our houses, to exhibit any tendency to the formation of nitre; while tufa and chalk, which differ from it only in porosity, nitrify with ease.

It is upon water that chalk and tufas exert their absorbing power. But these substances in contact with water produce no nitric acid when atmospheric air is withheld. But the water brings air with it, and the nitrifiable materials, possessed of humidity, continue to absorb air by means of that humidity.

Chemists have long known that all kinds of water contain air; but to MM. Gay-Lussac and Humboldt<sup>1</sup> we are indebted for a fact, which has more recently been confirmed by the latter philosopher and M. Provençal,<sup>2</sup> that the air in water contains more oxygen than atmospheric air does. The mean of ten experiments made by Humboldt and Provençal on air derived from water gives the proportion of oxygen as  $\frac{31.05}{10000}$ . The previous researches of Gay-Lussac and Humboldt made us acquainted with a still more interesting fact, that if aerated water be exposed to heat, and if we divide the air procured into any number of equal portions, the first portions contain less oxygen than the last, as is exhibited in the following table:—

Oxygen in 1000 parts of 1st portion of air, 24.0					
"	"	2d	"	"	26.8
"	"	3d	"	"	29.6
"	"	4th	"	"	33.0
"	"	5th	"	"	34.8

M. Longchamp's application of this fact I shall give in his own words, without abridgement,—the more so, as I consider it not altogether correct. "According to M. Berzelius, protoxide of azote contains 36.07 parts oxygen; the last portion, therefore, of the air obtained in the experiments of Gay-Lussac and Humboldt, contained almost as much oxygen as the oxide of azote possesses: and we perceive that water exercises such an action upon the oxygen and azote, as tends to combine these gases in a more intimate manner than they exist in the atmosphere. But if any other force should unite with that of the water, is it not reasonable to think that the molecular action of the gases will acquire more energy, and that there will result from these united forces a combination which will be nitric acid; whether this acid is formed in following out

<sup>1</sup> *Journ. de Phys.*, lx. 129.

<sup>2</sup> *Mém. d'Arcueil*, ii. 359.



the whole chain of compounds known and unknown of oxygen and azote, or is formed immediately by the first action of these gases? Now, the body which in nitrification seconds the action of the water, is the lime of the chalk. So then, tufa, chalk and nitrifiable materials act in nitrification both as absorbents of water and air, and as presenting a base which solicits the formation of nitric acid; and water acts as an absorbent of oxygen and azote, and in commencing the combination of these gases."

The greater portion of oxygen absorbed depends without doubt simply upon the greater absorbability of that gas than of azotic gas, and not, as Mons. L. supposes, upon water exerting "such an action upon the azote and oxygen as tends to unite them in a more intimate manner than they exist in the atmosphere." We embrace, however, M. Longchamp's fundamental proposition,—that it is from the action of the oxygen and azote, held in solution by water, upon the carbonate of lime, that the nitrate of lime results. All bodies, when in the liquid state, possess their powers of combination most energetically. Now I have formerly shown<sup>1</sup> that oxygen and azotic gases, when absorbed by water, are really in the liquid state; there is, therefore, some reason for that activity with which our theorist has invested them.

Such is the theory of M. Longchamp; and it appears to me to be, as far as it goes, a true explanation of the phenomena. The process of nitrification is constantly going on in nature, and in circumstances where no other agents appear to be employed, except carbonate of lime and the elements of the atmosphere. Hence, in circumstances in which animal matter is superadded to these agents, it is reasonable to think that the latter does not contribute, in any essential way, to the nitrification. Where nitrate of potash is the ultimate result, it appears to be established that nitrate of lime pre-existed, and that the nitrate of potash resulted from the decomposition of the nitrate of lime by some salt of potash.

But it cannot be denied that the nitrification of calcareous substances is greatly promoted by the contact, or, more generally, by the proximity, of putrescent vegetable and animal matter. The experiment of Thouvenel, to which M. Longchamp refers above, abundantly proves this; and the constant and universal practice in the formation of artificial nitre-beds strongly confirms it. This fact appears, therefore, to weigh heavily against the theory of M. Longchamp: it is however, in our opinion, susceptible of an explanation without any mutilation of that theory; and to this extension of the hypothesis we now proceed.

We are disposed to attribute the beneficial effect in nitrification of

<sup>1</sup> *Annals of Philosophy*, N. S. vol. xii. p. 69.



the decomposition of animal and vegetable matter to the plentiful supply of an element which exists at all times in the atmosphere in a perceptible proportion—carbonic acid gas. *The free carbonic acid renders a portion of the carbonate of lime soluble in the water or moisture, which must be present, and thereby enables the carbonate of lime to act more effectually upon the oxygen and azote, which the water has absorbed.* The oxygen, azote, and carbonate of lime are all liquefied, and in solution in the water; they are therefore in circumstances most favourable to their mutual action.

Carbonate of lime is altogether insoluble in pure water, while water saturated with carbonic acid dissolves 1-1500th part. According to Dr. Thomson:<sup>1</sup> “when carbonate of lime is rendered soluble in water by means of carbonic acid a bi-carbonate is formed, which seems only capable of existing in solution.” That carbonic acid is one of the most considerable products of the putrefaction of both animal and vegetable substances is well known.

Water in ordinary circumstances absorbs rather more than an equal volume of carbonic acid gas.

Now Thouvenel, without any view to this point, performed and has registered a series of experiments, which render it exceedingly probable that, of the products of putrefaction, it is the carbonic acid alone which contributes to the nitrification; inasmuch as when these products were deprived of their carbonic acid, by being passed through caustic potash or lime-water, before acting upon the chalk, their nitrifying power was lost; while otherwise their nitrifying power was sufficiently notable. I shall give Thouvenel's experiments, as reported by Messrs. Aikin in their Chemical Dictionary, which is still the best work we possess upon the chemical manufactures:—

“Having charged a retort with putrefying materials, Thouvenel connected with it three receivers in the manner of Woulfe's bottles, the last of which terminated in a tube communicating with a pneumatic apparatus. Four different sets of this apparatus were employed at the same time. In the first of these the two receivers nearest the retort were charged with four ounces of chalk diffused in distilled water, while the third receiver contained a solution of caustic potash. In the second set the two first receivers contained distilled water, and the last was charged with washed chalk. In the third set the two first receivers contained lime-water: and in the fourth set a solution of caustic potash; the third receiver in both cases holding the chalk. They were all equally exposed to the same temperature, namely, from 74° to 80° Fahr., for six months, and the changes which their contents had undergone were then examined.

<sup>1</sup> *First Principles*, ii. 296.



"The chalk in the first apparatus afforded 26 grains of nitrate of lime mixed with a little nitrate of ammonia; the potash in the third receiver had become saturated with carbonic acid, and had partly crystallized on the side of the receiver, but contained no nitre.

"In the second apparatus the water of the two first receivers had acquired a very putrid smell from the gas which had passed through it, and contained a little ammonia, but afforded no nitrous salt on evaporation: the chalk in the third receiver afforded by lixiviation no more than 4 grains of nitrated lime.

"In the third apparatus the lime-water had deposited its earth in the state of carbonate, and the supernatant fluid had a strong odour resembling ammonia and putrid garlic: by evaporation it yielded 5 or 6 grains of nitrated ammonia. The chalk in the third receiver gave only a slight trace of nitrate of lime.

"In the fourth apparatus the potash was crystallized, but contained no nitre: with sulphuric acid it effervesced strongly, giving out a very pungent and highly fetid gas: *the chalk in the third receiver gave no indications whatever of the presence of any nitrous salt.*

"The gas remaining in the receivers, and collected in the pneumatic apparatus, was in all the four experiments found to be slightly inflammable, although, when rising from the putrefying materials, it extinguished a taper immersed in it. This putrid inflammable gas was incapable by itself of nitrifying chalk; but when mixed with washed atmospheric air, *carbonic acid soon made its appearance*, and then the gas became capable of impregnating chalk with nitrous acid as at first."<sup>1</sup>

These experiments of Thouvenel, and particularly the last observation, point out carbonic acid as the important agent in nitrification, at least as distinctly as could be expected of experiments of this nature.

It has all along been observed in the management of artificial nitre-beds, that although free exposure to the atmosphere be indispensable to the progress of nitrification, yet a strong current of air is exceedingly prejudicial. The rapid circulation of the atmosphere would be attended with the quick dissipation of the carbonic acid gas, upon which we have supposed the superiority of these nitre-beds to depend.

The atmosphere at all times and places abounds in carbonic acid gas, as the exposure of lime-water would quickly indicate. In those chalks and calcareous soils, in which the spontaneous production of nitrous salts is observed, the activity of the carbonate of lime may, therefore, equally depend upon its *dissolution*, effected by the absorption of mois-

<sup>1</sup> Aikins' *Chemical Dictionary*, vol. ii. 160. From *Mém. Etrang. de l'Acad. des Sciences*, tom. xi. 503.



ture and carbonic acid from the atmosphere. It would still, however, be a curious subject of inquiry—whether these soils and chalks do not, in some cases, contain within themselves the carbonic acid necessary in conjunction with water to effect their partial solution, and be thus enabled to act to a greater extent upon the absorbed oxygen and azote—the elements of nitric acid?

Should this theory of the instrumentality of carbonic acid, in nitrification, be eventually substantiated, several improvements, in the artificial production of nitre, might evidently be deduced from it.

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#### IV.

### EXPERIMENTS ON THE ABSORPTION OF VAPOURS BY LIQUIDS.

From *Edin. Journ. of Science*, xvi. 1828, pp. 326-335. [Schweigger, *Journ.* liii. (= *Jahrb.* xxiii.) 1828, pp. 249-264.]

FROM theoretical considerations I was led to institute the following experiment:—Into a deep cylindrical jar as much water was poured as covered the bottom of it to the depth of half an inch. Within the jar, and an inch above the surface of the water, a porcelain basin, three inches in diameter, was supported, containing 500 grains of a saturated solution of chloride of sodium of the temperature  $57^{\circ}$ , which was observed to be also the temperature of the water below and of the air without. The mouth of the jar was finally covered over by a glass plate, and made nearly air-tight by means of lard. It was intended by this arrangement to preserve the solution of chloride of sodium in an atmosphere saturated, or nearly so, with aqueous vapour, to be supplied by the water at the bottom of the jar. For comparison another arrangement of a similar nature was made at the same time, with the only difference, that the porcelain basin contained 500 grains pure water instead of a saline solution. The two jars were set aside in a quiet place, not subject to great variations in temperature, and a specimen of the dry chloride of sodium made use of, was exposed freely to the air in their neighbourhood. At the expiration of six days the whole were examined: the salt exposed to the air did not present the slightest appearance of deliquescence. The basin of pure water in the second jar had lost three grains in weight, but the solution of chloride of sodium had increased in weight by 63 grains. This solution possessed no power to absorb and condense vapour from a temperature originally lower than that of the

<sup>1</sup> Read before the Royal Society of Edinburgh, March 3, 1828, then communicated to the *Edin. Journal of Science*.



water near it; while the circumstance of a loss, rather than an increase of weight, occurring in the other case, renders it improbable that any inequality of temperature took place during the continuance of the experiment, and operated in this way. The plain inference from the experiment was, that the chloride of sodium employed, although by itself not deliquescent, or incapable of absorbing vapour, yet possessed that property in a considerable degree when in solution, seeing that in six days it had absorbed nearly half its weight of water, the quantity of salt in solution being 143 grains, and the increase of weight 63 grains.

In a second preliminary experiment there were two cases similar to the preceding, and besides, the same quantities of saturated solutions of muriate of ammonia and of sulphate of magnesia were enclosed in jars containing a little water in a similar manner. The temperature on closing the jars was about  $58^{\circ}$ , and very equable during the experiment. In four days the basin of pure water was found to have lost 2.5 grains, but the solution of muriate of ammonia had increased 34 grains, of chloride of sodium 37 grains, and of sulphate of magnesia 8 grains. The increase in the case of sulphate of magnesia was the least, although it contained most saline matter.

In the further investigation of this subject, instead of separate jars, low tin canisters were employed, in which several vessels with solutions might be arranged at the same time. The vessels rested on a support of wire-cloth an inch from the bottom of the canister, the lowest part of the canister being occupied with water to the depth of half an inch. The canisters were provided with lids, which could be made air-tight. It had been found that Wedgewood porcelain basins unfailingly absorbed a portion of the water or of the saline solution which they contained, varying from one to twelve grains. The use of them was therefore discontinued, and hemispheres or capsules of glass three inches in diameter, and blown as like each other as possible, were employed in their place.

1. Solutions were formed of one part chloride of sodium in four parts water, and of anhydrous carbonate of potash and water in the same proportions. The carbonate of potash, which is deliquescent, was obtained by keeping the sesquicarbonate in a red heat till the excess of acid and the water which it contains were wholly expelled. Three of the glass capsules were placed in contact on the wire-cloth support of a small tin canister, with water below, but not in contact with them. These capsules contained respectively, 500 grains water, 500 grains of the solution of chloride of sodium, and 500 grains of the solution of carbonate of potash. They were less than half full. The observation being made that no inequality of temperature existed within the canister, its lid was applied, and the joinings made air-tight with lard. Upon examination at the expiration of six days, the capsule of water was found to



have lost 23 grains; that of the solution of chloride of sodium to have gained 39 grains; and the solution of carbonate of potash was found to have gained only 6·5 grains. Here it is evident that the solution of chloride of sodium had drawn vapour not only from the water below, but likewise to a large extent from the adjoining capsule of water, and most probably to a small extent from the solution of carbonate of potash, likewise in contact with it. The solution of chloride of sodium appears, therefore, to possess a manifest superiority in absorbing power over a similar solution of the deliquescent carbonate of potash.

2. In a large tin canister or box, eighteen inches long, nine broad, and four deep, with a wire-cloth support and water under it, precisely as in the foregoing case, ten capsules containing various solutions were arranged at the same time. To prevent the liquids from influencing each other, they were separated by temporary screens of pasteboard, so that each capsule was contained in a cell by itself; but all communicated equally, through the apertures of the wire-cloth, with the reservoir of water below. The results of this experiment are thrown into the form of a table. In the first column the composition of the solutions is given, of which 700 grains were always employed. When the proportion of salt in the solution is not expressed, it is to be understood that the solution was a saturated one at the temperature of the atmosphere, which varied during the experiment from  $55^{\circ}$  to  $42^{\circ}$ . In the second column the increase or loss of weight undergone by the different solutions, after being enclosed for six days, is expressed; and in the third column the additional increase or loss of weight, after further confinement for fourteen days. In a fourth column the boiling points of the solutions are subjoined, for a purpose which shall be presently explained.

Solutions.	Gain in 6 Days.	Gain in 14 Days.	
	Grs.	Grs.	
1. Chloride of sodium, . . . . .	35	66	224°
2. Sulphate of magnesia, . . . . .	7	16	214·5
3. Sulphate of soda, . . . . .	0	2	213
4. Carbonate of soda, . . . . .	2	7	214
5. Nitrate of potash, . . . . .	2	8	214
6. Muriate of ammonia, . . . . .	29	39	221
7. 1 carbonate of potash, 2 water, .	22	45	221
8. 1 chloride of calcium, 2 water, .	53	105	230·5
9. 1 chloride of calcium, 5 water, .	17	33	216·5
10. Water, . . . . .	-5	-3	212

From the experiments of this table, and from other experiments yet to be detailed, it is evident that not only the solutions of salts, which are deliquescent, but that the solutions of salts which are persistent in the air, and even of efflorescent salts, are capable of absorbing vapour in



an atmosphere nearly saturated with it. Some of the results are curious. It appears from the table that a saturated solution of common salt, which contains less than a third of its weight of a saline substance, which is not deliquescent, absorbs vapour much more powerfully than a solution of the deliquescent carbonate of potash in twice its weight of water. In fact, it appears that *all* saline solutions just as readily inhale as exhale vapour, according to the state of the atmosphere in which they exist. It is this proposition in all its generality which I wish to establish. As the powers to absorb and to emit vapour appear to be necessarily conjoined and of equal importance, it may be allowed us to say, that liquids *invaporate* when they take in their vapour, as they are said to evaporate when they give it out.

The column of boiling points is an index of the invaporating powers of the solutions. The superior invaporating power of chloride of sodium is distinctly connected with the high temperature at which it boils. We see that the power of water to emit vapour at these high temperatures is diminished in various degrees by the saline matter in solution. At low temperatures it is probably diminished according to the same rate; and saline solutions, unable to give out vapour of the tension of that in the atmosphere around them, necessarily become absorbents of that vapour, as is proved by these experiments.

3. The following table exhibits the weight acquired by solutions of the same salt, viz. chloride of sodium, in various proportions, and also by sea-water, by enclosure for five days. 500 grains of each solution were employed. The boiling points of the solutions are likewise subjoined.

	Gain in 5 Days.	Boiling Points.
	Grs.	
1. Saturated solution, chloride of sodium,	33	224°
2. 2 do. + 1 water, . . . . .	23	220
3. 2 do. + 2 water, . . . . .	17	217.5
4. 2 do. + 4 water, . . . . .	10	216
5. Sea-water, . . . . .	3	213

A capsule of pure water enclosed at the same time, instead of increasing in weight, lost 4 grains. The curious inference is deducible from this experiment, that sea-water is capable of absorbing moisture from air, perfectly saturated with it at the same temperature. The experiment with sea-water was several times repeated, and it always exhibited a slight invaporating power, while a capsule of pure water placed beside it lost weight.

4. Several saline solutions and acid liquors were formed, all of which boiled at one temperature, viz. 224°. 700 grains of each were employed,



and they were retained for five days in the tin vessel. In the second column the weight is expressed which each liquid acquired during that period. These liquids were afterwards withdrawn from the tin vessel and freely exposed to the air, that they might evaporate, in order that the connexion between their evaporating and invaporating power might be observed. The loss of each liquid by evaporation during twenty-four hours is placed against it in a third column.

Solutions.	Gain by Invapora- tion in 5 days.	Loss by Evapora- tion in 24 hours.
1. Chloride of sodium, . . .	+ 32 grs.	- 8.5 grs.
2. Chloride of calcium, . . .	+ 34	- 8.0
3. Carbonate of potash, . . .	+ 30	- 8.6
4. Tartaric acid, . . .	+ 31	- 8.4
5. Sulphuric acid (1.221), . . .	+ 34	- 8.1
6. Muriatic acid (1.125), . . .	+ 113	+ 2.1
7. Muriatic acid (1.089), . . .	+ 61	- 2.3
8. Nitric acid (1.206), . . .	+ 59	- 2.9

A capsule of pure water was allowed to evaporate spontaneously for the same time as the cases in the table. It lost 13.9 grains. The temperature of the air did not exceed  $45^{\circ}$ . The similarity of the point of ebullition seems to be attended with an analogous increase from invaporation and loss by evaporation in the saline solutions and in tartaric and sulphuric acids. The difference of the results in these cases is so small that it might depend on slight variations of the form of the capsules, or other accidental circumstances. But the absorbing power of the two cases of muriatic acid and of nitric acid, which boil at the same temperature, are exceedingly different. The stronger muriatic acid also actually gained weight when exposed to the air, instead of sustaining loss by evaporation, like the other cases. The weaker muriatic acid and the nitric acid likewise lost less by evaporation, as they gained more by invaporation than the saline solutions. The invaporating powers of liquids appear to be reciprocally proportional to their evaporating powers, as might be expected. This was observed very distinctly on exposing to the air various saline solutions of dissimilar absorbing power, when those which invaporated in the least degree evaporated most rapidly, and *vice versa*.

It has not, I believe, hitherto been noticed that muriatic acid is ever capable of increasing in weight when exposed to the air, as sulphuric and nitric acids are known to do, and as occurred in the case of the stronger muriatic acid in the foregoing experiment. But I have frequently observed muriatic acid, of all degrees of strength, intermediate between 1.190 and 1.100, to increase in weight by the absorption of hygrometric moisture, when the weather was damp and the temperature



not above  $55^{\circ}$ . When the acid is strong it emits muriatic acid gas at the same time that it absorbs aqueous vapour, till it becomes of specific gravity 1.0960. But when acid, diluted to any degree below that strength, is exposed in a dry atmosphere, no material quantity of the acid gas is emitted, but the acid concentrates by the emission of aqueous vapour, till its specific weight rises to 1.0960. The boiling point of muriatic acid is at a maximum when of that strength, as was observed by Mr. Dalton; and it consists of exactly one atom acid and sixteen atoms water, as Dr. Thomson remarked.

As evidence of the power of muriatic acid to absorb moisture from an atmosphere not particularly dry, and to increase in weight, I may be allowed to state one experiment, made lately in the month of January. Three small porcelain basins, each containing 200 grains of liquid, were exposed together, with paper covers, in a room in which there was no fire. The liquid in No. 1 was muriatic acid of specific gravity 1.185. In No. 2 the same, diluted with half its weight of water. In No. 3 pure water. It had been previously ascertained that the muriatic acid contained no sulphuric acid. The basins were weighed every twenty-four hours, and the following results obtained :—

Weight in Grains.		
No. 1.	No. 2.	No. 3.
200	200	200
209	204	194
219	216	187
227	224	160
235	220	133
242	223	105
247	221	93
245	210	70
244	200	50

5. The capacity of liquids of dissimilar composition to absorb the vapours of each other is also exceedingly general. We may always presume with safety, that, if two liquids are miscible in all proportions, the more fixed liquid is capable of absorbing the vapour of the more volatile liquid. Yet the only instances of such absorption which have been attended to are the absorption of aqueous vapour by sulphuric acid, and of the same vapour by nitric acid.

6. Alcohol and water are miscible liquids, of which water is the more fixed; and I find water to absorb the vapour of alcohol at the temperature of the atmosphere with considerable avidity.

Sulphuric acid also absorbs alcohol vapour with avidity, as was stated in a former communication. The following experiment was per-



formed with the view of ascertaining the relative intensity with which water absorbs the vapour of alcohol, and sulphuric acid the vapours of water and of alcohol.

(1.) A small Wedgewood basin, one inch and a half in diameter, containing 200 grains water, was supported over sulphuric acid in a cylindrical vessel, and closed in. Upon opening the jar after twelve hours, the water was found to have lost eleven grains. (2.) The acid was stirred up, and, instead of the water, 200 grains absolute alcohol were introduced into the basin, and the whole closed in as before. In twelve hours the alcohol was found to have lost sixty grains, and the sulphuric acid had acquired a reddish tinge. (3.) The sulphuric acid was now withdrawn from the jar, and pure water substituted as the absorbing liquid. The quantity of absolute alcohol in the basin being again increased to 200 grains, and the lid carefully luted down, in twelve hours the alcohol lost 45 grains, and the water below had acquired the taste of alcohol very sensibly. The vapour of sulphuric ether is absorbed with great avidity by alcohol, and with much less force by water.

The vapour of alcohol is likewise absorbed by castor oil, especially after some alcohol has been previously mixed with it, although with a very feeble force. Retained over alcohol for ten days 200 grains castor oil became 273 grains. Bichloride of mercury deliquesces in alcohol vapour, although slowly when in hard crystals. Twenty grains of the crystals (not reduced to powder), suspended in a capsule over alcohol, became in six days 29 grains, a portion being dissolved by the alcohol absorbed. A solution of bichloride of mercury in alcohol likewise exhibits an invaporating power when in an atmosphere of alcohol vapour.

It would be curious to know whether alcohol is capable of absorbing the vapour of water, as well as water is capable of absorbing the vapour of alcohol. It is difficult to determine the point directly, as the quantity of water absorbed might be very minute; but I am inclined to believe, from an indirect experiment, that alcohol does not possess such an absorbing power. A crystal of sulphate of soda was suspended over a small quantity of absolute alcohol very carefully prepared, by a thread, which was attached to the cork of the phial for a period of six months, without undergoing the slightest alteration in appearance. Now, if alcohol had possessed the power to absorb aqueous vapour, and to keep the atmosphere above it in a dry state, so far as aqueous vapour is concerned, the crystal would certainly have effloresced and fallen into powder.

The phenomena presented when pieces of camphor are placed at a little distance from alcohol are very remarkable. A number of small



pieces in a gauze bag were suspended within a glass jar which contained a little alcohol. In a few hours the camphor began to run into a liquid, which fell in drops, and in twenty-four hours the whole camphor had left the bag in that manner. It is evident, therefore, that solid camphor with relation to alcohol vapour is deliquescent. Forty grains camphor were suspended over alcohol, as in the previous case, with the difference that the camphor was contained in a little glass capsule. Five days afterwards the capsule contained a solution of camphor in alcohol weighing 105 grains. A little camphor, however, had passed down to the alcohol below, to which it communicated its taste and smell; but the quantity was so small that the alcohol, on being diluted with water, became only slightly opalescent. The temperature of the atmosphere during these experiments averaged about  $55^{\circ}$ .

The salt subcarbonate of ammonia is known to be possessed of considerable volatility, and also to be soluble in water. Enclosed with water in separate vessels it quickly passes over into the water. Thirty grains of dry subcarbonate reduced to powder were suspended in a glass capsule over a considerable quantity of cold water, the whole being contained in a close vessel as usual. Upon examination after five days, the capsule, instead of 30 grains of the dry salt, was found to contain 12 grains of a solution of it, the greater part of the salt having passed over into the reservoir of water below, to which it had imparted its taste and properties. The habitudes of subcarbonate of ammonia in an atmosphere saturated with aqueous vapour are therefore exceedingly different from those of any other salt, as, instead of attracting water or remaining unaffected, it is itself attracted by water and dissolved.

Such are the principal facts which have presented themselves in the investigation of the absorption of vapours by liquids.

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## V.

### ON THE INFLUENCE OF THE AIR IN DETERMINING THE CRYSTALLIZATION OF SALINE SOLUTIONS.

From *Edin. Roy. Soc. Trans.* xi. 1831, pp. 114-118, author's reprint. [*Phil. Mag.* iv. 1828, pp. 215-218; Silliman, *Journ.* xvii. 1830, pp. 373-374.]

THE phenomenon referred to has long been known, and popularly exhibited in the case of Glauber's salt, without any adequate explanation. A phial or flask is filled with a boiling saturated solution of sulphate of soda or Glauber's salt, and its mouth immediately stopped



by a cork, or a piece of bladder is tied tightly over it, while still hot. The solution, thus protected from the atmosphere, generally cools without crystallizing, although it contains a great excess of salt, and continues entirely liquid for hours, and even days. But upon withdrawing the stopper, or puncturing the bladder, and admitting air to the solution, it is immediately resolved into a spongy crystalline mass, with the evolution of much heat. The crystallization was attributed to the pressure of the atmosphere suddenly admitted, till it was shown that the same phenomenon occurred when air was admitted to a solution already subject to the atmospheric pressure. Recourse was likewise had to the supposed agency of solid particles floating in the air, and brought by means of it into contact with the solution; or it was supposed that the contact of gaseous molecules themselves might determine crystallization, as well as solid particles. But although the phenomenon has been the subject of much speculation among chemists, it is generally allowed that no satisfactory explanation of it has yet been proposed.

In experimenting upon this subject, it was found that hot concentrated solutions, in phials or other receivers, might be inverted over mercury in the pneumatic trough, and still remain liquid on cooling; and thus the causes which determine crystallization were more readily examined. For this purpose, it was absolutely necessary that the mercury in the trough should be previously heated to  $110^{\circ}$  or  $120^{\circ}$ ; for otherwise that part of the solution in contact with the mercury cooled so rapidly as to determine crystallization in the lower part of the receiver long before the upper part had fallen to the temperature of the atmosphere. In such cases, crystallization beginning on the surface of the mercury, advanced slowly and regularly through the solution. Above, there always remained a portion of the solution too weak to crystallize, being impoverished by the dense formation of crystals below. It was also necessary to clean the lower and external part of the receivers, when placed in the trough, from any adhering solution, as a communication of saline matter was sometimes formed between the solution in the receiver and the atmosphere without. When these precautions were attended to, saline solutions over mercury remained as long without crystallizing as when separated from the atmosphere in the usual mode.

Solutions which completely filled the receivers when placed in the trough allowed a portion of mercury to enter by contracting materially as they cooled. A bubble of air could thus be thrown up without expelling any of the solution from the receiver, and the crystallization determined without exposing the solution directly to the atmosphere.

The first observation made was, that solutions of sulphate of soda



sometimes did not crystallize at all upon the introduction of a bubble of air, or at least for a considerable time. This irregularity was chiefly observed in solutions formed at temperatures not exceeding  $150^{\circ}$  or  $170^{\circ}$ , although water dissolves more of the sulphate of soda at these inferior temperatures than at a boiling heat. Brisk ebullition for a few seconds, however, rendered the solution upon cooling amenable to the usual influence of the air. In all successful cases, crystallization commenced in the upper part of the receiver around the bubble of air, but pervaded the whole solution in a very few seconds. A light glass bead was thrown up into a solution without disturbing it.

It occurred to me that, since the effect of air could not be accounted for on mechanical principles, it might arise from a certain *chemical* action upon the solution. Water always holds in solution a certain portion of air, at the temperature of the atmosphere, which it parts with upon boiling. Cooled in a close vessel after boiling, and then exposed to the atmosphere, it reabsorbs its usual proportion of air with great avidity. Now, this absorbed air appears to affect in a minute degree the power of water to dissolve other bodies, at least a considerable part of it is extricated upon the solution of salts. When a bubble of air is thrown up into a solution of sulphate of soda, which has previously been boiled and deprived of all its air, a small quantity of air will certainly be absorbed by the solution around the bubble. A slight reduction in the solvent power of the menstruum will ensue at the spot where the air is dissolved. But the menstruum is greatly overloaded with saline matter, and ready to deposit; the slightest diminution of its solvent power may therefore decide the precipitation or crystallization of the unnatural excess of saline matter. The absorption of air may in this way commence and determine the precipitation of the excess of sulphate of soda in solution.

Here, too, we have an explanation of the fact just mentioned, that solutions of sulphate of soda, which have *not* been boiled, are less affected by exposure to the air than well-boiled solutions; for the former still retain the most of their air, and do not absorb air so eagerly on exposure as solutions which have been boiled.

But the theory was most powerfully confirmed by an experimental examination of the influence of other gases, besides atmospheric air, in determining crystallization. *Their influence was found to be precisely proportionate to the degree in which they are absorbed or dissolved by water and the saline solutions.*

To a solution of sulphate of soda over mercury, which had not been affected by a bubble of atmospheric air, a bubble of carbonic acid gas was added. Crystallization was instantly determined around the bubble, and thence through the whole mass. Water is capable of dissolving its



own volume of carbonic acid gas, and a solution of sulphate of soda, as strong as could be employed, was found by Saussure to absorb more than half its volume.

In a solution of sulphate of soda, which was rather weak, both common air and carbonic acid gas failed to destroy the equilibrium; but a small bubble of ammoniacal gas instantly determined crystallization.

When gases are employed which water dissolves abundantly, such as ammoniacal and sulphurous acid gases, the crystallization proceeds most vigorously. It is not deferred till the bubble of gas reaches the top of the receiver, as always happens with common air, and frequently with carbonic acid gas, but the track of the bubble becomes the common axis of innumerable crystalline planes, upon which it appears to be borne upwards; and sometimes before the ascent is completed, the bubble is entangled and arrested by crystalline arrangements which precede it.

The number of gases which are less soluble in water than atmospheric air is not considerable, but of these hydrogen gas was found to be decidedly less influential in determining crystallization.

Minute quantities of foreign liquids soluble in water likewise disposed the saline solution to immediate crystallization, as might be expected, and none with greater effect than alcohol. It is known that alcohol can precipitate sulphate of soda from its aqueous solutions. The soluble gases I suppose to possess a similar property.

These facts appear to warrant the conclusion that air determines the crystallization of supersaturated saline solutions by dissolving in the water, and thereby giving a shock to the feeble power by which the excess of salt is held in solution.

Before concluding, I may be allowed to make a remark on the usual description of the sudden congelation of the solution of sulphate of soda upon the admission of air. It is said that the solution expands in solidifying, in the same way as water does in becoming ice. But the expansion which takes place is merely temporary, and not due to such a cause, but entirely to a momentary dilatation of the whole contents of the phial, both liquid and solid, by the evolution of heat, which occurs on the instant of crystallizing, and which always amounts to  $20^{\circ}$  or  $30^{\circ}$ . That the salt does not permanently expand on crystallizing is easily proved by the sinking of a crystal in the densest solution of the salt which can be formed.



## VI.

A SHORT ACCOUNT OF EXPERIMENTAL RESEARCHES ON  
THE DIFFUSION OF GASES THROUGH EACH OTHER,  
AND THEIR SEPARATION BY MECHANICAL MEANS.

From *Quart. Journ. of Science*, ii. 1829, pp. 74-83. [Poggend, *Annal.* xvii. 1829, pp. 341-347 ; Schweigger, *Journ.* lviii. (= *Jahrb.* xxvii.) 1829, pp. 215-227.]

FRUITFUL as the miscibility of the gases has been in interesting speculations, the experimental information we possess on the subject amounts to little more than the well-established fact, that gases of a different nature, when brought into contact, do not arrange themselves according to their density, the heaviest undermost, and the lightest uppermost, but they spontaneously diffuse, mutually and equably, through each other, and so remain in an intimate state of mixture for any length of time. The beautiful illustrations of Mr. Dalton, by which this law was first developed, have rendered it familiar to every one. The subsequent experiments of Berthollet were made with uncommon care, and in most favourable circumstances, yet it is difficult to draw more from them than the same general fact ; unless perhaps that hydrogen is much more penetrating and diffusive than any of the other gases.<sup>1</sup> It is sufficiently evident, however, from Berthollet's experiments, that, in cases of gaseous mixture which are exactly similar, corresponding results may be expected, or that the diffusion is not accidental, but subject to fixed laws.

In the prosecution of further inquiry into the laws of the diffusion or miscibility of gases, much use was made of a cylindrical glass receiver A, 9 inches in length, and 0·9-inch internal diameter, divided into 150 equal parts, and provided with a stopper B, fitted into the mouth of the receiver by accurate grinding. The stopper was perforated longitudinally, cavity cylindrical, 0·34-inch in diameter, and 1·8 in length. Into the cavity of the stopper there was again ground a short piece of stout tube, having a bore of 0·07, or nearly  $\frac{1}{14.3}$  inch, and bent into a right angle in the middle ; such as C. These were the dimensions of tube A ; but after several experiments that tube was laid aside, and a second and a wider tube, of 0·12-inch bore and 2 inches in length, was ground into the aperture of the large stopper B, and bent in the middle, like tube C.



<sup>1</sup> Berthollet's experimental paper is contained in the *Mém. d'Arcueil*, vol. i. p. 463 ; but the whole experiments are given in a tabular form in Dr. Thomson's *System*, vol. iii. p. 33.



I. *On the Diffusion of the different Gases into Atmospheric Air.*

The receiver, above described, was filled in succession with various gases in a state of purity, and supported in a horizontal position upon a frame within a box, with the end of the bent tube pointing upwards, when the contained gas was heavier than air (*fig. 1*), and downwards, when the gas was lighter (*fig. 2*), to avoid any tendency of the gas to flow out of the receiver. After the gas had been allowed to diffuse into the air through the tube for a certain time, the receiver was transferred to the pneumatic trough, and the quantity of air which had entered, and gas that remained, ascertained. Two or three and sometimes more experiments were made on each gas, and the results found to be regular, or to vary within moderate limits.

FIG. 1.

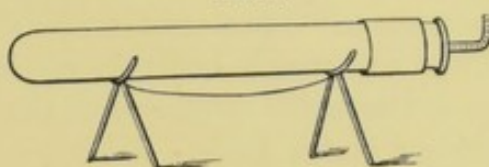
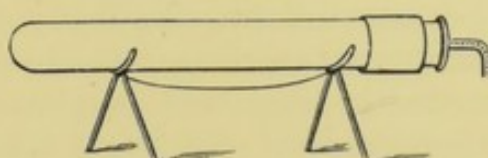


FIG. 2.



(1.) After diffusion for ten hours, through tube I, there was found in the receiver, of which the capacity = 150 parts—of

Hydrogen gas (sp. gr. 0.0694), . . . . .	8.3 parts.
Carburetted hydrogen of marshes (sp. gr. 0.5555), . . . . .	56
Ammoniacal gas (sp. gr. 0.59027), . . . . .	61
Olefiant gas (sp. gr. 0.9722), . . . . .	77.5
Carbonic acid (sp. gr. 1.5277), . . . . .	79.5
Sulphurous acid (sp. gr. 2.2222), . . . . .	81
Chlorine (sp. gr. 2.5), . . . . .	91

(2.) After diffusion for four hours through tube I—in 152 parts there was found—of

Hydrogen gas, . . . . .	28.1
Carburetted hydrogen, . . . . .	86
Ammoniacal gas, . . . . .	89
Olefiant gas, . . . . .	99
Carbonic acid, . . . . .	104
Sulphurous acid, . . . . .	110
Chlorine, . . . . .	116

There have, therefore, left the receiver in the same time—of

Hydrogen gas, . . . . .	123.9 parts.
Carburetted hydrogen, . . . . .	66
Ammoniacal gas, . . . . .	63
Olefiant gas, . . . . .	53
Carbonic acid gas, . . . . .	48
Sulphurous acid, . . . . .	42
Chlorine, . . . . .	36

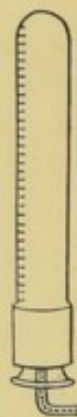


In deducing the comparative diffusiveness of the different gases from the table above, it is necessary to keep in mind the diminishing rate, according to which the latter portions of the gas leave the receiver. It was determined, with precision, in the case of olefiant gas, that that gas continues to leave a receiver, by diffusion, according to the same diminishing rate which holds in mechanical exhaustion by the air-pump. Hence the initial diffusions of the gases are even more varied than the numbers of the table. As much hydrogen gas left a receiver in two hours, as of carbonic acid in ten hours. Hence the former gas is five times more diffusive than the latter. In all cases the gases were necessitated to diffuse in *opposition* to the solicitation of gravity. Yet carburetted hydrogen and ammoniacal gases left the receiver in greater proportions than olefiant gas did, although the diffusion of the former gases was more opposed by mechanical causes.

It is evident that the diffusiveness of the gases is inversely as some function of their density—apparently the square root of their density.

The results, however, are much influenced by the mechanical resistance arising from gravity, which is not constant in gases of different densities, the position of the receiver remaining the same. The effect of the position of the receiver may be conceived from an experiment on hydrogen gas. The receiver, filled with hydrogen gas, was placed in an upright instead of a horizontal position (see *figure*). Other circumstances being the same as in the experiment of table (1), of 150 parts hydrogen 22.1 were found remaining in the receiver after diffusion for ten hours, instead of 8.3 parts, as in that experiment.

Although the stoppers fitted precisely, the additional precaution of luting the joinings was attended to. The properties of the receiver, too, were found not to be peculiar to it.



## II. *On the Diffusion of mixed Gases into Atmospheric Air.*

In the case of an intimate mixture of two gases, I was anxious to learn if each gas left the receiver, independently of the other, in the proportion of its individual diffusiveness—which would be a step gained in the solution of the important problem of the analysis of mixed gases by mechanical means.

For this purpose, the receiver was filled with 75 vols. hydrogen + 75 vols. olefiant gas, agitated and allowed to stand over water for 24 hours, that the mixture might be as perfect as possible. The receiver being then placed in the usual position, the mixed gases were allowed to



diffuse into the air for ten hours. The receiver thereafter was found to contain

Hydrogen gas,	.	.	.	.	.	3.5
Olefiant gas,	.	.	.	.	.	56.6
Air,	.	.	.	.	.	89.9
						<hr/>
						150.0

There have left the receiver—of

Hydrogen gas,	.	.	.	71.5 out of 75 parts.
Olefiant gas,	.	.	.	18.4      75

The more diffusive gas has, therefore, separated from the other, and left the receiver in greatest proportion.

Now, when the receiver contains nothing but pure olefiant gas, 72.5 parts of that gas leave the receiver in the circumstances of the preceding experiment. Hence, when the receiver is half filled with olefiant gas, we would expect the half of 72.5 parts, or 36.25 parts, to leave the receiver, and this happens when the complementary 75 parts are common air. But instead of 36.25 parts, only 18.4 olefiant gas leave the receiver in the last experiment. The disparity between the diffusion of each of the mixed gases, in that experiment, is actually greater than the disparity between the solitary diffusions of the same gases.

In the case of mixed gases, the law is—that the more diffusive gas leaves the receiver in a *greater* proportion than in the case of the solitary diffusion of the same gas, and the less diffusive gas in the mixture in a *less* proportion than in its solitary diffusion—a law of the diffusion of mixed gases, which was confirmed in upwards of forty experiments on diverse gaseous mixtures. Some of these experiments I shall subjoin.

(1.) The receiver was charged with

Carbonic acid,	.	.	.	.	75	} = 150
Hydrogen,	.	.	.	.	75	

which were allowed to mix intimately over night. The mixture was afterwards allowed to diffuse into the air through the tube for ten hours. Position horizontal, mouth of tube downwards. Thereafter contained,

Carbonic acid,	.	.	.	.	.	45
Hydrogen,	.	.	.	.	.	4.65
Air,	.	.	.	.	.	100.35
						<hr/>
						150.00

In this experiment, a portion of the carbonic acid may have *flowed* out, for at the end of the experiment the density of the gaseous mixture was greater than that of the atmosphere, while the mouth of the tube opened downwards.



(2.) Receiver charged with

Carbonic acid,	.	.	.	102	} = 152
Hydrogen,	.	.	.	50	

With tube II. Position of receiver horizontal, mouth upwards. After diffusing into the atmosphere for four hours, contained

Carbonic acid,	.	.	.	76
Hydrogen,	.	.	.	10.3
Air,	.	.	.	65.7

---

 152

(3.) Receiver charged with

Carbonic acid,	.	.	.	76	} = 152
Carbur. hydrogen (of marshes),	.	.	.	76	

Tube II, mouth upwards. After four hours, contained

Carbonic acid,	.	.	.	57
Carbur. hydrogen,	.	.	.	35.3
Air,	.	.	.	59.7

---

 152

Have left the receiver,

Carbonic acid,	.	.	.	19
Carbur. hydrogen,	.	.	.	40.7

or, twice as much carburetted hydrogen as carbonic acid has left the receiver. Of these gases individually, there left the receiver in the same circumstances,

Of Carbonic acid,	.	.	.	48
Carburetted hydrogen,	.	.	.	66

(4.) Receiver charged with

Carbonic acid,	.	.	.	52	} = 152
Carburetted hydrogen,	.	.	.	100	

Position, etc., as in preceding experiment. After four hours, contained

Carbonic acid,	.	.	.	39
Carbur. hydrogen,	.	.	.	51.6
Air,	.	.	.	61.4

---

 152

Have left the receiver,

Carbonic acid,	.	.	.	13
Carbur. hydrogen,	.	.	.	48.4

(5.) Receiver charged with

Carbonic acid,	.	.	.	31	} = 152
Carbur. hydrogen,	.	.	.	121	



Position, etc., as above. After four hours,

Carbonic acid, . . .	23
Carbur. hydrogen, . . .	71
Air, . . . . .	58
	<hr/>
	152

Have left the receiver,

Carbonic acid, . . .	8
Carbur. hydrogen, . . .	50

These three last experiments form a series. Suppose we had a mixture of two gases, of the same densities as carbonic acid and carburetted hydrogen, in equal volumes, but which could not be separated from each other by chemical means. Allow this gaseous mixture to diffuse for a certain time, as in Experiment 3, into a gaseous or vaporous atmosphere, which may afterwards be absorbed or condensed with facility. On condensing this atmosphere, there would remain a mixture, consisting of two parts of the light and one of the heavy gas.

By a similar diffusion of the mixture thus obtained, we would procure a third mixture, consisting of four parts of the light and one of the heavy gas (Experiment 4).

By a third diffusion, a mixture would be obtained of six or seven of the light and one of the heavy gas (Experiment 5).

In this way a specimen of the light gas would at last be eliminated, by a species of rectification, in a state of tolerable purity.

On the other hand, if a specimen of the dense gas be desired, a converse series of operations must be pursued. What remains in the receiver after diffusion must be preserved, accumulated, and submitted again and again to diffusion.

(6.) Receiver was charged with

Olefiant gas, . . .	76
Carburetted hydrogen, . . .	76
	} = 152

After four hours, contained,

Olefiant gas, . . .	47.75
Carbur. hydrogen, . . .	41.40
Air, . . . . .	62.85
	<hr/>
	152

Have left the receiver,

Olefiant gas, . . .	28.25
Carbur. hydrogen, . . .	34.60



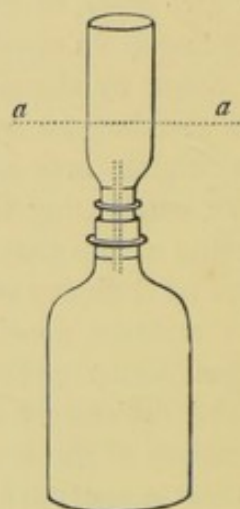
III. *Diffusion of Gases into other Atmospheres than Common Air.*

(1.) A phial, A, of 5·2 cubic inches, provided with a perforated cork, was filled with an intimate mixture of olefiant and hydrogen gases in equal proportions. The phial being held with its mouth undermost, a glass tube of 0·12 inch bore was thrust through the cork, and likewise quickly inserted into the perforated cork of another bottle, B, of 37

FIG. 1.



FIG. 2.



cubic inches, containing carbonic acid gas. The whole was then sunk in water till the surface of the water, *a, a* (*fig. 2*), rose above the joinings. After ten hours, the upper phial was removed, and its contents washed with lime-water. There remained a mixture, consisting of

Olefiant gas,	.	.	.	12
Hydrogen,	.	.	.	3·1

There can be no doubt that the olefiant gas would have been obtained in a state of greater purity had not the diffusion of the hydrogen gas been greatly impeded, 1st, from the direction in which it took place downwards; and, 2dly, from the density of the medium into which it diffused.

Had the mixture of olefiant gas and hydrogen been allowed to diffuse *upwards*, and into an atmosphere of specific gravity intermediate between that of its constituent gases—into steam or ammoniacal gas, for instance,—circumstances would have been most conducive to the unequal diffusion and separation of the mixed gases.



(2.) Hydrogen gas, in a tall receiver, is expanded by sulphuric ether, I find, four times more rapidly than common air. Mr. Leslie had already observed, that ice evaporates twice as rapidly in hydrogen gas as in common air; and he and Mr. Dalton found the cooling powers, or *mobility* of the different gases, to be inversely as their density.

(3.) Gases permeate with increased facility in both directions through the pores of porcelain tubes at high temperatures (Priestley), because, I believe, their tendency to diffusion, which is inversely as their density, is vastly increased by their rarefaction, and not from any dilatation of the pores of the porcelain, which must be utterly trivial in the most intense heat.

(4.) A tall receiver was  $\frac{3}{4}$ ths filled with a mixture of 2 hydrogen + 1 oxygen, which had remained mixed for three weeks, but was found sensibly pure before the experiment. A little ether being thrown up into the receiver, the experimental mixture rapidly expanded. The first bubble projected from the receiver by the expansion was received, deprived of all ether-vapour by washing, and, being exploded, left half its bulk of *pure hydrogen gas*.

(5.) The vapour of water appears, from the following experiment, to be more diffusive than the vapour of alcohol, as might be expected from the densities of these vapours. Of dilute alcohol (0.964), three ounces were exposed to spontaneous evaporation in a cylindrical jar two inches deep, and the same quantity in a jar six inches deep, but otherwise similar, the mouths of both jars being loosely covered with paper. When each of the vessels had lost half an ounce by evaporation, the remaining liquor was examined and found to contain sensibly more alcohol in the case of the deep than of the shallow jar. The difference, however, was altogether insufficient to enable us to account for the well-known experiment of the concentration of alcohol in a bladder, by referring it to the superior diffusiveness of water-vapour. But it is conceivable, and the subject is at present under investigation, that imperceptible pores, or orifices of excessive minuteness, may be altogether impassable (by diffusion) by gases of low diffusive power, that is, by dense gases, and passable only by gases of a certain diffusive energy. Hydrogen gas certainly escapes from a bladder more rapidly than any other gas, and probably from diffusion, as the place of the hydrogen is found occupied by common air. But to these investigations, and to certain theoretic considerations, I hope again to recur in a future paper.



## VII.

## OBSERVATIONS ON THE OXIDATION OF PHOSPHORUS.

From *Quart. Journ. of Science*, ii. 1829, pp. 83-88. [Poggend, *Annal.* xvii. 1829, pp. 375-380 ; Schweigger, *Journ.* lvii. (= *Jahrb.* xxvii.) 1829, pp. 230-240.]

WE are at present in possession of several curious facts respecting the insensible combustion of phosphorus at low temperatures.

1. In pure oxygen gas, under the atmospheric pressure, and at temperatures below  $64^{\circ}$ , the usual white smoke is not seen around phosphorus in daylight, and it is not luminous in the dark. No absorption of oxygen takes place.

2. A slight expansion of the oxygen gas, produced by diminishing the pressure upon it two or three inches below the usual pressure of the atmosphere, occasions phosphorus to be acted upon by pure oxygen, and to undergo slow combustion.

3. By diluting oxygen with certain gases, such as hydrogen, azote, protoxide of azote, carbonic oxide, carbonic acid, etc., the oxygen becomes capable of supporting the slow combustion of phosphorus even under the atmospheric pressure, as well as when rarefied by reduced pressure. Hence phosphorus is luminous in common air. The proportion of foreign gas necessarily varies according to the nature of the gas.

4. Certain other gases do not qualify oxygen to act upon phosphorus at low temperatures, in whatever quantity they may be added to it. This is the case with olefiant gas, and with azote obtained by the action of a paste of sulphur and iron on common air.

The first and third of these facts have been known for a long time ; the second was discovered by M. Bellani de Monza ; and the fourth appears to have been first observed by M. Thénard (*Traité de Chimie*, t. i. p. 236, where the subject is treated at length).

In experimenting upon this subject, another curious fact was noticed. The presence of a minute quantity of certain gases and vapours entirely prevents the usual action of phosphorus upon the oxygen of common air. Thus the slow combustion of phosphorus does not take place at all, at the temp. of  $66^{\circ}$ , in mixtures of

	Volumes of air.
1 volume olefiant gas and . . . . .	450
1 ditto vapour of sulphuric ether and . . . . .	150
1 ditto vapour of naphtha and . . . . .	1820
1 ditto vapour of oil of turpentine and . . . . .	4444



A stick of phosphorus was repeatedly left for upwards of twenty-four hours over water in air containing only one four-hundredth part of its bulk of pure olefiant gas, during the hot weather of July and August 1828, thermometer frequently above  $70^{\circ}$ , without diminishing the bulk of the air in contact. A slight expansion, amounting sometimes to  $\frac{1}{100}$ th part, occurred on several occasions. A stick of phosphorus, with a few drops of water, was corked up in a large retort, 213 cubic inches in capacity, and containing common air, with which  $\frac{1}{20}$ th of its bulk of pure olefiant gas had been mixed. During three months the phosphorus never became luminous, although its surface was gradually covered with a thin white crust. The water present was found to have become slightly acidulous.

The influence of a minute quantity of ether-vapour, in extinguishing the combustion of phosphorus at low temperatures, may be exhibited in a striking manner. Introduce two or three moist sticks of phosphorus into a pint-stoppered phial, into which, when filled with the white fumes, pour a little ether-vapour from the ether bottle. In a few seconds the fumes entirely disappear, and the air around the phosphorus becomes perfectly transparent. If the bottle is now stopped, white fumes do not again appear in it till the ether has passed entirely into acetic acid by combining with oxygen, which requires a few days.

Phosphorus is not luminous in the dark in air slightly impregnated with any other essential oil, as well as oil of turpentine. In an open two-ounce phial, phosphorus will appear brightly luminous in the dark; but the moment the phial is stopped with a cork, which has formerly confined an essential oil, and still sensibly retains its odour, the light begins to fade, and disappears entirely in a few seconds. The light from phosphorus in air at  $63^{\circ}$  F. is extinguished by the addition of four per cent. of chlorine gas, or twenty per cent. of sulphuretted hydrogen. The vapour from strong alcohol of about  $80^{\circ}$  in temperature extinguishes luminous phosphorus. But the vapours from camphor, sulphur, iodine, benzoic acid, carbonate of ammonia, iodide of carbon, do not produce that effect—thermometer  $67^{\circ}$ . Held in the mouth of a bottle containing strong muriatic acid, phosphorus appears to become more brilliant. But this is not the case with nitric or nitrous acids, which sensibly impair the light. The vapour from the liquor condensed in the vessels of the Portable Oil Gas Company, and coal gas, protect phosphorus from oxidation.

It is evident, from these experiments, that phosphorus cannot be used to withdraw oxygen from gaseous mixtures containing olefiant gas, or the different compounds of carbon and hydrogen allied to that gas. It may be employed as a test of their presence even in very minute quantity.



The influence of those gases in preventing the oxidation of phosphorus in air appears even at elevated temperatures. Phosphorus may be melted and kept for any length of time at  $212^{\circ}$ , without alteration, in air containing an equal volume of olefiant gas. In three parts air, with two parts sulphuric ether, phosphorus became faintly and transiently luminous in the dark at  $215^{\circ}$ —weak lambent flashes, which disappeared entirely at  $210^{\circ}$ , and were repeatedly revived and extinguished by alternately elevating and lowering the temperature between these limits. A pretty strong combustion occurred at  $240^{\circ}$ . The following table exhibits the temperature at which phosphorus first becomes faintly luminous in the dark in air containing different gaseous substances:—

In 1 volume of air and 1 volume of olefiant gas, at . . .	200° F.
3                   "                   2                   "                   vapour of ether, at . . .	215
111               "               1               "               vapour of naphtha, . . .	170
166               "               1               "               vapour of turpentine, at	186

The manner in which the influence of these gases is modified by barometric pressure is the most curious part of the subject. The proportion necessary to prevent combustion depends entirely upon the density of the gases. Thus, although less than one four-hundredth part of olefiant gas prevents the combustion of phosphorus—barometer 29 inches—phosphorus has been observed in a luminous state, under the pressure of half an inch mercury, in air containing so much as an equal volume of that gas.

In the following table, the first column of fractions expresses the largest proportion of olefiant gas, in a mixture of air and that gas, which allows phosphorus to be luminous under the pressure placed against it. A greater proportion of olefiant gas extinguishes at that pressure.

PHOSPHORUS LUMINOUS.				
Proportion of Olefiant Gas.	Olefiant Gas	+	Air	Barometric Pressure.
$\frac{1}{3}$	1	+	2	1.4 inches.
$\frac{1}{5}$	1	+	4	2.3
$\frac{1}{10}$	1	+	9	3.2
$\frac{1}{20}$	1	+	19	5.0
$\frac{1}{30}$	1	+	29	10.3
$\frac{1}{40}$	1	+	39	12.1
$\frac{1}{50}$	1	+	49	16.5
$\frac{1}{100}$	1	+	99	25.5
$\frac{1}{200}$	1	+	199	26.4
$\frac{1}{400}$	1	+	449	29.0



Thermometer at  $70^{\circ}$ . When phosphorus is luminous above the mercurial column in a barometer tube, at the greatest pressure possible for a particular mixture, a slight inclination of the tube from its vertical position, which has the effect of condensing the gas, extinguishes the light; while, on bringing back the tube to its vertical position, the phosphorus again becomes luminous.

The influence of other vapour on the oxidation of phosphorus, at various pressures, did not present any material differences from that of olefiant gas just detailed.

Naphtha and turpentine vapours appeared to lose their negative influence very rapidly as the pressure was reduced.

Carburetted hydrogen of marshes impedes to a certain degree, but does not altogether prevent, the oxidation of phosphorus. Its effect vanishes over a mercurial column of a few inches, a circumstance which will be attended to with advantage in removing, by means of phosphorus, the small portion of oxygen generally found in that gas.

The sulphuret of phosphorus and phosphuretted hydrogen gas are likewise protected from oxidation, to a certain extent, by olefiant gas, sulphuric ether, etc., although less powerfully than phosphorus, in proportion to their higher accendibility.

The oxidation of potassium appears likewise, from several comparative experiments, to be considerably retarded in dry air containing a fourth or fifth of its bulk of ether-vapour or olefiant gas, particularly of the latter. A piece of potassium, about the size of a pea, confined for a month in dry air, containing a fifth of its bulk of olefiant gas, was merely covered by a thin coating of grey oxide; while another piece of potassium, in similar circumstances, with the exception of the olefiant gas, was deeply penetrated with fissures of a kernel white.

The interference of those gases in preventing the oxidation of phosphorus, etc., is probably allied to the influence of the same and several other gases in preventing the accension of the explosive mixture of oxygen and hydrogen by the electric spark, first observed by Sir H. Davy (*Essay on Flame*), and since confirmed and investigated by Dr. Henry (*Phil. Trans.*, 1824), and Dr. Turner (*Edin. Phil. Journal*, vol. xi.) Olefiant gas was found to act most powerfully, half a volume preventing the combustion of the explosive mixture, that is, defending the hydrogen from oxidation; and here, as in the case of phosphorus, the olefiant gas seemed to suspend the usual action between the supporter and combustible, without undergoing any change itself. If the nature of this *influence* of olefiant gas is the same in both cases, it forms a singular and interesting subject of inquiry, readily accessible in its most minute details in the case of phosphorus.



## VIII.

## NOTICE OF THE SINGULAR INFLATION OF A BLADDER.

From *Quart. Journ. of Science*, ii. 1829, pp. 88, 89. [Schweigger, *Journ.* lvii.  
(=*Jahrb.* xxvii.) 1829, pp. 227-229.]

IN the course of an investigation respecting the passage of mixed gases through capillary openings, the following singular observation was made.

A sound bladder with stopcock was filled about two-thirds with coal gas, and the stopcock shut; the bladder was passed up in this flaccid state into a bell-jar receiver, filled with carbonic acid gas, and standing over water. The bladder was thus introduced into an atmosphere of carbonic acid gas. In the course of twelve hours, instead of being in the flaccid state in which it was left, the bladder was found distended to the utmost, and on the very point of bursting, while most of the carbonic acid gas in the receiver had disappeared. The bladder actually burst in the neck in withdrawing it from under the receiver. It was found to contain 35 parts of carbonic acid gas by volume in 100. The substance of the bladder was quite fresh to the smell, and appeared to have undergone no change. The carbonic acid gas, remaining without in the bell-jar, had acquired a very little coal gas.

The conclusion is unavoidable, that the close bladder was inflated by the insinuation of carbonic acid gas from without.

In a second experiment, a bladder containing rather less coal gas, and similarly placed in an atmosphere of carbonic acid gas, being fully inflated in fifteen hours, was found to have acquired 40 parts in 100 of this latter gas. A small portion of coal gas left the bladder as before.

A close bladder, half filled with common air, was fully inflated in like manner in the course of twenty-four hours. The entrance of carbonic acid gas into the bladder depends, therefore, upon no peculiar property of coal gas. The bladder, partially filled with coal gas, did not expand at all in the same bell-jar containing common air or water merely.

M. Dutrochet will probably view, in these experiments, the discovery of *endosmose* acting upon aeriform matter, as he observed it to act upon



bodies in the liquid state. Unaware of the speculations of that philosopher at the time the experiments were made, I fabricated the following theory to account for them, to which I am still disposed to adhere, although it does not involve the new power.

The jar of carbonic acid gas standing over water, the bladder was moist, and we know it to be porous. Between the air in the bladder and the carbonic acid gas without, there existed capillary canals through the substance of the bladder filled with water. The surface of water at the outer extremity of these canals being exposed to carbonic acid, a gas soluble in water would necessarily absorb it. But the gas in solution, when, permeating through a canal, it arrived at the surface of the inner extremity, would rise, as necessarily, into the air in the bladder and expand it. Nothing but the presence of carbonic acid gas within could prevent the disengagement of that gas. The force by which water is held in minute capillary tubes might retain that liquid in the pores of the bladder, and enable it to act in the transit of the gas, even after the pressure within the bladder had become considerable.

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## IX.

### CHEMICAL OBSERVATIONS ON THE APPLICATION OF SPONGY PLATINUM TO EUDIOMETRY.

From *Quart. Journ. of Science*, ii. 1829, pp. 354-359. [*Erdm. Journ. Tech. Chem.* viii. 1830, pp. 20-27.]

IN explaining the action of cold spongy platinum in disposing the union of mixed oxygen and hydrogen gases, it seems necessary to suppose that hydrogen is really accendible at common temperatures, but that its point of accension is unnaturally elevated in ordinary circumstances when it is not in contact with highly-divided matter, just as the boiling point of water and other liquids is elevated in smooth glass vessels. This view may be correct, although it only shifts the difficulty; for we have still to explain why hydrogen, if so accendible, does *not* take fire at superior temperatures when out of contact with minutely-divided matter. But there is an apparent analogy between the circumstances of the suspension of the combustion in the one case, and of the



ebullition in the other, on which the mind can rest with some satisfaction.

Soon after the discovery of Doebereiner, it occurred to both Dr. Henry and Dr. Turner to apply the principle to the analysis of mixed gases. But they immediately found that hydrogen could not at all times be withdrawn from a gaseous mixture by the action of spongy platinum, although the required addition of oxygen was made, as the action of that substance was paralysed or entirely suspended by the presence of certain gases in the mixture. The following table of Dr. Henry's exhibits the sum of our information on this subject.

"The first column exhibits the number of volumes of each gas required to render one volume of an explosive mixture of hydrogen and oxygen (in the usual proportion of two hydrogen to one oxygen) unflammable by the discharge of a Leyden jar; while the second column shows the number of volumes of each gas necessary, in some cases, to render one volume of an explosive mixture insensible to the action of the sponge, and in other cases indicates the number which may be added without preventing immediate combination.

"In the first column, the numbers marked with an asterisk were determined by Sir H. Davy: the remaining numbers in that column, and the whole of the second, are derived from my own experiments:—

One volume of explosive mixture was rendered incapable of being inflamed by electricity when mixed with

Effect of adding the same gases to one volume of explosive mixture on the action of the sponge.

About *8 vols. of hydrogen . .	not prevented by many vols.
" 6 " nitrogen . .	ditto.
" *9 " oxygen . .	not prevented by 10 vols.
" *11 " nitrous oxide . .	ditto.
" 1.5 " cyanogen . .	prevented by 1 vol.
" *1 " carbonized hydr. .	not prevented by 10 vols.
" 4 " carbonic oxide . .	prevented by $\frac{1}{2}$ vol.
" *0.5 " olefiant gas . .	prevented by 1.5 vol.
" *2 " muriatic acid . .	not prevented by 6 vols.
" 2 " ammoniacal . .	not prevented by 10 vols.
" 3 " carbonic acid . .	ditto.

From other observations of Dr. Henry, carbonic oxide appears to retard the combustion of hydrogen, by taking the precedence of the latter in uniting with oxygen, from superior inflammability. This I found to be much more strikingly the case with sulphuretted hydrogen



gas, which Dr. Turner found to suspend the action of the sponge, when present even in the most minute proportion. When mixed with oxygen, this gas slowly disappeared under the influence of a dried clay pellet, containing spongy platinum; the hydrogen only uniting with the oxygen, and the sulphur being deposited in the ball, which was soon thereby rendered inactive, but not till it had destroyed two or three hundred times its bulk of sulphuretted hydrogen in the course of twenty-four hours. In a mixture of sulphuretted hydrogen, hydrogen and oxygen gases in equal volumes, the oxygen united in twenty-four hours to the hydrogen of the sulphuretted hydrogen, nearly to the entire exclusion of the free hydrogen; but the union of the last with the remaining oxygen was determined in a few seconds by throwing up a fresh platinum ball.

Sulphurous acid gas is as efficient in this way as sulphuretted hydrogen (Turner); yet, upon trial, the sponge had no effect in determining the union of oxygen and sulphurous acid, even with the presence of moisture.

Olefiant gas in my hands was at first as powerful in preventing the combustion of explosive mixture as it was found to be by both Henry and Turner; but on washing that gas more sedulously with caustic potash, its interference was found to depend on a trace of impurities, for the ball always acted on explosive mixture within a few minutes, however largely diluted with this gas, if properly purified. Indeed, I had frequent occasion to separate hydrogen from olefiant gas, and found cold spongy platinum most effectual for the purpose. Neither did sulphuric acid vapour retard the action of the platinum; indeed, the other allowed the action to go on so rapidly, that from the elevation of temperature it was itself slightly acted upon, carbonic acid always appearing. The same was the case with the vapours of naphtha and the essential oils.

The action of these gases here, therefore, is unlike the action of the same gases and vapours in protecting phosphorus from oxidation.

The influence of sulphurous acid and sulphuretted hydrogen is not impaired by diminishing the barometric pressure.



## X.

ON THE LAW OF THE DIFFUSION OF GASES.<sup>1</sup>

From *Phil. Mag.* ii. 1833, pp. 175-190, 269-276, 351-358. [*Poggend, Annal.* xxviii. 1833, pp. 331-358 ; *Edin. Roy. Soc. Trans.* xii. 1834, pp. 222-258.]

It is the object of this paper to establish with numerical exactness the following law of the diffusion of gases :—

“The diffusion or spontaneous intermixture of two gases in contact is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas.”

These replacing volumes of the gases may be named *equivalent volumes of diffusion*, and are as follows :—air, 1 ; hydrogen, 3·7947 ; carburetted hydrogen, 1·3414 ; water-vapour, 1·2649 ; nitrogen, 1·0140 ; oxygen, 0·9487 ; carbonic acid, 0·8091 ; chlorine, 0·6325, etc.—numbers which are inversely proportional to the square roots of the densities of these gases, being the reciprocals of the square roots of the densities, the density of air being assumed as unity.

If the two gases are separated at the outset by a screen having apertures of insensible magnitude, the interchange of “equivalent volumes of diffusion” takes place through these apertures, being effected by a force of the highest intensity ; and if the gases are of unequal density, there is a consequent accumulation on the side of the heavy gas, and loss on the side of the light gas. In the case of air, for instance, on the one side of the screen, and hydrogen gas on the other, a process of exchanging 1 measure of air for 3·7947 measures of hydrogen, through the apertures, is commenced, and continues till the gases on both sides of the screen are in a state of uniform mixture. Experiments on this principle can be made with ease and precision, as will appear in the sequel, and afford an elegant demonstration of the law.

There is a singular observation of Doebereiner, which chemists seem to have neglected as wholly inexplicable, on the escape of hydrogen gas by a fissure or crack in glass-receivers, which belongs to this subject, and from which I set out in the inquiry. Having occasion, while engaged in his researches on spongy platinum, to collect large quantities of hydrogen gas, he accidentally made use of a jar which had a slight crack or fissure in it. He was surprised to find that the water of the pneumatic trough rose into this jar one and a half inches in twelve

<sup>1</sup> Read before the Royal Society of Edinburgh, Dec. 19, 1831, and now reprinted from the *Edin. Phil. Trans.*, with an Appendix communicated by the author.



hours, and that, after twenty-four hours, the height of the water was two inches two-thirds above the level of the water-trough. During the experiment, neither the height of the barometer nor the temperature of the place had sensibly altered.

In other experiments, he substituted glass vessels of very different forms, tubes, bell-jars, flasks, all of which had fissures. In every one of these vessels, filled with hydrogen, the water rose, after some hours, to a certain height. On covering one of these vessels, containing hydrogen, by a receiver—or on filling the vessel with atmospheric air, oxygen, or azote, instead of hydrogen—he never observed a change in the original volume of the gas. He thinks it probable that the phenomenon is due to the capillary action of the fissure, and that the hydrogen only is attracted by the fissures, and escapes through them on account of the extreme smallness of its atoms.<sup>1</sup>

This explanation is rendered improbable by the circumstance, that hydrogen, of all the gases, was condensed and absorbed with greatest difficulty, and in smallest quantity, by charcoal and the other porous substances, tried by Saussure. And we have no reason to suppose that the particles of hydrogen are smaller than those of the other gases.

On repeating Doebereiner's experiment, and varying the circumstances, it appeared that hydrogen never escapes outwards by the fissure without a certain proportion of air returning inwards. In the experiment, however, as originally performed, it is evident, that, as soon as the water rises in the jar above its outer level, air will begin to be forced into the jar mechanically through the fissure, by the pressure of the atmosphere, independently of what we shall suppose enters by diffusion. But if we press down the jar of hydrogen to a certain depth in the water-trough, so that the level of the water without is kept constantly higher than the level of the water within the jar, then, on the contrary, a portion of the hydrogen will be forced out mechanically by the pressure to which the gas is subject. In the last circumstances, however, no air can enter by the fissure, and mix with the hydrogen, except by diffusion, or in exchange for hydrogen. Now, in a great number of experiments of this kind, the air which entered by diffusion amounted to between one-fifth and one-fourth of the hydrogen, which left the receiver at the same time. But when the circumstances were reversed, and the column of water allowed to rise in the jar above the level of the water-trough, the quantity of air which entered by diffusion was increased by a portion which entered mechanically; and varied from a third to a fourth part of the hydrogen, which escaped at the same time. The results, therefore, oscillate, as they should do, about our theoretical

<sup>1</sup> "Sur l'Action capillaire des Fissures, etc." *Annales de Chimie et de Physique*, t. 24, pp. 332-334. 1823.



number. One volume air should replace 3.7947 volumes hydrogen; or the whole hydrogen, on escaping from the jar, should be replaced by little more than one-fourth of its bulk of air, and a very great contraction ensue.

But it is unnecessary to detail experiments made with the jar with the fissure, as with every precaution they were not precise, although at all times compatible with, and indeed illustrative of, the law. Thus a sensible contraction always took place in the bulk of the gaseous contents of the jar when filled with carburetted hydrogen of marshes, or with coal-gas, which, like hydrogen, are lighter than air, and ought therefore to be replaced by less than equal volumes of air. With olefiant gas and carbonic oxide, which approach closely to the density of air, no contraction was perceptible, not attributable to other causes, although the gases as usual wholly escaped. In the case of carbonic acid, which is heavier than air, a slight, but positive, expansion appeared to take place, the experiment being performed over mercury.

But the same fissure or opening never allows the process of diffusion to go on with the same degree of rapidity in two successive experiments, principally, I believe, from its size changing with variations in its condition in regard to humidity. The fissures appear to be extremely minute, for we cannot cause either air or the gas employed to flow through them mechanically, at the same rate as it passes by the agency of diffusion, without the application of considerable pressure. Artificial chinks, such as that obtained by pressing together ground glass-plates, or in phials fitted with accurately ground glass-stoppers, allow gas to pass through under the slightest pressure, and do not answer for the experiment.

The effects were made much more striking, in some respects, by the discovery that Wedgewood stoneware tubes, such as are used in furnace experiments, admit from their porous structure, of being substituted, instead of jars with fissures. When shut at one end, as they are sometimes made, they may be managed like other cylindrical gas receivers. Those which are unglazed are most suitable; but do not answer the purpose, if either very dry or too damp, being permeable by a gas under the slightest pressure in the one case, and perfectly air-tight in the other. The following experiment illustrates the force and rapidity with which diffusion proceeds. A stoneware cylinder was entirely filled with hydrogen gas over water, and transferred to the mercurial trough: in forty minutes the mercury rose to a height of  $2\frac{1}{2}$  inches in the receiver above the level of the mercury in the trough; half of the hydrogen had escaped, and had been replaced by about a third of its volume of air.

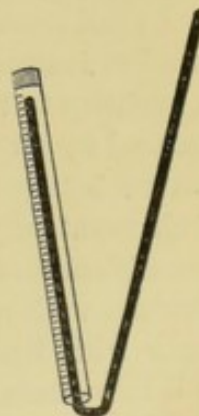
But these modes were superseded by the use of Paris-plaster as the porous intermedium.



A simple instrument, which I shall call a diffusion-tube, was constructed as follows. A glass-tube open at both ends was selected, half an inch in diameter, and from six to fourteen inches in length. A cylinder of wood, somewhat less in diameter, was introduced into the tube, so as to occupy the whole of it, with the exception of about one-fifth of an inch at one extremity, which space was filled with a paste of Paris-plaster of the usual consistence for castes. In the course of a few minutes the plaster set, and, withdrawing the wooden cylinder, the tube formed a receiver closed with an immoveable plug of stucco. The less water employed in slaking the Paris-plaster the more dense is the plug, and the more suitable for the purpose. In the wet state the plug is air-tight; it was therefore dried, either by exposure to the air for a day, or by placing the instrument in a temperature of  $200^{\circ}$  F. for a few hours; and thereafter was permeable by gases, even in the most humid atmosphere, if not positively wetted. The tube was finally graduated by means of mercury into hundredths of a cubic inch, and the notation, as is usual with gas-receivers, counted from the top.

When such a diffusion-tube, six inches in length, was filled with hydrogen over mercury, the diffusion, or exchange of air for hydrogen, instantly commenced, through the minute pores of the stucco, and proceeded with so much force and rapidity, that within three minutes the mercury attained a height in the receiver of upwards of two inches above its level in the trough. Within twenty minutes the whole of the hydrogen had escaped.

In conducting such experiments over water, it was necessary to avoid wetting the plug. With this view, before filling the diffusion-tube with hydrogen, the air was withdrawn by placing the tube upon the short limb of an empty syphon (see figure), which did not reach, but came within half an inch of the plug, and then sinking the instrument in the water-trough, so that the air escaped by the syphon, with the exception of a small measure, which was noted. The diffusion-tube was then filled up, either entirely, or to a certain extent, with the gas to be diffused.



The ascent of the water in the tube, when hydrogen is diffused, forms a striking experiment. In a diffusion-tube fourteen inches long, the water rises six or eight inches in as many minutes. The column of water attains in a short time its maximum height, at which, however, it is never long sustained; for, as in Doebeiner's experiment, air is all along entering mechanically through the porous plug, in such circumstances, from the pressure of the atmosphere; and after the diffusion is over, the water subsides, in the course of



several hours, to the general level. In experiments made with the purpose of determining the proportion between the gas diffused and the return-air, it was therefore necessary to guard against any inequality of pressure, which was managed much more easily when the tube was standing over water than over mercury.

The capacity of a mass of stucco to absorb and condense in its pores the various gases was made the subject of experiment, as this property might interfere with the results of diffusion. The mass was previously dried at 200° F. It absorbed at the temperature of the atmosphere, which at the time was 78°.

6.5	volumes ammoniacal gas,
0.75	„ sulphurous acid gas,
0.5	„ cyanogen,
0.45	„ sulphuretted hydrogen,
0.25	„ carbonic acid.

Oxygen, hydrogen, nitrogen, carbonic oxide, olefiant gas, coal-gas were not absorbed in a sensible proportion, even when the temperature was 58°. It is evident, therefore, that the absorbent power which stucco enjoys, as a porous substance, is inconsiderable. Placed in humid air, the same mass of stucco absorbed 1½ per cent. of hygrometric moisture. In setting, 100 parts of the stucco had retained twenty-six parts water uncombined, which escaped on drying at a moderate temperature, so as to avoid decomposing the hydrated sulphate of lime. It can be shown from this, that the vacuities must have amounted to one-third of the volume of the mass.

I shall treat in succession of the escape of the different gases from a diffusion instrument into air. As the contained gas bears no proportion in quantity to the external air, the gas escapes entirely, and is wholly replaced by air. It is of the utmost importance to determine the proportion between the volume of gas diffused, and the replacing volume of air eventually found in the instrument. We thus obtain the *equivalent diffusion-volume* of the gas, which it will be convenient to state in numbers with reference to the replacing volume of air as unity. I shall begin with hydrogen gas, although attended with peculiar difficulties, as it introduces in a distinct manner to our notice several circumstances which may slightly modify the results of diffusion.

### I. *Diffusion-volume of Hydrogen Gas.*

I shall in this paper adopt the specific gravities of the gases generally received in this country. Of hydrogen the specific gravity is



0.0694 (air=1), of which number the square root is 0.2635. Now, according to our law, 1 volume hydrogen should be replaced by 0.2635 air. But to have the replacing volume of air=1,

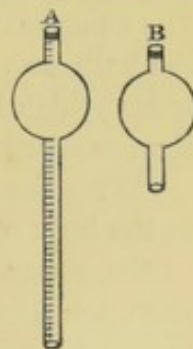
$$0.2635 : 1 :: 1 : 3.7947 ;$$

or,  $\frac{1}{0.2635} = 3.7947$ ; that is, 1 air should replace 3.7947 hydrogen.

With the specific gravity of hydrogen adopted by Berzelius, namely, 0.06885, the equivalent diffusion-volume of hydrogen is 3.8149.

In a diffusion-tube standing over water, temperature  $65^{\circ}$ , 88 volumes hydrogen were replaced by 26 air; 84 hydrogen by 25 air; and in another tube, 130 hydrogen by 38 air. The quantity of return-air is here related to the hydrogen diffused, as 1 to 3.38, 3.36, and 3.42, numbers which approach to, but fall short of, the theoretical diffusion-volume of hydrogen, namely, 3.79. But the hydrogen in these experiments was saturated with vapour at  $65^{\circ}$ , which would make its density 0.0809, and reduce its diffusion-volume to 3.5161; while the air without, being comparatively dry, would be somewhat expanded *after* it entered the diffusion-tube, by the ascent of vapour into it. This would occasion the quantity of return-air to appear greater than it should be; but it is difficult to find elements for a proper correction, as not only the quantity of vapour in the atmosphere must be taken into account, but also the hygrometric state of the plug itself. The increased return-air, however, evidently lowers the diffusion-volume of the hydrogen gas.

With the view of increasing the capacity of the instrument, and the number of its divisions, and of obviating the interference of vapour, the mode of performing the experiment was varied. On a tube, four-tenths of an inch in diameter, a bulb of two inches in diameter was blown, as in figures A and B. The tube above and below the bulb, in the case of A, was graduated into two-hundredths of a cubic inch. The upper end of the tube was closed by stucco, as in the case of the simple diffusion-tube. The general mode of proceeding will be best conceived from the recital of the details of a particular experiment.



The diffusion-instrument employed in the following experiment contained 855 measures, and was of the form A. The stucco plug was unusually large, being 0.6 inch in length, which occasioned the diffusion to be slow. At the commencement of the experiment the thermometer stood at  $68^{\circ}$ , and the barometer 29.73 inches. The bulb being sunk in water with the air-syphon in it, the whole air was withdrawn, with the exception of 12 measures, and the instrument filled up



with newly made hydrogen gas. So that at the outset we had in the instrument,

Air with its vapour, . . . . .	12
Hydrogen, . . . . .	823.83
Vapour (accompanying the hydrogen at 68°)	19.17
	<hr/>
	855.00

As soon as it was filled, it was placed in a glass-jar, of about the same height, with a little water left in the bottom, and in proportion as the water rose in the tube of A, from the subsequent contraction, the jar was filled up by repeated additions of water, so as to keep the surface of the water, within and without the tube, as nearly as possible at the same level. With the view of having the external air in a constant state in regard to humidity, means were taken to saturate it. A small cone of damp paper was inverted, like an extinguisher, over the upper part of the instrument; the jar containing the instrument was placed on the shelf of the pneumatic trough, and a bell-jar with an opening at the top, which could be shut at pleasure, inverted over the whole. The return-air must therefore have been in the same state, in regard to humidity, as the hydrogen itself. Aqueous vapour would diffuse neither outwards nor inwards, as it existed in the same proportion on both sides of the plug; but dry hydrogen only would be exchanged for dry air, in the proportion of their equivalent diffusion-volumes.

In the first thirty-four minutes, the gaseous contents of the bulb were diminished by 95 measures, and ultimately, in twenty-six and a half hours, they were reduced to 227 measures, which were common air. The contraction in this and other cases, in which the water rose into the bulb, was determined by weighing, at the end of the experiment, the water which had entered; a mode which admits of even greater nicety than measuring the bulk of residuary gas in a graduated vessel.

With the view of obtaining elements for a correction for any change in the bulk of the gas, which might take place during the continuance of the experiment, from changes in temperature, pressure or from solution of the gas in water, a receiver was made of the same tube, with a bulb of nearly the same capacity as the diffusion-instrument, but close at the top. This receiver was also nearly filled at the commencement of the experiment with hydrogen gas, and the quantity of gas noted, the tube being graduated. The hydrogen in this standard receiver contracted  $\frac{1}{8}$ nd part during the experiment. We have therefore to increase the quantity of air found ultimately in the diffusion-receiver by  $\frac{1}{8}$ nd part. In this way the residuary air is increased to 229.8 measures, 12 of which, or, more correctly, 11.85 ( $= 12 - \frac{1}{8}(12)$ ), were present from the beginning.





The temperature was also  $68^{\circ}$  at the end of the experiment, the same as at the beginning. The ultimate contents of the diffusion-instrument may be stated with sufficient accuracy as follows:—

Air and vapour originally present,	.	.	11.85
Dry air which has entered,	.	.	212.84
Vapour in ditto,	.	.	5.11
			<hr/>
			229.80

The conclusion is, that 823.83 measures dry hydrogen have been replaced by 212.84 dry air. Now,

$$\frac{823.83}{212.84} = 3.87 = \text{diffusion volume of hydrogen.}$$

The diffusion-volume of hydrogen comes out above the theoretical number in this experiment, but an addition of not more than 2 per cent. to the quantity of return-air would reduce it below the theoretical number. The quantity of vapour which was supported by the hydrogen at the commencement of the experiment was 19.17 measures, but at the end of the experiment we find only 5.11 measures vapour; the difference has condensed from the loss of a permanently elastic fluid necessary to support it.

As the quantity of hydrogen and of return-air is amplified in the same proportion by vapour, provided the temperature be the same at the beginning and end of the experiment, it is unnecessary to know the absolute quantity of vapour in either case in determining the diffusion-volume of hydrogen. We may simply divide the gross amount of hydrogen gas diffused by the gross amount of return-air; the quotient is the diffusion-volume of hydrogen.

*Experiment 2.*—The thickness of the stucco-plug in the instrument used above was reduced from six-tenths to two-tenths of an inch, by cutting away the upper portion. The instrument, of the same capacity as before, was now entirely filled with hydrogen gas. This was effected by first filling up with hydrogen, leaving a small quantity of air in the upper part of the instrument, as in the previous experiment, then withdrawing this impure hydrogen by the air-syphon, and filling up a second or third time with the same gas, whereupon the proportion of air remaining ceased to be appreciable. The apertures of the plug were closed, by pressing the finger upon its upper surface; and in this manner any diffusion of the hydrogen was carefully guarded against till the process of filling was completed. The diffusion was so rapid in the case of the thin plug that this additional precaution was absolutely required. Care was taken to have the return-air saturated with moisture in this and every other experiment of the same kind, and inequality of pressure was avoided.

At the beginning of the experiment, the instrument contained 855



measures hydrogen, saturated with vapour at  $62^{\circ}$ ; in three minutes a contraction of 95 measures took place, and in the course of an hour the diffusion was sensibly at an end. The instrument, however, was exposed for two hours longer, that the diffusion might certainly be complete. During intervals so short, uniformity of temperature might be counted upon, with certain precautions; and the variations in atmospheric pressure were generally so minute, that they might be neglected with impunity. Corrections for temperature and pressure might therefore be dispensed with, which was a great advantage. 855 measures hydrogen were found eventually to be replaced by 226.5 measures air, both saturated with vapour at  $62^{\circ}$ .

$$\frac{855}{226.5} = 3.774 = \text{diffusion-volume of hydrogen.} \quad \text{This determination}$$

is somewhat below the theoretical diffusion-volume, 3.79, while the preceding determination was in excess.

*Experiment 3.*—Another diffusion-instrument of the form B, with a dense plug, one-tenth of an inch in thickness, was filled with water, which was then poured into a counterpoised phial, and found to weigh 1085.7 grains. When filled over water, 1085.7 grain-measures of gas are therefore introduced into this instrument, and in this way we express most correctly its capacity. The instrument, after the plug was dried, was entirely filled with hydrogen gas, as in the preceding experiment, thermometer  $61^{\circ}$ . The bulk of the diffusion appeared to be over in an hour and a half, but five hours were allowed to the experiment. Thereafter the water, which had entered the instrument, was poured into a counterpoised phial, and found to weigh 800.6 grains. This last quantity represents the contraction, and subtracting it from 1085.7, we have the return-air equal to 285.1 grain measures. Now,

$$\frac{1085.7}{285.1} = 3.808 = \text{diffusion-volume of hydrogen gas.}$$

*Experiment 4.*—Same bulb, circumstances the same, but thermometer  $62^{\circ}$ . Time allowed for the diffusion four hours.

1085.7 measures hydrogen were replaced by 286.1 measures air.

$$\frac{1085.7}{286.1} = 3.795 = \text{diffusion-volume of hydrogen.}$$

*Experiment 5.*—Same bulb, etc., thermometer  $61^{\circ}$ . Time five hours.

1085.7 measures hydrogen were replaced by 278.4 measures air.

$$\frac{1085.7}{278.4} = 3.900 = \text{diffusion-volume of hydrogen.}$$

*Experiment 6.*—Same bulb, but in this and the succeeding experiment the bulb was attached to the end of a balance, and counterpoised, so that it adjusted itself spontaneously in the jar filled with water, in which it floated. Thermometer  $60^{\circ}$ .



1085·7 measures hydrogen were replaced by 279·1 measures air.

$$\frac{1085\cdot7}{279\cdot1} = 3\cdot890 = \text{diffusion-volume of hydrogen.}$$

*Experiment 7.*—Same repeated. Thermometer 61°.

1085·7 measures hydrogen were replaced by 282·2 measures air.

$$\frac{1085\cdot7}{282\cdot2} = 3\cdot847 = \text{diffusion-volume of hydrogen.}$$

The results of these five last experiments, with the same instruments, are, in one view,

Measures of Return Air.	Diffusion-volume of Hydrogen.
285·1	3·808
286·1	3·795
278·4	3·900
279·1	3·890
282·2	3·847
<hr/>	<hr/>
Mean, 282·2	Mean, 3·848

New hydrogen gas was made for each experiment by the moderate action of dilute sulphuric acid on zinc, and it was collected in the diffusion-instrument from the beak of the retort. The observations could not be made with so much accuracy as to entitle us to place any reliance on more than two decimal places of the calculated diffusion-volumes. A great variety of experiments were performed on the diffusion of hydrogen with the diffusion-bulbs employed above, and several others of similar construction, principally with the view of discovering the cause of the slight variations in the results, and why the quantity of return-air was pretty uniformly somewhat less than the theoretical quantity, which has the effect of increasing the proportion of the hydrogen diffusion-volume.

It appears that when the stucco-plug is in a parched state, the quantity of return-air is uniformly greater than it should be. Thus 3·65 and 3·69 were the diffusion-volumes of hydrogen deduced from an experiment, in the one case with a plug which had been dried at 100°, and subsequently exposed for several hours to the air, and in the other case with a plug merely dried in air, temperature 68°. The obvious cause of this is, that the air is dried in passing through the plug, and is subsequently expanded while in the diffusion-instrument by the ascent of vapour into it. Hence, the first time a diffusion-bulb is tried, it generally gives the diffusion-volume of hydrogen below the truth.

On the other hand, I apprehend that, when the pores of the stucco



are saturated with hygrometric moisture, which, from the circumstances of the experiments, must be almost always the case, the hydrogen, in making its way through the plug, actually avails itself to a small extent of this moisture, inducing it to vaporize, and exchanging places with it instead of air. Hydrogen, which escapes in this way, will not be represented by return-air, the quantity of which is thus diminished. This process, however, is extremely intricate, and has not yet been fully investigated. Its effect is insensible in the case of the other gases, of which the diffusion-volumes approach more closely to that of air.

The more dense and compact the plaster-plug, the more correct appear to be its general indications. On this account I compress the plug, while moist, before it sets. When the plug is of a loose structure, and probably contains sensible vacuities in its substance, diffusion goes on with increased rapidity; but I have observed that the proportion of return-air is notably diminished in the case of the diffusion of hydrogen. Thus, in a set of experiments with a diffusion-bulb, having a plug of this description, and little more than one-tenth of an inch in thickness, I obtained, as the diffusion-volume of hydrogen, 4.05, 4.04, and 4.00. This plug had been somewhat thicker at one time, and then gave 3.93 as the diffusion-volume of hydrogen. These experiments exhibit an extreme case of this deviation. It appears to depend upon some physical property of hydrogen gas which is peculiar to it. To obtain light upon this subject, I was led to investigate the rate at which air, hydrogen, and the other gases flow through the stucco-plug into a vacuum under the influence of mechanical pressure.

A small bell-jar, with an opening at top, was used, which opening was closed with a plug of Paris-plaster of half an inch in thickness, over which a brass cap and stopcock were fitted and cemented. This receiver was placed on the plate of an air-pump in perfect order, and exhausted. When the stopcock of the receiver was closed, nothing entered the exhausted receiver; but on opening it, either air entered, forcing its way through the pores of the stucco, or any gas which might be conducted to it, by means of a flexible tube from a proper magazine.

The time was noted in which the mercury of the gauge-barometer, in communication with the receiver, fell two inches, always setting out with gas of the tension of one inch mercury in the receiver, and stopping exactly when it attained a tension of three inches.

Air entered, according to eight or ten experiments made on different days, in within ten seconds, more or less, of ten minutes, and so whether the air was saturated with aqueous vapour or dry.

The same volume of different gases entered in the times expressed in the following table, under the same pressure, or beginning at a pressure of 29 inches mercury, and terminating with a pressure of 27 inches:—



	Minutes.	Seconds.
Air, dry, . . . . .	10	0
Air, saturated with moisture at 60°, . . . . .	10	0
Carbonic acid, . . . . .	10	0
Nitrogen, . . . . .	10	0
Oxygen, . . . . .	10	0
Carbonic oxide, . . . . .	9	30
Olefiant Gas, . . . . .	7	50
Coal Gas, . . . . .	7	0
Hydrogen, . . . . .	4	0

In repetitions of the experiments, the numbers oscillated 10, or 12, sometimes 20 seconds, on either side of the numbers given in the table, from circumstances which could not easily be appreciated. As the mercury in the gauge fell not continuously, but by leaps, from adhesion to the glass, the experiments are not susceptible of the greatest accuracy.

The greater the pressure the more rapidly are gases forced through the pores of the plug; but the quantity of gas which penetrates in any given time is not exactly proportional to the pressure, at least in the case of air and hydrogen. By doubling the pressure, we do not quite so much as double the quantity of gas forced through; or a fixed quantity of gas does not enter in half time under double pressure, as will be evident from the following table of observations. Pressure of atmosphere 30 inches.

Height of Gauge Barometer in inches of Mercury or Pressure.	AIR. Interval of Time in falling one inch by Gauge.		HYDROGEN. Interval of Time in falling one inch by Gauge.	
	Minutes.	Seconds.	Minutes.	Seconds.
29	0	0	0	0
28	5	0	1	50
27	5	23	2	0
26	5	15	1	55
25	5	30	1	55
24	5	35	2	0
23	5	45	2	2
22	6	0	2	13
21	6	5	2	10
20	6	30	2	35
19	6	35	2	30
18	7	3	2	40
17	7	12	2	50
16	7	35	3	10
15	8	10	3	30
14	8	40	3	35
13	9	10	4	5
12	9	55	4	10
11	11	0	4	15
10	11	40	4	30
9	12	30	5	20
8	14	15	7	40



The ratio of the times, in hydrogen and air, is not greatly different at different pressures. Thus the mercurial column was depressed 18 inches, or from 29 to 11 inches.

By air, in . 7283 seconds,

By hydrogen, in 3025 seconds,

$$\frac{7348}{3025} = 2.408 = \text{ratio of hydrogen,}$$

$$1. = \text{rate of air.}$$

It was found that the kind of gas in the receiver made no difference on the velocity with which hydrogen entered under a certain pressure. Hydrogen entered as rapidly against hydrogen in the receiver of a certain tension, as against air of the same tension. Thus,

Barometer Gauge. Height.	Hydrogen entered against Hydrogen. (From preceding Table.)		Hydrogen entered against Air.	
	Time.		Time.	
Inches.	Min.	Sec.	Min.	Sec.
15	0	0	0	0
14	3	37	3	35
13	3	56	4	5

It is evident from this, that the air does not diffuse out against so strong a pressure and the inward current of hydrogen.

When this jar, of which the capacity was 65 cubic inches, was used as a diffusion-instrument, and filled over water with hydrogen, one-fourth of the hydrogen which it contained escaped by diffusion into air in the first hour. Now, we find by the table (p. 55), that hydrogen penetrates the plug with greater velocity when passing into a vacuum or into the exhausted receiver. The exhausted receiver was filled one-fourth in about fifteen minutes; hence a certain quantity of hydrogen passed through the same porous plug, by the pressure of the atmosphere, into a vacuum in fifteen minutes; by spontaneous diffusion into air in sixty minutes; or the velocity of diffusion was one-fourth the velocity of mechanical pressure.

This was a dense and excellent plug; and in others of a looser texture, the velocity of diffusion was much less than a fourth.

Dried bladder answers for showing the diffusion of hydrogen when stretched over the open end of the tube receiver. The diffusion, however, through a single thickness of bladder, is effected at least twenty times more slowly than through a thickness of one inch of stucco. While, on the other hand, either air or hydrogen, under mechanical pressure, passes more readily through bladder than a great thickness of stucco. Goldbeaters' skin is even more permeable by gases under a slight pressure than bladder, and less suitable for diffusion.



The superior aptitude of stucco for exhibiting the unequal diffusion of gases of different densities, seems to depend upon its pores being excessively numerous, but exceedingly minute, making in the aggregate a considerable channel. In the bladder, or goldbeaters' skin, the pores I suppose to be few in number but wide, making, however, when added together, but a small channel. Air passes through them but little impeded by friction.

Dry and sound cork answers exceedingly well as a substitute for the stucco-plug. The diffusion takes place slowly, but is not apt to be deranged by a slight mechanical pressure. So do thin laminæ of many granular minerals, such as the flexible magnesian limestone, etc.; charcoal also, and woods, if not too porous, may be applied to the purpose.

It might occur, in explanation of our experiments with the diffusion-instrument, to take Mr. Dalton's hypothesis, and suppose, in the case of hydrogen, the external air to be a vacuum to the hydrogen, and the hydrogen a vacuum to the air, and that the *inequality* of the diffusion depends upon the hydrogen *being least resisted in passing through the plug*. The experiments on the permeability of the stucco by gases under pressure, above detailed, were projected with a view to settle this point among others; and they are evidently incompatible with such an application of the theory, for hydrogen passes 2.4 times more swiftly, and not 3.8 times, as in the diffusion experiments. Carbonic acid, too, permeates the plug, under pressure, as rapidly as air does, or even somewhat more rapidly, for our results inclined to this side rather than to the other; whereas carbonic acid diffuses through the plug more slowly than air does, or is replaced by more than an equal volume of air, as will presently appear.

Those experiments, previously narrated, are perhaps sufficient to establish the law in regard to hydrogen, particularly when we find it hold in the case of other gases.

As hydrogen is a very light gas, I was anxious to establish the law also in regard to a heavy gas, such as carbonic acid.

## II. *Diffusion of Carbonic Acid Gas.*

The most satisfactory experiments with carbonic acid gas were performed by confining it over a solution of common salt, saturated in the cold, which absorbs this gas very slowly, and, instead of the diffusion-instrument with bulb, a long diffusion-tube was found most suitable.

*Experiment 1.*—Thermometer  $64^{\circ}$ : dew-point  $53^{\circ}$ . Barometer 30.13. Left in diffusion-tube 17 air, and filled up over brine to 197 with carbonic acid gas, which gives 180 carbonic acid. As brine boils at  $222^{\circ}$  or  $224^{\circ}$ , that is  $11^{\circ}$  or  $12^{\circ}$  above the boiling point of water, we may suppose it



to be proportionally less vaporous at low temperatures, and take the tension of its vapour at  $64^{\circ}$  to be that of water at  $53^{\circ}$ , which was also the dew-point. This was confirmed by confining 847 volumes of atmospheric air over brine at the time; the air was not expanded by vapour rising into it from the brine, nor did it contract.

The initial contents of the diffusion are therefore,

Air and vapour, . . . . .	17.
Carbonic acid gas, . . . . .	177.6
Vapour, . . . . .	2.4
	<hr/>
	197.0

An expansion took place of 4 measures in ten minutes, and of 40 measures in five hours. A standard tube of the same diameter as the diffusion-tube, sealed at the top, had been filled with carbonic acid and placed over brine, to mark the absorption of the gas. One measure of gas was absorbed during the continuance of the above experiment. The expansion, therefore, in the diffusion-case has really been 41 and not 40, or, probably even more than 41, as undoubtedly a greater absorption of gas by the brine occurred in the diffusion-tube than in the standard-tube, from the motion of the liquid in the former during the course of the expansion of its gaseous contents, while the liquid in the other was quite at rest, and  $177.6 - 1$ , or 176.6 carbonic acid gas only have been exposed to diffusion. The diffusion was allowed to take place into the open air, which had the same proportion of vapour as the carbonic acid.

The specific gravity of carbonic acid gas is 1.527, of which the square root is 1.2360, and the reciprocal of the square root 0.8091. Hence one volume air should replace 0.8091 carbonic acid gas, which is the theoretical diffusion-volume of this gas.

In the experiment, 176.6 carbonic acid are replaced by 217.6 air.

Here, the expansion upon 176.6 carbonic acid being replaced by air is  $41 +$  parts by experiment, while it is 41.68 parts by theory.

The diffusion-volume of carbonic acid gas is,

0.812 by experiment,

0.809 by theory.

*Experiment 2.*—In another experiment, conducted in the same manner, thermometer  $64^{\circ}$ , barometer 30.00, the initial contents of the diffusion-tube were,

Carbonic acid and vapour, 201.

The final contents,

Air and vapour, . . . . . 245.

Correcting for loss of gas by absorption, the final contents would be,

Air and vapour, . . . . . 246.

As the proportion of vapour in the gas at the first, and in the air



finally is the same, we may say that carbonic acid is replaced by air in the proportion of 201 to 246.

$$\frac{201}{246} = 0.813 = \text{diffusion-volume of carbonic acid.}$$

*Experiment 3.*—In a third experiment over brine, thermometer 62°, barometer 29.65, carbonic acid and vapour, . . . 169  
 Replaced by air and vapour, . . . 205  
 Or, allowing for absorption, by air and vapour, . . . 206

$$\frac{169}{206} = 0.816 = \text{diffusion-volume of carbonic acid.}$$

But extreme accuracy is quite out of the question in the case of carbonic acid, from the vagueness of the small correction for absorption of the gas by the brine, and from the absorbent action of the plug, which affects, more or less, all the condensible gases.

The experiment in the case of this gas had been performed repeatedly over water itself, in different diffusion-tubes, and always with an eventual increase to the gaseous contents of the tube of within 2 per cent. of the theoretical quantity; but this mode, and the corrections for absorption, are decidedly inferior in precision to the preceding.

3. *Chlorine.*—This gas, from its high density, should afford a good illustration of the law, were other circumstances equally favourable, as the specific gravity of chlorine is about 2.5, of which the square root is 1.5811, and the reciprocal of the square root 0.6325. 100 measures of chlorine should be replaced by 158.11 air; or 1 air should replace 0.6325 chlorine, which is its diffusion-volume.

*Experiment.*—Thermometer 64°. To a diffusion-tube over water, with 5 measures air, 80 chlorine gas were added, making together 85 measures, which, diffusing into damp air, expanded 3 measures in the first eight minutes, 18 measures in eighty-two minutes, and, finally, 19 measures in one hundred and six minutes; but the same gas, in a close standard tube of the same diameter, contracted, owing to absorption of the gas by water, 5 measures in eight minutes, 15 measures in thirty-three minutes, and 18 measures in thirty-nine minutes, the rate of absorption diminishing evidently from the water in the tube becoming saturated and abiding in it. But the absorption of gas by water in the two experiments cannot be well compared; for, in the diffusion experiment, the chlorine is rapidly diluted with return-air, which protects it from absorption, and, indeed, before the end of the experiment, must occasion a portion of the dissolved chlorine gas to reassume the gaseous form, vaporizing away from the water which held it in solution, and rising into the upper part of the tube. The absorption in the diffusion-case would certainly be overrated at one-half of what occurred in the comparative experiment in the same time. At the outset, however, we



may presume that the same absorption took place in both cases. Hence the expansion in the diffusion experiment would be  $3 + 5$ , or 8 measures to the first eight minutes. The absorption, however, would tell two ways in lessening the expansion; *first*, so much gas has disappeared by absorption, the quantity to be added to the expansion; *second*, so much less chlorine has really been submitted to diffusion; 80 parts have not been diffused, but 80 diminished by this quantity.

Merely adding the observed absorption in the first thirty-nine minutes, namely, 18 measures to the expansion observed of 19 measures, we have an expansion from diffusion of 37 measures, which approaches, as near as we can expect from the method, to 45 measures, the theoretical expansion on 78 measures dry chlorine. We may therefore presume that the diffusion of chlorine is not incompatible with the law.

4. *Sulphurous Acid Gas*.—Over mercury. To diffusion-tube with 7 measures air, 66 dry sulphurous acid gas were added, which were allowed to diffuse into dry air. An expansion occurred of

5 measures in 9 minutes,			
13	„	23	„
30	„	85	„
31	„	108	„

at which last expansion it remained steady.

Assuming the specific gravity of sulphurous gas at 2.222, its square root is 1.4907, of which the reciprocal is 0.6708.

67.08 sulphurous gas should be replaced by 100 air.

We have 66 sulphurous gas, and expansion 31, or,

66 sulphurous acid are replaced by 97.00 air, by experiment;

66 „ „ „ 98.39 air, by theory.

The diffusion-volume of sulphurous acid gas is,

0.68 by experiment,

0.67 by theory.

5. *Protoxide of Nitrogen*.—In an experiment with this gas, dry, over mercury, allowing for a quantity of nitrogen which it contained, 51 measures were replaced in ninety minutes by 62 dry air. Taking the specific gravity of this gas at 1.2577, its root is 1.2360, of which the reciprocal is 0.8091.

Diffusion-volume 0.82 by experiment,

„ „ 0.81 by theory.

6. *Cyanogen*.—Also over mercury. First deprived of hydrocyanic acid by peroxide of mercury, and dried, an expansion always resulted from diffusion, but it never amounted to the theoretical quantity. Taking 1.8105 as the specific gravity of cyanogen, the square root is 1.3456, and the reciprocal of the square root 0.7432.

Hence, 1 cyanogen is replaced by 1.3456 air; and

1 air replaces, 0.7432 cyanogen.



1st, 83 cyanogen were replaced by  $99\frac{1}{2}$  air; 2nd, 75 cyanogen by 90 air; 3d, 50 cyanogen by 63 air. The last experiment is the most favourable. But 100 cyanogen are replaced, according to that experiment, by 126 air only, instead of 134. This deviation from the law depends on the property of the plaster-plug, which it shares with all porous bodies, to absorb and condense a portion of all those gases which, like cyanogen, are easily liquefied. It is evident, that if a portion of the cyanogen is withdrawn in this way, a certain contraction is occasioned, and again really less of the gas is submitted to diffusion; and from both causes, the expansion is less than it ought to be. It is possible, also, that the cyanogen may have contained a little nitrogen.

7. *Muriatic Acid Gas*.—Specific gravity 1.28472; square root, 1.1334; reciprocal of square root 0.8823. Hence,

1 muriatic acid should be replaced by 1.2847 air; and

1 air should replace 0.8823 muriatic acid.

In the case of this gas, the expansion from diffusion was overpowered by the absorbent property of the plug.

94 measures contracted to 88 in ten minutes, and remained at that quantity for nine minutes, and then expanded to 90 measures in twenty-five minutes more. The plug, upon a subsequent examination, appeared to be injured, and rendered too permeable, by a chemical action of the muriatic acid upon the hydrated sulphate of lime.

8. *Ammoniacal Gas*.—Density 0.5902. Square root 0.76825; reciprocal of square root 1.3016. Hence,

1 ammoniacal gas should be replaced by 0.76825 air; and

1 air should replace 1.3016 ammoniacal gas.

But in the case of this gas, as with muriatic acid, the result of diffusion is altogether deranged by condensation of gas in the porous plug, which, in these experiments, was half an inch in thickness. It is remarkable, however, that when the tube was filled with ammoniacal gas in the usual way, the final contraction was by no means excessive, indeed, never quite so great as it should have been from diffusion alone, independently of the contraction from absorption. This was found to arise from the absorption by the plug being so rapid, that, during the progress of filling the tube with gas, the plug became nearly saturated with gas, taking up ten or twelve times its bulk, and consequently, a great deal more gas was introduced into the tube than its capacity.

9. *Sulphuretted Hydrogen Gas*.—Prepared from sulphuret of antimony, by the action of muriatic acid. Density, 1.1805. Root, 1.0855. Reciprocal of root, 0.9204.

In the case of this gas, 69 measures were replaced by 73 air. In this experiment, 100 air replaced 95 instead of 92 sulphuretted hydrogen.



But we may refer the diminution to the absorption of the gas by the plug, and to its partial decomposition, as the mercury exposed to the gas became black. The air which entered contributed to this decomposition.

As carbonic acid is one of the gases condensed by the plug, like the preceding examples, but to a less extent, we can now understand why the return-air was always a little under the theoretical quantity, in the careful experiments on that gas, of which an account was formerly given.

In the case of the gases which follow, the specific gravity approaches so closely to that of air, that their accordance with the law requires every precaution.

10. *Oxygen Gas*.—Specific gravity, 1.111. Square root, 1.0541. Reciprocal, 0.9487.

100 oxygen should be replaced by 105.41 air; and

100 air should replace 94.87 oxygen.

When confined in a straight diffusion-tube, there is uniformly an expansion; but it is unnecessary to recount experiments performed with the straight tube, as the divisions are not minute.

*Experiment 1*.—Thermometer  $64^{\circ}$ . Barometer 29.82 inches. Diffusion-instrument with bulb, divided into two hundredths of a cubic inch; also standard bulb and tube, close at top, to afford corrections for changes in temperature and pressure, as before explained. Both diffusion-instrument and standard were filled with pure oxygen from chlorate of potash, and placed in glasses over water, covered by a bell-jar, of which the inside was moistened. A few minutes were purposely allowed to elapse before the quantity of gas in either instrument was noted, as the quantity oscillated for a little. The diffusion-instrument contained 795 measures oxygen, and the standard 828 at the outset. In two hours the expansion in diffusion-instrument, corrected from the standard, was 6 measures; in four hours and a half, 13 measures; in fifteen hours, 29 measures; in twenty hours, 34 measures; in twenty-nine hours, 41 measures; in thirty-eight hours, the expansion was at a maximum, namely, 43 measures. In explanation of the long duration of this and the following experiments, it may be stated, that the plug was fully half an inch in thickness.

795 measures oxygen and vapour have therefore been replaced by 838 measures air and vapour.

$$\frac{795}{838} = 0.9487 = \text{diffusion-volume of oxygen by experiment.}$$

This is the exact theoretic number; a coincidence, however, which we must view as accidental.

*Experiment 2*. In a careful repetition of this experiment with another



specimen of oxygen gas, the results approached very closely to the preceding; but the return-air was in slight excess above the theoretical quantity. Thus,

1 oxygen was replaced by 1.056 air, by experiment.

1 " " 1.054 air, by theory.

Oxygen, therefore, affords a most striking confirmation of the law.

11. *Nitrogen*.—Prepared by burning an excess of phosphorus in a confined portion of air, and allowing the residuary gas to stand over water for several days.

Specific gravity, 0.9722. Root, 0.9860. Reciprocal of root, 1.0140. 100 nitrogen should be replaced by 98.60; and 100 air should replace 101.40 nitrogen.

Thermometer 66°. Barometer 29.23. Diffusion into moist air as in the preceding experiments.

836 measures contracted 3 measures in two hours and forty minutes, as corrected by standard; and 13 measures in eighteen hours, which was the maximum contraction; for in twenty-three hours and a half from the beginning of experiment, a contraction of 12 measures was indicated. Taking the last as the true result,

$$\frac{836}{834} = 1.0143 = \text{diffusion-volume of nitrogen by experiment.}$$

$$1.0140 = \text{diffusion-volume of nitrogen by theory.}$$

12. *Olefiant Gas*.—Specific gravity likewise 0.972, etc., as in nitrogen. The gas was carefully made, collected in a low receiver, allowed to stand over water for twenty-four hours, and finally washed with caustic ley.

Thermometer 59°. Barometer 29.83. 800 measures of this gas were replaced by 785 measures of air, in twenty-five hours, correcting from standard.

$$\frac{800}{785} = 1.0191 = \text{diffusion-volume of olefiant gas, by experiment.}$$

The contraction in this experiment is a little above the theoretical quantity. In another experiment with different gas, the contraction was even greater, indicating a diffusion-volume = 1.0303; but the presence of a minute quantity of carburetted hydrogen, or some lighter hydro-carburet, was suspected, from the rapidity of the contraction in this case.

13. *Carbonic Oxide*.—Specific gravity, 0.9722, etc., as in the case of nitrogen. Gas prepared by the action of sulphuric acid on crystallized oxalic acid, well washed with caustic ley.

On 803 measures carbonic oxide and vapour, a contraction of 11 measures in fifty hours, 12 measures in eighty-nine hours, 12 measures in ninety-seven hours; or 803 became 791. The diffusion was slower



than usual, from the plug having been partially wetted in filling the instrument with gas.

$$\frac{815}{803} = 1.0149 = \text{diffusion-volume of carbonic oxide, by experiment.}$$

$$1.0140 = \text{diffusion-volume of carbonic oxide, by theory.}$$

In the case of the last three gases, when the experiment was performed over water in a diffusion-tube, with free exposure to the dry atmosphere, instead of any contraction ensuing, a positive expansion generally occurred, which was to be attributed to the return air, which was comparatively dry, being expanded after entering the receiver.

14. *Carburetted Hydrogen of Marshes*.—Specific gravity, 0.555. Diffusion-volume, 1.3414.

In an experiment with this gas, deducting a small quantity of air which it contained, 252 measures were replaced by 187 air.

$$\frac{252}{187} = 1.344 = \text{diffusion-volume, by experiment.}$$

$$1.341 = \text{diffusion-volume, by theory.}$$

These are all the permanent gases which could conveniently be submitted to diffusion. Vapours cannot be rigidly examined, as they are all condensible in the pores of the stucco. The following Table exhibits a summary of the results:—

*Table of Equivalent Diffusion-volumes of Gases; Air = 1.*

	By Experiment.	By Theory.	Spec. Gravity.
Hydrogen, . . . . .	3.83	3.7947	0.694
Carburetted Hydrogen, . . .	1.344	1.3414	0.555
Olefiant Gas, . . . . .	1.0191	1.0140	0.972
Carbonic Oxide, . . . . .	1.0149	1.0140	0.972
Nitrogen, . . . . .	1.0143	1.0140	0.972
Oxygen, . . . . .	0.9487	0.9487	0.111
Sulphuretted Hydrogen, . .	0.95	0.9204	1.1805
Protoxide of Nitrogen, . . .	0.82	0.8091	1.527
Carbonic Acid, . . . . .	0.812	0.8091	1.527
Sulphurous Acid, . . . . .	0.68	0.6708	2.222

In the diffusion-volumes of oxygen, nitrogen, and carbonic oxide, the correspondence between theory and experiment is as close as could be desired. Indeed, admitting our law, I believe that the specific gravity of these gases can be determined by experiments on the principle of diffusion, with greater accuracy than by the ordinary means. But, to be of value, experiments performed with this important object in view, would require to be conducted with extreme care, in the most favourable circumstances, as regards uniformity of temperature, and to be frequently repeated. The diffusion-bulbs might also be considerably increased in



size, and a greater minuteness of observation attained. Even in the most successful experiments recited in this paper, we cannot depend upon the absolute accuracy of the third decimal figure. In the case of carbonic acid gas, protoxide of nitrogen, sulphuretted hydrogen, and sulphurous acid, the process of diffusion is interfered with in a greater or lesser degree by the absorbent action which all porous bodies exercise upon gases. Fortunately, however, the absorbent power of stucco is very low in degree.

The density of any gas diffused into air, both being in the same state as to aqueous vapour, is obtained by the formula

$$D = \left(\frac{A}{G}\right)^2;$$

where G is the volume of gas submitted to diffusion, and A the volume of return-air. In operating upon gases lighter than air, the most useful instrument is a bulb of about two inches in diameter blown upon half-inch tube, of which about an inch may be left on either side of the bulb. The capacity of the instrument, *used as a gas-receiver over water*, is most simply determined by filling it with water, and weighing the water which it contains, and which can be poured from it into a counterpoised phial. Then, after any experiment, the return-air may be found from the weight of the water which has entered the instrument, determined in the same manner. By proceeding in this way, we avoid wetting the stucco after every experiment. A hood of damp paper may be inverted over the upper tube while the diffusion is going on, and the whole counterpoised in a tumbler of water, being suspended from one of the arms of the beam of a balance, the scale on that side being removed. An experiment with the bulb will generally occupy several hours. But with a plain diffusion-tube, a much shorter time will suffice.

A peculiar advantage of this mode of taking the specific gravity of gases, besides its simplicity, is, that we can operate upon a most minute quantity of gas: it is possible to come within 100th of the specific gravity, operating upon no more than one cubic inch of gas.

It is to be regretted that this method is not so fully available in the case of coal-gas as might be expected. The density of that gaseous mixture appears to depend, in no inconsiderable measure, upon the presence of a small quantity of the heavier hydro-carburets, such as naphtha-vapour; and these are apt to be absorbed and withdrawn in part by the water during the continuance of a diffusion experiment. I have observed coal-gas to contract  $\frac{1}{10}$ th of its bulk by standing over water, without agitation, for forty-eight hours, and from the loss of the denser portion of it. But in the case of this gas, the experiment should succeed over brine, which absorbs much less of the gas than water does.



The process of diffusion may be managed so as to demonstrate relations in density. The short upper tubes of two diffusion-bulbs, not closed by plaster, but open, were connected by means of thick caoutchouc adopters, with the two ends of a short piece of straight tube, in which there was a diaphragm of plaster  $\frac{1}{4}$ th of an inch in thickness, and equidistant from either end of the tube. The apparatus being proved air-tight, and the plug in a proper condition for diffusion, one of the diffusion-bulbs was filled with nitrogen gas, and the other with carbonic oxide, and the bulbs placed upright in separate contiguous glasses containing water. The quantity of gas in each was carefully observed at the beginning of the experiment; and after the expiry of twenty-four hours, when it was found to be identically the same as at first; at least, if a contraction or expansion took place, it was the same in both bulbs, and therefore entirely due to changes in temperature or pressure. Now, the gases were found by analysis to be uniformly diffused through both bulbs; so that nitrogen and carbonic oxide are of the same density, or at least do not differ more than  $\frac{1}{300}$ th part, which was the limit of the observation in the case of these experiments. It appears, also, that inequality of density is not an essential requisite in diffusion.

I had occasion to remark, more than once, a singular accident to the stucco plugs. After being disused for some days or weeks, and left in the interval exposed to the air, which might be either dry or damp at the time, the plugs occasionally, on a new trial, did not permit diffusion to take place through their pores, at least immediately. Hydrogen, however, always opened a passage in the course of two or three minutes, and then the diffusion proceeded as rapidly as ever. Carburated hydrogen, and the other gases, often required a longer period. A slight heat restored the action of the plug. The obstruction could not be attributed to moisture, nor to anything but dust.

It may be mentioned that there was nothing peculiar in a mixture of two gases in the proportion of the numbers expressing their diffusion-volumes;—nothing that could be considered an indication of mutual saturation.

Evaporation, or the elevation of vapour from a liquid into air, or any other gas, comes now to be explained on the principles of diffusion. The powerful disposition of the particles of different gaseous bodies to exchange positions may as effectually induce the first separation of vapour from the surface of the liquid, as a vacuum would do. Once elevated, the vapour will be propagated to any distance by exchanging positions with a train of particles of air, according to the law of diffusion. The length to which this diffusion proceeds, in a confined portion of air, is limited by a property of vapour, namely, that the particles of any



vapour condense when they approximate within a certain distance. Hence, the quantity of vapour which rises into air has the same limit as that which rises into a vacuum, and is the same.

I may be allowed to mention an application of the law of diffusion, in explanation of the mechanism of respiration. The cavity into which air enters during respiration consists, first, of a large tube, the windpipe; secondly, of smaller tubes, into which the windpipe diverges; and, thirdly, of a series of still smaller tubes, diverging from the last, themselves ramifying to an indeterminate extent, till at last the tubes cease to be of sensible magnitude, but are believed to terminate in shut sacs. The capacity of the whole cavity cannot easily be determined, but we may estimate it at 300 cubic inches. In a natural expiration, about 20 cubic inches, or  $\frac{1}{15}$ th of the contents, are thrown out from the application of a general pressure to the whole. But it is evident that these twenty cubic inches will be the twenty cubic inches nearest the outlet, or the contents of the larger tubes. The contents of the second-sized tubes will advance at the same time into the largest tubes, but no further, and will recede again into their original depositories on the next inspiration, which will fill the larger tubes with fresh air; which identical quantity will again be expelled in the next expiration. This illustration is perhaps too strongly stated; but it is evident that, in ordinary respiration, the slight mechanical compression will have little or no effect in emptying the most distant tubes, or the ultimate air-cells, of their contents. The bulk of the air, also, is not altered during respiration, although, for a quantity of oxygen, carbonic acid gas is substituted. This substitution, which is the great end of respiration, undoubtedly takes place most abundantly in the minute and distant air-cells, which present the largest surface to the blood; and the carbonic acid there produced must be moved along the smaller tubes by the diffusion process (which we know to be extremely energetic, and also inevitable), till it is thrown into the larger tubes, from which it can be expelled by the ordinary action of respiration. But the action of diffusion is always twofold; at the same time that carbonic acid is being carried outward from the air-cells, oxygen is carried inward in exchange, and thus the necessary circulation kept up throughout the whole lungs.

Further, by a forced expiration, from 160 to 178 cubic inches may be expelled, after which there still remain in the lungs about 120 cubic inches, which are not under the control of the respiratory action.

There can be no doubt that much of this quantity occupies constantly and permanently the most minute tubes and air-cells, for it can scarcely be withdrawn by means of the air-pump. Now, the question has arisen, how these ultimate tubes and air-cells are so powerfully



inflated; for they are not distended by the action of muscular fibre, of which they are known to be destitute. This state of distention must be highly useful by exposing surface, and the law of diffusion enables us to account for it. The heavy carbonic acid which these minute cells may contain is not merely exchanged for oxygen, but for a larger volume of oxygen, in the proportion of the diffusion-volumes of carbonic acid and oxygen, namely, 81 carbonic acid are replaced by 95 oxygen. The resistance to passage through the most minute tubes is overcome by the diffusion action, as in the case of the pores of the stucco-plug, and there follows a tendency to accumulation on the side originally occupied by the carbonic acid. This accumulation is limited by the increased facility with which the air-vessels can empty themselves mechanically of a portion of their contents from their distended state.

In the law of diffusion of gases, we have, therefore, a singular provision for the full and permanent inflation of the ultimate air-cells of the lungs.

But it is in the respiration of insects that the operation of this law will be most distinctly perceived. The minute air-tubes accompanying the blood-vessels to every organ, and like them ramifying till they cease to be visible under the most powerful microscope, are kept distended during the most lively movements of the little animals, and the necessary gaseous circulation maintained, wholly, we may presume, by the agency of diffusion.

In regard to the terms of the law of diffusion: "The diffusion, or spontaneous intermixture of two gases in contact, is effected by an interchange in position of *indefinitely minute volumes of the gases*." My experiments, published on a former occasion, on the diffusion of mixed gases (*Quarterly Journal of Science*, p. 28, Sept. 1829), afford the first demonstration of the fact that diffusion takes place between the ultimate particles of gases, and not between sensible masses, and therefore that diffusion cannot be the result of accident. For, in the case of a mixture of two gases escaping from a receiver into the atmosphere, by apertures of 0.12 and 0.07 inch in diameter, it was not so much of the mixture which left the receiver in a given time, but a certain proportion of each of the mixed gases, independently of the other, corresponding to its individual diffusiveness. The same separation of mixed gases occurred in diffusion through the pores of stucco, or the fissure of a cracked jar.

"Which volumes are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas." This may be demonstrated when different gases communicate by very narrow channels, or by very small apertures, and and when inequality of pressure is guarded against. In the case of a gas communicating with the air by a wide aperture, on the other hand,



although the diffusion or intermixture takes place precisely in the same way, still the result is different; for where a contraction takes place from the process of diffusion, the air flows in mechanically through the aperture, wholly unresisted, and makes up the deficiency. A gas, however, of large diffusion-volume escapes, in these circumstances, *in a shorter time* than a gas of small diffusion-volume. Indeed, it was the conclusion of the former paper, that gases diffuse more or less rapidly according to some function of their densities, "apparently inversely as the square root of their densities." The advantage, in illustrating the process of diffusion of minute apertures or channels of communication, such as we have in the stucco-plug, depends upon the circumstance that, when a contraction or expansion takes place in the gaseous contents of a diffusion-instrument, any current in an outward or inward direction is prevented by frictional resistance; so that the simple result of diffusion is exhibited, not complicated by the effect of any other force.

The law at which we have arrived (which is merely a description of the appearances, and involves, I believe, nothing hypothetic) is certainly not provided for in the corpuscular philosophy of the day, and is altogether so extraordinary that I may be excused for not speculating further upon its cause, till its various bearings, and certain collateral subjects, be fully investigated.

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#### SUPPLEMENTARY OBSERVATIONS

##### ON THE LAW OF THE DIFFUSION OF GASES.

It is curious that intermixture takes place more rapidly in the case of some gases than in that of others, although still in conformity with the law of diffusion. Thus the process goes on with much greater activity in the case of hydrogen, olefiant gas, and coal gas diffusing into air, than in the case of chlorine, carbonic acid, carbonic oxide, etc., diffusing into the same medium. This is very observable on comparing the times as stated in describing the experiments on each gas.

The circumstance of the apertures being in the upper part of the diffusion-instruments, and opening upwards, may be supposed to give the light gases an advantage in diffusing; but I am disposed to attribute little of the inequality in question to this cause. From a diffusion-bulb, in which the upper tube was curved and bent downwards, hydrogen gas was found to escape with its wonted rapidity.

This inequality in the velocity of diffusion is strikingly illustrated in the following results, obtained from experiments with different gases,



submitted in turn to diffusion from the same instrument. In a certain time, the same in all the experiments, a quantity of air entered, by diffusion, which varied with the gas diffusing.

In a given time,

With chlorine in the diffusion-tube 0.302 vol. air entered.

With carbonic acid . . . . . 0.623 ”

With hydrogen . . . . . 1.277 ”

It appears, then, that the process of diffusion into air through stucco is four times more rapid in the case of hydrogen than in that of chlorine, and twice as rapid in the case of the former gas as in carbonic acid. The process of diffusion might be said to proceed at a uniform rate, if the same quantity of air entered the instrument in the same time, whatever gas was diffused, and although the quantity of gas which escaped was variable of course, and proportional to the respective diffusion-volume of the gas. But this exchange of diffusion-volumes takes place more rapidly, it appears, in the case of some gases than of others.

A table of experiments is given in the body of the paper (p. 55) on the rate of passage of different gases through the pores of stucco under the influence of pressure. The rate appears to be the same in the case of air, nitrogen, oxygen, and carbonic acid, from which carbonic oxide deviates in a small degree. But hydrogen, and, it is remarkable, olefiant gas and coal gas, which contain hydrogen, are less resisted than the preceding class. Upon reconsideration, I am inclined to connect with this fact the apparent deviation of hydrogen from the law of diffusion, which is noticed in the paper. It is there shown that more hydrogen passes out than the exact quantity proportional to the return-air. The same deviation from the law may be remarked in the experiments detailed on olefiant gas. It is also very noticeable in the case of coal gas. But these are gases which, like hydrogen, are less resisted than common air in their passage through stucco. There appears to exist an inaptitude on the part of a stucco intermedium to exhibit the exact effect of diffusion, in the case of gases, on either side of it, which are not capable of permeating through it with equal facility; that gas which experiences least frictional resistance diffusing through in a quantity somewhat greater than it should do.

There can be no doubt that the velocity of diffusion noticed above is likewise influenced by the variable resistance which the gases experience in passing through the stucco. But I am not prepared to say that the variation depends entirely on this cause, and is therefore accidental to the mode in which the diffusion takes place. The diffusion or intermixture of *light* gases appears to take place in all circumstances with greater rapidity than that of heavy gases.

THOMAS GRAHAM.

GLASGOW, Sept. 7, 1832.



## XI.

ON PHOSPHURETTED HYDROGEN.<sup>1</sup>

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FEW substances have been made the subject of experimental inquiry more frequently than the compounds of phosphorus and hydrogen, and no subject is so remarkable for the various and conflicting results which it has presented to chemists of the greatest acuteness and practical skill. The obscurity which long hung over the subject has been dispelled, however, in a great measure, by the recent investigations of Henry Rose of Berlin. Although baffled in his early researches, that philosopher returned again and again to the subject, and at last succeeded in determining the chemical functions and true constitution of phosphuretted hydrogen. He has shown it to be analogous to ammonia in chemical character and composition. But hitherto two compounds of phosphorus and hydrogen had generally been admitted to exist, which were believed to differ in composition, as they do in properties, one being spontaneously inflammable in atmospheric air, and the other not so. Rose establishes beyond all doubt that these gases are essentially of the same composition, and of the same specific gravity ; and, indeed, that they are mutually convertible, each into the other, without any addition or subtraction of matter that could be perceived. In explanation of their possessing different properties, under the same composition, allusion is made by Rose to *Isomerism*, or the doctrine that two bodies may exist identical in composition, but differing in properties. Certainly the existence of *two gases*, constituted alike, and yet possessing different properties, if established, would afford a firm basis for this doctrine.

It was the importance of the theoretical results which might be looked for, that induced me to attempt to continue the investigation beyond the point to which it had been carried by Rose.

Holding the general doctrine of *Isomerism* as problematical, my inquiries were directed to the discovery, in one or other of the gases, of some adventitious matter, to the presence of which the peculiarities of the species might be attributed.

It is to be understood that the spontaneously inflammable gas made use of in my experiments was prepared by the well-known process of heating phosphorus, lime, and water together. This gas is spoken of as "the self-accendible gas," or as "the gas from phosphuret of lime." The other gas, which is *not* spontaneously inflammable, was prepared by

<sup>1</sup> Read before the Royal Society of Edinburgh 1st Dec. 1834.



heating hydrated phosphorous acid, or by allowing the preceding species, contained in low receivers, to stand over water for twenty-four hours. It is described as "the non-accendible gas," the gas from phosphorous acid. The accendibility of the gas was judged of by allowing it to escape in bubbles into the air from the receiver containing it, either over water or mercury. The experiments were all made when the temperature of the atmosphere was between  $60^{\circ}$  and  $70^{\circ}$  Fahrenheit.

1. In the process by which the self-accendible gas is procured, free phosphorus distils over, of which a trace, in the state of vapour, may well be supposed to remain in the gas for some time. Hence the idea has generally presented itself, that the free and highly accendible phosphorus present may be the cause of the spontaneous inflammability of the gas. Dr. Dalton, who all along maintained the opinion, which has finally been established by Rose, that the two gases are of the same composition, was in the habit of referring the spontaneous inflammability of the one species to this cause. The speedy loss of the property in question, in the case of gas confined over water, seemed to favour this view. I find, however, that if a small quantity of phosphuretted hydrogen, when not self-accendible, be added to a confined portion of air, sticks of phosphorus introduced into that air do not smoke, that phosphorus has no disposition to combine with oxygen when phosphuretted hydrogen is present. In a transparent mixture of one volume phosphuretted hydrogen with one thousand volumes, or any smaller proportion of air, sticks of phosphorus remain unaffected, but the phosphuretted hydrogen itself always undergoes a slow oxidation. In a mixture of one volume phosphuretted hydrogen and two thousand volumes air, phosphorus smoked strongly for some time; but at a certain period the action ceased, long before the oxygen of the air was exhausted. A minute proportion of phosphuretted hydrogen is, therefore, sufficient to protect phosphorus from oxidation, in which respect this gas resembles the hydrocarburets and essential oils, which have been shown to be equally efficacious in protecting phosphorus from oxidation. All these bodies appear to act in this respect in one way, namely, by taking the precedence of phosphorus in the process of oxygenation. Phosphorus therefore being less oxidable than phosphuretted hydrogen itself, cannot be supposed to take fire and to inflame the gas, or to be the cause of the accendibility of the gas at low temperatures.

On sending electric sparks through non-accendible phosphuretted hydrogen itself, phosphorus is deposited, but the gas, when still cloudy from the phosphorus suspended in it, proved to be non-inflammable on passing it into air.

The loss of accendibility in the case of gas confined over water is certainly wholly unconnected with the deposition of any free phos-



phorus from the gas, which may occur, but is due to the rise of *oxygen* from the water into the gas. It was observed that water, which had been boiled to deprive it of all air, and which was then passed up to self-accendible gas confined over mercury, did not affect the gas in the course of forty-eight hours. In this case, moreover, the gas was agitated with the water. The gas continues in general spontaneously inflammable over mercury for forty-eight hours, and sometimes for three or four days, but ceases to be so in a very short time after the admission of a small proportion of air, particularly if the air be added in a gradual manner. Thus, if to the gas be passed up one-twentieth part of its bulk of cork or of dry stucco, containing air in its pores, a white smoke appears in the gas, and it ceases to be spontaneously inflammable in the course of a few minutes. The same mass of stucco, warmed before being passed up into the gas, so as to expel the air it contained, did not produce the same effect. The self-accendible gas always deposits on standing a solid matter, containing phosphorus, of a lively yellow colour, but in quantity too minute for analysis. This matter is not acted on by any of the ordinary solvents, such as alcohol, ether, alkalies, or muriatic acid, but is destroyed by chlorine-water, and by nitric acid. The precipitation of this matter is most rapid in the case of gas over water, and is indicative of deterioration of the gas.

2. The self-accendible gas procured from phosphorus, water, and lime is always mixed with free hydrogen, varying in quantity from 25 to 50 per cent.; while the non-accendible gas from phosphorous acid contains no hydrogen gas, but is pure. Rose concludes that the spontaneous inflammability of the first species cannot depend upon this hydrogen, for the other species is not made self-accendible by the addition to it of any proportion of free hydrogen. On trying the experiment, however, I obtained a different result. A quantity of gas had lost its self-accendibility by standing over water for two or three hours; to my surprise, the addition to this gas of hydrogen, in any proportion from one-third of a volume to three volumes, restored the self-accendibility of the gas. Spontaneous inflammability was likewise communicated, in some cases, to the gas procured from phosphorous acid merely by adding hydrogen to it. It was early perceived, however, in the course of the investigation, that hydrogen did not uniformly communicate the property in question, and that its influence depended on something accidental and not essential to the gas. For instance, the hydrogen which comes over almost pure towards the end of the process for phosphuretted hydrogen had none of this property, nor did it appear in hydrogen obtained from the following sources:—from the electric decomposition of water, from the decomposition of steam by iron, from the action of water on amalgam of potassium, or from the action of muriatic, arsenic,



or phosphoric acid on zinc. Even in the case of the action of sulphuric acid on zinc or iron, which had first afforded hydrogen possessing the property in question, it turned out that only the hydrogen evolved at an early period of the action is efficient, while the gas evolved after the vivacity of the action is impaired is nearly, and sometimes entirely, destitute of any influence. The activity of the hydrogen was in short traced to a slight impregnation of *nitrous acid vapour*, which it possessed. The sulphuric acid of commerce always contains a small portion of some acid of nitrogen, probably the hyponitrous, from which, I find, it cannot be freed by boiling or concentration continued for any length of time. On quickly mixing sulphuric acid with two or three volumes of water, the presence of nitrous acid is attested by its peculiar odour, and almost certainly by the appearance of brown fumes. That the hydrogen did not owe the property in question to a trace of nitric oxide, which, combining with oxygen, might, by a slight consequent evolution of heat, have an effect in kindling the phosphuretted hydrogen, was proved by the fact that the property in question could not be imparted to hydrogen by any proportion of nitric oxide; but to this point there will be occasion to recur.

At an earlier stage in the inquiry, some experiments were made upon the effect of other gases than hydrogen upon phosphuretted hydrogen. None, with the exception of sulphuretted hydrogen (evolved by the action of sulphuric acid on sulphuret of iron, and which therefore contains free hydrogen), appeared to favour the accendibility of the gas. On the contrary, the addition of all others, and even of hydrogen and sulphuretted hydrogen themselves above a certain proportion, distinctly impeded or destroyed the accendibility of this gas. Thus, one volume phosphuretted hydrogen ceased to be spontaneously inflammable when mixed with the following proportions of different gases:—

With 5 volumes hydrogen,			
„ 2	„	carbonic acid,	
„ 3	„	nitrogen,	
„ 1 volume		olefiant gas,	
„ $\frac{1}{2}$	„	sulphuretted hydrogen,	
„ $\frac{1}{10}$	„	nitric oxide,	
„ $\frac{1}{20}$	„	muriatic acid,	
„ $\frac{1}{3}$	„	ammoniacal gas.	

It is to be remarked, however, in reference to the preceding table, that some specimens of phosphuretted hydrogen appear to be more highly accendible than others, and that there is considerable latitude in the proportion of foreign gas, which may be requisite for destroying the spontaneous inflammability of a given specimen. Often a much smaller portion suffices than is stated in the table. I have found half



a volume of carbonic acid or of nitrogen to produce the effect. Of course the introduction of any trace of air, with the gases, must be carefully guarded against. Nitrous acid, when present in hydrogen in too small a proportion to enable that gas to communicate spontaneous inflammability to phosphuretted hydrogen, or to be perceived by the smell, may be detected by the effect of the hydrogen upon a prepared mixture of non-accendible phosphuretted hydrogen and air, which mixture may be had quite free from white smoke and transparent. The addition of hydrogen to this mixture occasions the immediate appearance of a dense white smoke, the oxidation of the phosphorus being partially induced, if even an infinitesimal proportion of nitrous acid exist in the hydrogen. Although the oxidation of the phosphorus takes place at the expense of the air present, and only when air is present, yet the nitrous acid appears to be speedily consumed; the fumes soon ceasing but appearing again on every subsequent addition of active hydrogen, till several volumes have been added, or till the oxygen of the air present is exhausted.

That the influence of hydrogen was referable to the nitrous impregnation appeared also from the fact that phosphuretted hydrogen, which had lost its spontaneous inflammability, was rendered as actively inflammable as ever by passing it, bubble by bubble, into an inverted receiver filled with sulphuric acid, recently diluted with three measures of water and cooled. The gas was now capable of igniting spontaneously, when passed into air, without the intervention of hydrogen. The same diluted acid lost the smell of nitrous acid by exposure to air in a shallow vessel for a few hours, and thereafter was found unfit for the purpose in question. Phosphuretted hydrogen, which had acquired spontaneous inflammability from a nitrous impregnation, appeared to retain that property as long as the phosphuretted hydrogen, which is spontaneously inflammable as first prepared.

Hydrogen gas, too, which had received a nitrous impregnation by being passed through a diluted sulphuric acid, retained, in one case, after being confined for twenty-four hours over water, the power of rendering phosphuretted hydrogen spontaneously inflammable. From the preceding results and other considerations, it seemed not unlikely that the spontaneous inflammability of phosphuretted hydrogen may be an accidental property, and depend upon the occasional presence of some foreign body in minute quantity. The inquiry suggests itself, Is there a *peculiar principle* in the self-accendible gas, and what is it?

3. It was very soon found that a peculiar principle is withdrawn from the gas by *porous absorbents*, such as wood, charcoal, and baked clay, which substances are capable of destroying the inflammability of



several hundred times their volume of gas. Thus, in one experiment, to 500 measures of highly accendible phosphuretted hydrogen, one measure of charcoal, recently heated to redness, and cooled under the surface of mercury, was passed up. In the course of five minutes a contraction of eight or ten measures occurred, without any oxidation of the gas, for no air was introduced with the charcoal. The gas was still spontaneously inflammable, but ceased to be so in the course of half an hour. It was found, in fact, by different experiments, that wood-charcoal can absorb about ten times its volume of phosphuretted hydrogen gas itself; that the phosphuretted hydrogen and the peculiar principle are absorbed indiscriminately at first by the charcoal, but that by-and-bye the peculiar principle comes to be entirely absorbed by the charcoal, without any further absorption of phosphuretted hydrogen.

When the phosphuretted hydrogen did not exceed fifty or sixty times the bulk of the charcoal, the peculiar principle was entirely withdrawn in five minutes, and the gas ceased to be self-accendible. Charcoal, which had been drenched in water, was without effect upon the gas. On heating the charcoal saturated with gas, in a retort filled with water, phosphuretted hydrogen was given off, which, however, was not self-accendible, and all my attempts failed to isolate the peculiar principle by separating it from the charcoal. It was quite clear that the peculiar principle formed but a very small proportion of the volume of the phosphuretted hydrogen, evidently much less than one per cent. of the bulk of the gas.

Spongy platinum introduced into the gas did not exercise any sensible absorbent effect, and no quantity of it seemed sufficient to withdraw the peculiar principle from a small bulk of the phosphuretted hydrogen.

Stucco, likewise, was without effect upon the gas, at least when access of air was guarded against at the same time. But both of these substances are known to possess a very low absorbent power.

4. Phosphuretted hydrogen transferred to a receiver over mercury, the inside of which is moistened by a strong solution of *caustic potash*, always loses its spontaneous accendibility, although by no means rapidly, several hours being generally required.

5. Certain *acids* appear to have a remarkable power in withdrawing the principle of inflammability from phosphuretted hydrogen.

Let phosphuretted hydrogen be transferred into a jar inverted over mercury, of which jar the inner surface has been moistened with concentrated phosphorous acid. A small quantity of a milk-white matter immediately appears in the acid where exposed to the gas, and in two or three minutes the gas has ceased to be spontaneously inflammable



without any appreciable diminution of its volume having occurred. This white matter, although very sensible to the eye, exists only in the most minute quantity. It is not crystalline, and perhaps is not even solid. The introduction of concentrated phosphoric acid into the gas was attended by similar phenomena, and the gas lost its spontaneous inflammability in the course of half an hour.

A strong solution of arsenic acid acts as rapidly in withdrawing the peculiar principle as phosphoric acid does, but the arsenic acid soon begins to react upon the phosphuretted hydrogen itself, a dark copper-coloured incrustation soon forming upon the surface of the gas-receiver, which matter is probably a phosphuret of arsenic. Concentrated sulphuric acid is capable of absorbing phosphuretted hydrogen itself, which the preceding acids are not, but even sulphuric acid appears to absorb the peculiar principle, in the first instance, by a more active affinity than it exerts upon the gas itself. Dilute phosphorous, phosphoric, and arsenic acids, react in the same manner upon phosphuretted hydrogen, but not so rapidly as the concentrated acids do.

6. The following liquids are capable of dissolving the quantity of phosphuretted hydrogen gas placed against their names, at 65° Fahr.

Alcohol (sp. gr. 850),	.	.	.	.	$\frac{1}{2}$ volume.
Sulphuric ether,	.	.	.	.	2
Oil of turpentine,	.	.	.	.	$3\frac{1}{4}$

The *essential oils* and most of the *hydrocarburets* appear to withdraw, or to negative the peculiar principle in spontaneously inflammable phosphuretted hydrogen in a rapid manner. If a jar be moistened, in the slightest degree, with oil of turpentine, coal-tar naphtha, or by the liquid distilled from caoutchouc, and then be used as a receiver for containing self-accendible gas, either over water or mercury, the gas is found to lose its spontaneous inflammability in a very few minutes. White fumes often appear in the gas at the same time, but these I am satisfied are due to the evolution of some gaseous oxygen from the liquids, and appear in the case of the portion of gas which is first brought into contact with the liquid, but do not occur in the case of subsequent additions of gas, although the liquid remains capable of destroying the spontaneous accendibility of many portions of gas, successively exposed to it. It is not easy to decide whether the vapours destroy irrecoverably the peculiar substance of spontaneous inflammability, or merely negative the action of that principle by their presence.

I am inclined to think, however, that they destroy that principle, for the action is not so rapid as the diffusion of the vapour through the gas, the impregnation appearing to be fully accomplished, and yet the



loss of inflammability not occurring sometimes for two or three minutes afterwards, particularly in the case of naphtha, a portion of that pure liquid, in which potassium had been preserved, being used in the experiment. A small addition of ether-vapour also destroys the inflammability of phosphuretted hydrogen, although a distinct interval must elapse before the change occurs, such as a quarter or half of an hour.

The action of alcohol vapour is much slower, generally requiring two or three hours. Pure olefiant gas, containing no air, added in the proportion of 10 or 20 per cent., eventually destroys the spontaneous inflammability, but requires a period of not less than twenty or thirty hours.

Olefiant gas has a negative influence of quite a different character, which has already been alluded to, and which is in action the moment the gases are mixed, but which does not appear unless the proportion of olefiant gas be very considerable. It is probable that ether-vapour and the gaseous hydrocarburets likewise have an influence of the same kind. An astonishingly minute quantity of an essential oil suffices to destroy the inflammability of the gas over mercury, if allowed an hour or two to act. Hence it is very difficult to preserve gas in the inflammable condition, in the mercurial trough, if any portion of the mercury has been soiled by an essential oil.

7. The action of *potassium* on the peculiar principle is equally remarkable. A most minute quantity of this metal, or of its amalgam, destroys the self-accendibility of the gas in a few minutes, without occasioning any sensible reduction of volume that could be measured.

The fact is, potassium, or its amalgam, is without effect upon phosphuretted hydrogen itself, at the temperature of the air, neither absorbing nor decomposing the gas; but upon the peculiar principle the action of this metal is rapid and certain. One grain of potassium, amalgamated with fifty pounds of mercury, rendered that large quantity of mercury quite unfit for retaining gas over it, in the self-accendible condition, for more than a few minutes. In such experiments the interference of naphtha vapour was perfectly excluded. Zinc and tin, either by themselves or in the state of amalgam, have no sensible effect upon self-accendible gas, at least in a period of five or six hours. Protoxide of mercury speedily withdraws the peculiar principle, but afterwards also reacts slowly upon the gas itself. On the other hand, the peroxide of the same metal is nowise injurious to the self-accendible gas. Arsenious acid in powder acts in the same manner as protoxide of mercury. The solution of proto-sulphate of iron, if previously boiled to deprive it of air, is without effect upon the gas.

The extraordinary action of potassium, and that also perhaps of the essential oils, seemed to point to the existence of an oxygenated prin-



ciple, as the cause of the spontaneous inflammability of phosphuretted hydrogen.

It is sufficiently evident that the proportion in which this principle exists to the whole gas, is exceedingly small, too minute to afford any hope of isolating that principle. The nitrous impregnation, too, which was found adequate to render gas spontaneously inflammable, shows to how minute a quantity of matter the spontaneous inflammability of phosphuretted hydrogen may at times be owing. It seemed within the bounds of possibility that the gas might owe its spontaneous inflammability, in ordinary circumstances, if not to nitrous acid, at least to some other principle analogous to that substance. This led to a careful examination of the properties of phosphuretted hydrogen made inflammable by means of nitrous acid; a subject of much interest, as illustrating the effect of a most minute and almost infinitesimal quantity of foreign admixture, in communicating so striking a property as spontaneous inflammability to a chemical body, independently of the light which it may throw upon the constitution of ordinary phosphuretted hydrogen.

8. Phosphuretted hydrogen, which had lost all trace of spontaneous inflammability by standing a day or two over water, or the gas from hydrated phosphorous acid, might be impregnated with nitrous acid, and made spontaneously inflammable in various ways. It was ascertained that the gas obtained, by either process, was affected in the same way. Such gas only, entirely destitute of spontaneous inflammability, was employed in the following experiments:—

(1.) The nitrous acid of Dulong may be added directly to the gas over mercury, a glass spherule, or the bore of a short piece of thermometer tube being filled with the liquid, and passed up to the gas. When *nitric acid* is brought into contact with the gas in this manner, a violent action occurs; but with *nitrous acid* the evolution of white fumes is very slight. The nitrous acid is absorbed in part by the mercury, but this absorption is slow, provided the quantity of gas be considerable with which the acid vapour is mixed. If the quantity of gas primarily impregnated with nitrous acid, in the manner described, be small, or the impregnation of nitrous acid considerable, the gas exhibits no disposition to smoke or to take fire, when passed into air. It has not become spontaneously accendible. On diluting the gas with a large proportion of unimpregnated phosphuretted hydrogen, no reaction is indicated, but the whole becomes spontaneously accendible in a high degree. In fact, it was discovered that the gas is not accendible when the nitrous acid exceeds a certain proportion, which is by no means considerable.

(2.) Allow a single drop of nitrous acid to fall into a dry glass jar, which may be of small dimensions. Fill the jar with mercury, and



invert it without loss of time in the mercurial trough, a bubble of gas will collect in the upper part of the jar, which bubble is chiefly nitrous acid vapour. One cubic inch or so of phosphuretted hydrogen, or of hydrogen itself, may then be added to the gas in the jar, and this is our nitrous impregnating mixture. Suppose this mixture to contain one-twentieth of its bulk of nitrous acid vapour. The addition of it, in any proportion, to phosphuretted hydrogen, is not attended by the slightest production of white fumes; in fact no reaction appears to take place. But the addition of a single bubble of this mixture, not exceeding one-tenth of an inch in volume, to five or six cubic inches of phosphuretted hydrogen, will render the whole highly accendible, so that every bubble passed into the air will take fire.

(3.) In the above arrangement, a drop of the strongest nitric acid may be substituted for the nitrous acid, in the preparation of the impregnating mixture. The nitric acid acts on the mercury, and nitric oxide, charged with nitrous acid, is collected, which may be diluted with hydrogen as above.

The preceding processes uniformly afford a nitrous impregnating mixture which may be depended upon; but when the experiment is attempted over water, there is not the same certainty of the impregnation being successful. I have often, however, made hydrogen highly suitable for the purpose, by passing it through a column of fluid composed of nitric acid recently diluted with water, provided that the acid had been fuming from the presence of nitrous acid; or by passing hydrogen through recently diluted sulphuric acid, as has already been stated.

In regard to the proper proportion of nitrous acid vapour to the phosphuretted hydrogen, I am satisfied that the proportion most efficacious is somewhere between 1 part nitrous acid to 1000, and 1 to 10,000 phosphuretted hydrogen. One volume nitrous acid vapour to 100 gas, or to less gas, is never accendible, but becomes so on diluting it with enough of phosphuretted hydrogen.

I was anxious to discover how far nitric oxide interferes in the phenomenon. The nitrous acid is never free from, but always accompanied with, a certain proportion of this gas.

9. *Action of Nitric Oxide.*—In a table formerly given, nitric oxide is set down as incompatible with the accendibility of the good gas from phosphuret of lime, when the proportion of the first is so great as one-tenth of the whole mixture.

In fact, the best inflammable gas, when mixed with nitric oxide, in quantity from two volumes to one-tenth of a volume, exhibited no symptoms of spontaneous inflammability. The nitric oxide forms red fumes when the mixture meets the air, but the phosphuretted hydrogen



does not even smoke, so that the oxidation of the nitric oxide has not a kindling effect upon the phosphuretted hydrogen, but the very reverse. A mixture of one volume nitric oxide, with twenty volumes good phosphuretted hydrogen (self accendible *per se*), is still self-accendible; the bubble, however, does not take fire the instant it bursts in the air, but after rising to a little height, and then explodes with a puff like loose grains of gunpowder, and not with the usual snap, the oxidation of the nitric oxide preceding the oxidation of the phosphuretted hydrogen by a sensible interval. Nitric oxide, in a considerably smaller proportion than one-twentieth volume, exhibits a sensible effect in retarding the combustion of self-accendible gas, but does not altogether prevent it. In the case of phosphuretted hydrogen, which was not self-accendible, small additions of nitric oxide, such as 1 to 100, to 500, to 1000, or to 2000 volumes phosphuretted hydrogen, did not induce self-accendibility, when the nitric oxide employed had been previously washed with caustic alkali. The experiment was tried with three different specimens of washed nitric oxide. But nitric oxide, which had not been washed with alkali, particularly if it resulted from a turbulent action of the nitric acid on copper, and came overcharged with red fumes, and was withal newly collected, was pretty often efficient in making the gas self-accendible. The proper proportion of such nitric oxide for this purpose was found to be 1 volume to a quantity between 1000 and 2000 volumes of phosphuretted hydrogen. A greater or a less proportion of the nitric oxide failed to produce the desired effect. All these experiments with nitric oxide were made over water.

It is well known that a mixture of phosphuretted hydrogen and nitric oxide may be exploded by a bubble of oxygen gas, a method of firing these gases first practised, I believe, by Dr. Thomson. But pure nitric oxide was found by Dr. Dalton to oxygenate phosphuretted hydrogen in a gradual manner, when the two gases are left together. It is probable, therefore, that it is by acting itself upon phosphuretted hydrogen that nitric oxide prevents atmospheric air from acting upon that gas in our experiments. It is conceivable that the oxygenating action of nitric oxide upon phosphuretted hydrogen, like that of air upon the same gas, may be promoted by the presence of nitrous acid, which will explain Dr. Thomson's experiments.

The impregnating nitrous mixture of the foregoing experiments was not destitute of nitric oxide, but what proves that the efficiency of the mixture did not depend upon the last-mentioned ingredient, is the circumstance, that the mixture lost its virtue by standing over mercury for a week, during which period the acid-vapour was absorbed by the mercury, but the nitric oxide remained, as appeared on admitting air



to the gaseous mixture. Hence we may conclude that when nitric oxide acts in producing inflammability in phosphuretted hydrogen, it is from the nitrous acid which it occasionally contains.

It is certainly, however, very curious that nitric oxide is not quite equivalent to nitrous acid, in producing the change in question upon phosphuretted hydrogen, seeing that the nitric oxide passes immediately into nitrous acid upon meeting air. Whether the negative influence of nitric oxide upon really accendible gas is sufficient to account for this anomaly, I am doubtful. It may be thought that nitrous acid and phosphuretted hydrogen, when in contact for a short time, react upon each other, with the production of some entirely new and highly accendible body. But this supposition seems not to quadrate with the fact, that the impregnating mixture requires to be diluted by so large a proportion of phosphuretted hydrogen, before the whole becomes spontaneously accendible. Nor is it supported by any visible signs of reaction between the nitrous acid and phosphuretted hydrogen. Indeed, nitrous acid-vapour appears to be compatible with phosphuretted hydrogen, to an extent which could not have been anticipated.

Again, that nitrous acid, or at least some acid compound of nitrogen, continues to exist in what we may now call the *nitrous phosphuretted hydrogen gas*, appears to be corroborated by the properties which this self-accendible gas is found to possess.

10. *Properties of nitrous phosphuretted hydrogen.*

(1.) This gas loses its self-accendibility when kept over mercury, in a period varying from six to twenty-four hours, according to the amount of nitrous impregnation.

It is remarkable that this gas continues, in general, inflammable for a longer time when confined over water than over mercury, which is the reverse of what occurs with the gas from phosphuret of lime.

(2.) The factitious gas is deprived of its spontaneous inflammability by charcoal and other porous absorbents, by essential oils and hydrocarurets, and by amalgam of potassium, and quite as rapidly as is its natural prototype.

(3.) Phosphorous acid, and concentrated sulphuric acid, appear likewise to withdraw the nitrous principle, although phosphoric acid does not. The agency of these acids probably exemplifies the disposition of nitrous acid to combine with other acids. The action of potassium and of essential oils upon nitrous acid, requires no explanation. Potassium has, I find, no action upon pure nitric oxide in the cold.

(4.) A cubic inch of this gas, passed up into a receiver, of which the inside was moistened with caustic alkali, had its accendibility sensibly impaired in fifteen minutes, but not completely destroyed in less than an hour.



In conclusion, the statement of the above properties is abundantly sufficient to prove that a strong analogy subsists between our nitrous phosphuretted hydrogen and the self-accendible gas, which has been so long in the hands of chemists. The peculiar principle of the last may therefore possibly be an oxygenated body. That principle cannot be nitrous acid, but it may be a compound of phosphorus and oxygen,  $\ddot{P}$ , analogous to nitrous acid. In all the reactions by which self-accendible phosphuretted hydrogen is produced, we have the simultaneous formation of compounds of phosphorus and oxygen, such as hypophosphorous and phosphoric acids. The compound  $\ddot{P}$  is hypothetical, however, and has not yet been formed directly. Its existence is only surmised from the parallelism which appears to be established between nitrogen and phosphorus, and between their compounds; phosphuretted hydrogen itself corresponding with ammonia, phosphoric, and phosphorous acids, with nitric and hyponitrous acids. The peroxide of chlorine of Davy and Stadion  $\ddot{Cl}$ , corresponds with nitrous acid, and with our hypothetical oxide of phosphorus, which we may speak of as the peroxide of phosphorus.

The peroxide of phosphorus would appear to resemble the peroxide of chlorine, in being acted on more slowly by mercury and by alkalies, than is the case with nitrous acid. It is to be admitted, however, that I did not succeed in producing an inflammable phosphuretted hydrogen by the agency of peroxide of chlorine—that there is no *chlorous* phosphuretted hydrogen. The reason is, that peroxide of chlorine is incompatible with phosphuretted hydrogen, reacting upon that gas the instant of mixture.

As to the mode in which nitrous acid vapour, in a proportion so minute, contributes to the accendibility of phosphuretted hydrogen, I have been able to form no distinct idea. The most likely conjecture is, that the nitrous acid, or resulting hyponitrous acid, combines with some product of the oxygenation of phosphuretted hydrogen, and thereby disposes or promotes the occurrence of that change. The oxygenation of pure hydrogen itself, under the influence of a clean plate of platinum, is not promoted in a sensible degree by any nitrous impregnation. Sulphurous acid and muriatic acid gases, and vapour of acetic acid, appeared to contribute nothing to the accendibility of phosphuretted hydrogen.

It appears, then, that the two phosphuretted hydrogens are not isomeric bodies, but that the peculiarities of the spontaneously inflammable species depend upon the presence of adventitious matter:

That the vapour of some acid of nitrogen, which, in the present state of our knowledge of that class of compounds, seems to be the nitrous



acid, is capable of rendering phosphuretted hydrogen spontaneously inflammable, when present to the extent of *one ten-thousandth part* of the volume of the gas :

That the last gas has a general resemblance to phosphuretted hydrogen, as obtained in the spontaneously inflammable state by ordinary processes, which, it is probable, owes its ready accendibility to the presence of an equally minute trace of a volatile compound of *phosphorus and oxygen*, analogous to nitrous acid.

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## XII.

### ON A NEW PROPERTY OF GASES.

*From Report of Brit. Assoc. for the Advancement of Science, 1845 (Part ii.), p. 28.*

AFTER explaining the law which regulated the diffusion of gases, and stating the fact, that the lighter gases diffused themselves much more speedily than the more dense ones—the velocity of their diffusion being equal to the square root of their densities—he proceeded to relate his experiments on the passage of gases into a vacuum. To this passage the term effusion has been applied. The velocity of air being 1, the velocity of oxygen was found to be 0.9500 by experiment, and by calculation 0.9487. Carbonic acid being much heavier than air, gave the number 0.821, the theoretical number being 0.812. Carburetted hydrogen gave 0.1322 as the velocity of its effusion, the theoretical number being 1.341. Hydrogen gave as the velocity of effusion 3.613 by experiment, which was nearly the amount given by theory (0.379). The interference of friction, even of minute orifices, was then described, and shown to admit of easy correction. Some useful applications were mentioned; as in the manufacture of coal-gas, where it is desirable to ascertain the quality, as well as the quantity of gas manufactured. As the gas will pass the orifice on its way to a vacuum the quicker the lighter it is, and the more slowly as it increases in density, and as the superior carburetted hydrogen is heaviest, it would be easy to construct an instrument to register this velocity, and thus mark at once the required quality and quantity of gas. It was also proposed that an instrument might be used in mines to detect the presence of light carburetted hydrogen (fire-damp). The passage of gases under pressure through porous bodies was termed, by Prof. Graham, transpiration. The mode adopted in experiment was, to take a glass receiver, open at the top, which was



closed with a plate of stucco. This was placed on an air-pump, and the air exhausted by the pump, the velocity with which the air passed through the stucco being marked by the mercurial gauge of the pump. The transpiration of atmospheric air was found to be more rapid than that of oxygen. Carbonic acid is found to be more transpirable than oxygen, or even, under low pressure, than atmospheric air. The transpiration of hydrogen is one-third more rapid than that of oxygen. The applicability of this process of experimenting to the explanation of exosmose and endosmose action in the passage of fluids through porous bodies was pointed out.

### XIII.

#### ON THE COMPOSITION OF THE FIRE-DAMP OF THE NEWCASTLE COAL MINES.

From *Memoirs of Chem. Society*, iii. 1845-48, pp. 7-10.

SOME years ago I examined the gas of these mines with the same result as Dr. Henry, Davy, and Dr. Turner had previously obtained, namely, that it contains no other combustible ingredient than light carburetted hydrogen. But the analysis of the gas of the coal mines in Germany, subsequently published, showing the presence of other gases, particularly of olefiant gas, has rendered a new examination of the gas of the English mines desirable. The gases were—1, from a seam named the Five-Quarter seam, in the Gateshead colliery, where the gas is collected as it issues, and used for lighting the mine; 2, the gas of Hebburn colliery, which issues from a bore let down into the Bensham seam—a seam of coal which is highly charged with gas, and has been the cause of many accidents; and 3, gas from Killingworth colliery, in the neighbourhood of Jarrow, where the last great explosion occurred. This last gas issues from a fissure in a stratum of sandstone, and has been kept uninterruptedly burning, as the means of lighting the horse-road in the mine, for upwards of ten years, without any sensible diminution in its quantity. The gases were collected personally by my friend Mr. J. Hutchinson, with every requisite precaution to insure their purity, and prevent admixture of atmospheric air.

The usual eudiometrical process of firing the gases with oxygen was sufficient to prove that they all consisted of light carburetted hydrogen, with the exception of a few per cent. The results were as follows:—



*Gateshead Gas.*—Specific gravity 0·5802.

Carburetted hydrogen,	94·2
Nitrogen,	4·5
Oxygen,	1·3
	<hr/>
	100·0

The density of such a mixture is, by calculation, 0·5813.

*Killingworth Gas.*—Specific gravity 0·6306.

Carburetted hydrogen,	82·5
Nitrogen,	16·5
Oxygen,	1·0
	<hr/>
	100·0

The theoretical density of this gas, deduced from its composition, is 0·6308.

The Hebburn gas was of specific gravity 0·6327.

Seventy-nine measures of the Killingworth gas, mixed with an equal volume of chlorine, left in the dark for eighteen hours, and afterwards washed with alkali, were reduced to seventy-five measures, from which the presence of four measures of olefiant gas might be inferred. \* But in a comparative experiment made at the same time on 25·3 measures of pure gas of the acetates, mixed with an equal volume of chlorine, a contraction occurred of 1·3 measure; that is in exactly the same proportion as with the fire-damp.

It was observed that phosphorus remains strongly luminous in these gases, mixed with a little air, while the addition to them of one-four-hundredth part of olefiant gas, or even a smaller proportion of the volatile hydrocarbon vapours, destroyed this property. Olefiant gas itself, and all the allied hydrocarbons, were thus excluded.

Another property of pure light carburetted hydrogen, observed by myself, enabled me to exclude other combustible gases, namely, that the former gas is capable of entirely resisting the oxidating action of platinum black, and yet permits other gases to be oxidated, which are mixed with it even in the smallest proportion, such as carbonic oxide and hydrogen the first slowly and the last very rapidly; air or oxygen gas being, of course, also present in the mixture. Now platinum black had not the smallest action on a mixture of the gas from the mines with air. No moisture appeared or sensible contraction, and no trace of carbonic acid could be discovered after a protracted contact of twenty-four hours; while, with the addition of one per cent. of hydrogen, the first effects were conspicuously evident in three minutes, and with the same proportion of carbonic oxide, the gas became capable of affecting lime-water in half an hour. These experiments were repeated upon each of the three specimens of fire-damp.



Potassium fused in the fire-damp did not become covered with the green fusible compound of carbonic oxide, nor occasion any contraction. Indeed, however carefully the heat was applied to the potassium by means of an oil-bath, a slight permanent expansion always ensued. The same thing occurred in pure gas of the acetates. It appeared that potassium could not be heated above  $300^{\circ}$  Fahr. in pure carburetted hydrogen, without causing a decomposition and the evolution of free hydrogen gas.

The gas was also inodorous, and clearly contained no appreciable quantity of any other combustible gas than light carburetted hydrogen. The only additional matters present were nitrogen and oxygen; the specimen collected in the most favourable circumstances for the exclusion of atmospheric air, namely, that from the Bensham seam, still containing 0.6 per cent. of oxygen. The gases also contained no carbonic acid.

It is worthy of observation that nothing oxidable, at the temperature of the air, is found in a volatile state associated with the perfect coal of the Newcastle beds. The remarkable absence of oxidability in light carburetted hydrogen appears to have preserved that alone of all the combustible gases originally evolved in the formation of coal, and which are still found accompanying the imperfect lignite coal of Germany, of which the gas has been examined. This fact is of geological interest, as it proves that an almost indefinitely protracted oxidating action of the air must be taken into account in the formation of coal, air finding a gradual access through the thickest beds of superimposed strata, whether these strata be in a dry state or humid.

In regard to measures for preventing the explosion of the gas in coal mines, and of mitigating the effects of such accidents, I confine myself to two suggestions. The first has reference to the length of time which the fire-damp, from its lightness, continues near the roof, without mixing uniformly with the air circulating through the workings. It was found that a glass jar, of six inches in length and one inch in diameter, filled with fire-damp, and left open with its mouth downwards, continued to retain an explosive mixture for twenty minutes. Now it is very desirable that the fire-damp should be mingled as soon as possible with the whole circulating stream of air, as beyond a certain degree of dilution it ceases to be explosive. Mr. Buddle has stated, "that immediately to the leeward of a blower, though for a considerable way the current may be highly explosive, it often happens that after it has travelled a greater distance in the air-course, it becomes perfectly blended and mixed with the air, so that we can go into it with candles; hence, before we had the use of the Davy lamp, we intentionally made 'long runs,' for the purpose of mixing the air." It is recommended that means be taken to



promote an early intermixture of the fire-damp and air; the smallest force is sufficient for this purpose, as a downward velocity of a few inches in the second will bring the light gas from the roof to the floor. The circulating stream might be agitated most easily by a light portable wheel, with vanes, turned by a boy, and so placed as to impel the air in the direction of the ventilation, and not to impede the draft. The gas at the roof undoubtedly often acts as an explosive train, conveying the combustion to a great distance through the mine, while its continuity would be broken by such mixing, and an explosion, when it occurred, be confined within narrower limits.

Secondly, no effective means exist for succouring the miners after the occurrence of an explosion, although a large proportion of the deaths is not occasioned by fire, or injuries from the force of the explosion, but from suffocation by the after-damp, or carbonic acid gas, which diffuses itself afterwards through all parts of the mine. It is suggested that a cast-iron pipe, from eight to twelve inches in diameter, be permanently fixed in every shaft, with blowing apparatus, above, by which air could be thrown down, and the shaft itself immediately ventilated after the occurrence of an explosion. It is also desirable that, by means of fixed or flexible tubes, this auxiliary circulation should be further extended, and carried as far as practicable into the workings.

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#### XIV.

##### OF THE MOTION OF GASES.<sup>1</sup> PART I.

From *Phil. Trans.* iv. 1846, pp. 573-632 ; ii. 1849, pp. 349-362.

THE spontaneous intermixture of different gases, and their passage under pressure through apertures in thin plates and by tubes, form a class of phenomena of which the laws have been only partially established by experiment. The separation of two gases by a porous screen, such as a plate of dry stucco, will prevent for a short time any sensible intermixture arising from slight inequalities of pressure, but such a barrier is readily overcome by the diffusive power of the gases, which is fully equal to their whole elastic force. Hence a cylindrical glass jar with a stucco top, filled with any gas and standing over water, affords the means of demonstrating the unequal diffusive velocities of air and the gas, by the final contraction or expansion of the gaseous contents of the jar, after the escape of the gas is completed. Compared with the

<sup>1</sup> Received June 18 ; Read June 18, 1846.



volume of air which has entered, the volume of gas which has passed simultaneously outwards is found to be in the inverse proportion of the square root of the specific gravity of the gas. The diffusive velocities therefore of different gases are inversely as the square root of their densities; or the times of diffusion of equal volumes directly as the square root of the densities of the gases.<sup>1</sup>

Such is also the theoretical law of the passage of gases into a vacuum, according to the well-known theorem that the molecules of a gas rush into a vacuum with the velocity they would acquire by falling from the summit of an atmosphere of the gas of the same density throughout; while the height of such an atmosphere, composed of different gases, is inversely as their specific gravities. This is a particular case of the general law of the movement of fluids, well established by observation for liquids, and extended by analogy to gases. The experiments which have already been made upon air and other gases, by M. P. S. Girard<sup>2</sup> and by Mr. Faraday,<sup>3</sup> are sufficient to show that the discharge of light is more rapid than that of heavy gases; and are interesting as first approximations, although incomplete and lending a very imperfect support to the theoretical law. Indeed some results obtained by these experimenters and others, appear wholly inconsistent with that law, such as Mr. Faraday's curious observations of the change of the relative rates of hydrogen and olefiant gases in passing through a capillary tube under different pressures; and my own observation, that carbonic acid gas is forced by pressure through a porous mass of stucco as quickly or more so than air is, although more than a half heavier; and that other gases pass in times which have no obvious relation to their diffusive velocities.<sup>4</sup>

In studying this subject, I found that it was necessary to keep entirely apart the two cases of the passage of a gas through a small aperture in a thin plate and its passage through a tube of sensible length. The phenomena of the first class then became well-defined and simple, and quite agreeable to theory. Those of the second class also attained a high degree of regularity, where the tubes were of great length, or being short were of extremely small diameter. Capillary glass tubes, which varied in length from twenty feet to two inches, were found equally available and gave similar results, where a sufficient resistance was offered to the passage of the gas.

The rate of discharge of different gases from capillary tubes appears to be independent of the nature of the material of the tube, in so far as

<sup>1</sup> On the Law of the Diffusion of Gases; *Transactions of the Royal Society of Edinburgh*, vol. xii. p. 222; or *Phil. Mag.*, 1834, vol. ii. pp. 175, 269, 351. See *ante*, p. 44.

<sup>2</sup> *Annales de Chimie*, etc., 2de Sér., t. 16, p. 129.

<sup>3</sup> *Quarterly Journal of Science*, vol. iii. p. 354; and vol. vii. p. 106.

<sup>4</sup> *Edinburgh Transactions*, xii. 238. (Paper at p. 44, *ante*.)



the rates were found to be similar for tubes of glass and copper, and even for a porous mass of stucco. But while the discharge by apertures in thin plates is found to be dependent in all gases upon a constant function of their specific gravity, the discharge of the same gases from tubes has no uniform relation to the density of the gases. Both hydrogen and carbonic acid, for instance, pass more quickly through a tube than oxygen, although the one is lighter and the other heavier than that gas. I shall assume then for the present, that in the passage of gases through tubes we have the interference of a new and peculiar property of gases; and on the ground of a radical difference in agency speak of the two classes of phenomena under different names. The passage of gases into a vacuum through an aperture in a thin plate I shall refer to as the *Effusion* of gases, and to their passage through a tube as the *Transpiration* of gases. The determination of the coefficients of effusion and transpiration of various gases will be the principal object of the following paper.

#### PART I.—EFFUSION OF GASES.

##### 1. *Effusion into a Vacuum by a glass jet.*

The glass jet was formed from a short piece of a capillary thermometer tube, of which the bore was cylindrical, to which a conical termination was given by drawing it out when softened by heat and breaking the point. The aperture at the point of the jet was cylindrical, in a flat surface, and so small that it could only be seen distinctly by means of a magnifying-glass; its size, compared with other apertures, may be expressed by the statement that one cubic inch of air of the usual tension passed into a vacuum through this aperture in 2.18 seconds. By means of a perforated cork this glass jet was fixed within a block-tin tube, through which the gas was to be drawn; with the point of the tube directed towards the magazine of gas, so that the gas in passing towards the vacuum entered the conical point of the jet instead of issuing from it. This form of the aperture reduced the rubbing surface of glass to a thin ring, or made it equivalent to an aperture in a very thin plate; but the mode of placing the jet, or direction in which the current passed through the aperture, was found afterwards to be of little consequence.

The gas for an experiment was contained in a glass jar, of an elliptical form, balanced like a gasometer over water, and terminated at top and bottom with two short hollow cylindrical axes, of an inch in diameter; its capacity between two marks, one on each of the cylindrical ends, being 227 cubic inches. From this gasometer the gas was conveyed directly into a U-shaped drying tube, 18 inches in length and 0.8 inch in diameter, filled in some cases with fragments of chloride of calcium, in



others with fragments of pumice-stone soaked in oil of vitriol; the pumice, when used, having been first washed with water, to deprive it of soluble chlorides. From the drying tube, the gas entered the tin tube occupied by the glass jet, one end of that tub being connected with the drying tube, and the other with an exhausted receiver on the plate of an air-pump. The apparatus described is exhibited in fig. 1 of Plate XXXIII., with the exception of the elliptical gasometer, the place of which is occupied there by the counterpoised jar A in the water trough. The gas was thus forced through the minute aperture by the whole atmospheric pressure. In making an experiment with any other gas than atmospheric air, a considerable quantity of the gas was first blown through the drying tube, from the gasometer, to displace the air in the former; and to do this quickly an opening was made into the air-channel beyond the drying tube, at G, by which gas might be allowed to escape into the atmosphere without proceeding further or being drawn through the glass aperture into the vacuum. This side aperture was closed by a brass screw and leather washer. In making an experiment, the gasometer was filled with the gas to be effused, and then connected with the air-pump receiver, in which a constant degree of exhaustion was maintained by continued pumping. The interval of time was noted in seconds, which was required for the passage of a constant volume of gas, amounting to 227 cubic inches, namely, that contained between the two marks in the elliptical gasometer. Or, the volume of gas effused was more strictly 227 cubic inches, minus the volume of aqueous vapour which saturates air at the temperature of the experiment; the vapour being withdrawn from the gas, after it left the elliptical measure and before it reached the effusion aperture. It is scarcely necessary to add that great care is necessary during these and all other experiments on gases, to maintain a uniform temperature. The use of a fire or stove in the room in which the experiments were conducted was therefore avoided, and such arrangements made that the temperature was kept for five or six hours within a range of a single degree of Fahrenheit's scale.

*Hydrogen.*—In the experiments first made with air and hydrogen the temperature was 59° Fahr., and the height of the barometer 30·14 inches; a uniform exhaustion was maintained in the air-pump receiver of 29·3 inches, as observed by the gauge barometer attached.

The constant volume of dry air passed into the vacuum, or was effused, in three experiments, in 494, 495, and again in 495 seconds.

The constant volume of dry hydrogen was effused, in two experiments, in 137 and again in 137 seconds. Calculating from 495 seconds as the time for air, we have—

Time of effusion of air,	.	.	.	.	1·
Time of effusion of hydrogen,	.	.	.	.	0·277



Or, the result may be otherwise expressed, taking the reciprocals of the last numbers :

Velocity of effusion of air, . . . . .	1
Velocity of effusion of hydrogen, . . . . .	3.613

The specific gravity of hydrogen gas, according to the most recent and exact determination, that of Regnault, is 0.06926, referred to air as unity; of which the square root is 0.2632, and the reciprocal of the square root 3.7994; to which the numbers for the time and velocity of hydrogen above certainly approximate.

*Oxygen and Nitrogen.*—Temperature 60°; exhaustion maintained at 29.3 inches. The constant volume of air was effused in 494 seconds, of oxygen in 520 seconds, and of nitrogen in 486 seconds, in one experiment made upon each gas. Hence the following results :

	Time of effusion.	Square root of density.	Velocity of effusion.	Reciprocal of square root of density.
Air, . . . . .	1	1	1	1
Oxygen, . . . . .	1.053	1.0515	0.9500	0.9510
Nitrogen, . . . . .	0.984	0.9856	1.0164	1.0146

The densities made use of are those of M. Regnault, namely, 1.10563 for oxygen, and 0.97137 for nitrogen. It will be observed, that the times of effusion of these two gases correspond as closely with the square roots of their densities as the mode of observation will admit of; the times observed being within one second of the theoretical times.

*Carbonic Oxide.*—This gas was prepared by the action of oil of vitriol upon pure crystallized oxalic acid, and subsequent washing with alkali. The temperature during the effusive experiment was 60° 3; the usual exhaustion was maintained. The time of effusion of air was 494 seconds; of the same volume of carbonic oxide 488 seconds :

	Time of effusion, air = 1.	Square root of density.	Velocity of effusion.	Reciprocal of square root.
Carbonic oxide, .	0.987	0.9838	1.0123	1.0165

The effusion-rate of this gas approaches therefore very closely to the theoretical number. In the calculations the density of carbonic oxide is taken at 0.96779, as found by Wrede.

*Carburetted Hydrogen, CH<sub>2</sub>.*—This was the gas of the acetates, prepared by heating a mixture of acetate of soda with dry hydrate of potash and lime.

The temperature of the gases effused being 59° 5, and the exhaustion 29.3 inches; the constant volume of air passed through the aperture in 493 seconds, of carburetted hydrogen in 373 seconds :



	Time, air = 1.	Theoretical time.	Velocity.	Theoretical velocity.
Carburetted hydrogen,	0.756	0.7449	1.322	1.3424

The density of carburetted hydrogen is taken at 0.5549 in the calculations.

*Carbonic Acid and Nitrous Oxide.*—In the first experiment with carbonic acid, the gasometer with the gas was floated as usual over water; thermometer  $58^{\circ}5$ . The effusion of air took place in 495 seconds, of carbonic acid in 595 seconds. To diminish the loss of the latter gas occasioned by its solubility in water, a second experiment was made over brine: the time required by the carbonic acid was now 603 seconds. The velocity of effusion of carbonic acid is by the first experiment 0.832; by the second it approaches more nearly the theoretical number, calculated from 1.52901 (Regnault) as the density of this gas, as appears below:

	Time, air = 1.	Theoretical time.	Velocity.	Theoretical velocity.
Carbonic acid, . . .	1.218	1.2365	0.821	0.8087

The observation on nitrous oxide was made on a different occasion, with a temperature of  $62^{\circ}5$ . The time of effusion of air was then 488 seconds; of nitrous oxide 585 seconds, the gas being collected over water:

	Time, air, = 1.	Theoretical time.	Velocity.	Theoretical velocity.
Nitrous oxide, . . .	1.199	1.2365	0.834	0.8087

The specific gravity of nitrous oxide is assumed in the calculations to be the same as that of carbonic acid. The time of effusion of both of these gases is shortened by the loss of a portion of the gas, by solution in the water of the pneumatic trough during the period of the experiment, and falls below the theoretical number. In carbonic acid over brine, where the injury is least from this cause, the observed velocity is, however, still within one-seventieth part of that calculated from the specific gravity of the gas.

*Olefiant Gas.*—When this gas is prepared by heating sulphuric acid, of specific gravity 1.6, with strong alcohol at the temperature of  $320^{\circ}$ , in the proportion of six parts of the former to one of the latter, it appears



to come off at first very pure, as it is entirely absorbed by the perchloride of antimony, and contains therefore no carbonic oxide. But it is really contaminated, I find, by a portion of another heavier gas or vapour (not ether vapour), which cannot be entirely removed from it by washing with alkaline water, oil of vitriol, or strong alcohol, and which may raise the density of the gas above that of air. As the evolution of gas proceeds, the proportion of the heavy compound diminishes, and it finally disappears, and the gas attains its theoretical density; but it is then again contaminated with more or less carbonic oxide. The latter gas, however, being of sensibly the same density as olefiant gas, is not likely to exert any influence upon its effusion rate. But before these facts were ascertained this jet became unserviceable from an accident, and the experiments made with it were all made upon the dense olefiant gas, and gave an effusion time which slightly exceeded that of air.

## 2. *Effusion into a Vacuum by a perforated brass plate A.*

A minute circular aperture was made by means of a fine drill in a thin plate of sheet brass  $\frac{1}{28}$ th of an inch thick, and the opening still further diminished by blows from a small hammer, of which the surface was rounded. A small disc of the brass plate was then punched out, having the aperture in the centre, which was soldered upon the end of a short piece of brass tube, of quill size, so as to close the end of the cylinder. This brass tube was then fixed, by means of a perforated cork, within the tin tube, used as formerly, for conveying the gas from the gasometer jar to the air-pump receiver; so that the gas should necessarily flow through the small aperture in its passage, as before through the glass jet. The aperture was of an irregular triangular form, in consequence of the hammering of the plate. One cubic inch of air of usual tension passed into a vacuum through this aperture in 12.56 seconds. The volume of gas effused in an experiment was the same as before, and the other arrangements similar, but the aperture in the brass plate being smaller than that of the glass jet, the effusion was considerably slower.

The constant volume of 227 cubic inches of the following gases passed into a vacuum of 29.3 inches by the attached mercurial gauge, at the temperature of 63° 3, in the following times:—

- (1.) Air in 47' 32", or 2852 seconds.
- (2.) Nitrogen in 46' 47", or 2807 seconds.
- (3.) Oxygen in 50' 1", or 3001 seconds.
- (4.) Hydrogen in 13' 8", or 788 seconds.
- (5.) Carbonic acid (over brine) in 56' 54", or 3414 seconds.



These results, referred to air as unity, are as follows :—

	Time of effusion.	Theoretical time.	Velocity of effusion.	Theoretical velocity.
Air, . . . . .	1	1	1	1
Nitrogen, . . . . .	0·9842	0·9856	1·0160	1·0146
Oxygen, . . . . .	1·0502	1·0515	0·9503	0·9510
Hydrogen, . . . . .	0·2763	0·2632	3·607	3·7994
Carbonic acid, . . . .	1·1971	1·2365	0·8354	0·8087

The experimental results of the velocity of effusion of nitrogen and oxygen accord very closely with theory, the velocity of the first being only 0·0014 in excess, and the second 0·0007 in deficiency. Indeed the differences fall within the unavoidable errors of observation in determining the specific gravity of these gases, unless conducted with the greatest precautions. Of hydrogen, the velocity of effusion observed is 3·607 times instead of 3·80 times greater than air. It thus suffers a small but sensible reduction of its velocity, which can be referred, as will afterwards appear, to the thickness of the plate and the aperture being in consequence sensibly tubular. A portion of the carbonic acid gas must have been absorbed by the brine during the long continuance of the experiment, nearly an hour; to which the quickness of the rate of that gas may be referred; the velocity of its passage being thus apparently increased from 0·81 to 0·835.

The experiment was varied by observing the time in which gas entered a vacuous receiver upon the plate of the air-pump, in quantity sufficient to depress the gauge barometer from 28 to 23 inches. An exhaustion was always made at first of upwards of 29 inches, and the instant noted at which the mercury passed the 28th and 23rd inches of the scale. The times of effusion were as follows, the temperature being 66° :—

	Experiments.				Velocity of effusion.	
	1.	2.	3.	Mean.	Observed.	Calculated.
Air, . . . . .	474	474	...	474	1	1
Oxygen, . . . . .	501	502	499	500·7	0·9467	0·9510
Nitrogen, . . . . .	468	469	...	468·5	1·0117	1·0146
Olefiant gas, . . . . .	467	469	...	468	1·0128	1·0147
Carburetted hydrogen, .	357	...	...	337	1·3278	1·3369
Carbonic acid, . . . .	573	573	...	573	0·8272	0·8087

The same close correspondence is manifest here between the observed and calculated velocities.

The whole results leave no doubt of the truth of the general law, that *different gases pass through minute apertures into a vacuum in times which are as the square roots of their respective specific gravities; or with*



*velocities which are inversely as the square roots of their specific gravities ; that is, according to the same law as gases diffuse into each other.*

It appears that the proper effect of effusion can only be brought out in a perfect manner when the gas passes through an aperture in a plate of no sensible thickness, for when the opening becomes a tube, however short, the effluent gas meets a new resistance which varies in the different gases according to an entirely different law from their rates of effusion, namely, the resistance of transpiration. The deviation is most considerable in hydrogen, which rapidly loses velocity if carried through a tubular opening, when compared with air. This was illustrated by experiments made upon the glass jet of the former observations ; which was operated upon in four different conditions as to length. The point had been drawn out rather long at first, so that it admitted of portions of 0·2 inch, 0·1 inch, and 0·07 inch, being broken off successively before it was reduced to the form of a blunt cone, which it had when used in the experiments already detailed. Air and hydrogen were effused from this jet into the exhausted receiver till the mercurial gauge fell from 28 to 4 inches, with the jet in the different states described.

When the glass jet was of greatest length, the time of air was 335 and 337 seconds in two experiments, and of hydrogen 120 seconds in two experiments ; which give 2·800 as the velocity of effusion of hydrogen.

After the first portion was broken from the point, by which of course the aperture was enlarged, the time of air was 175 seconds in two experiments, of hydrogen 55 and 56 seconds ; giving 3·153 for the effusive velocity of hydrogen.

After the second abridgment in its length, the time of passage of air by the jet was 110 seconds in two experiments, of hydrogen, 33, 32 and 33 seconds in three experiments ; giving 3·33 for the velocity of hydrogen.

When still further reduced in length, a larger jar being used as the vacuum receiver, the time of air was in two experiments 408 and 410 seconds ; of hydrogen in three experiments, 122, 120 and 122 seconds, giving 3·38 for the velocity of hydrogen. Thus, as the jet was progressively shortened, the relative velocity of the passage of hydrogen continually rose, passing through the numbers 2·8, 3·153, 3·33 and 3·38. By reversing the direction of the stream of gas through the aperture in its last condition, the effect of friction was still further diminished, and the velocity of hydrogen raised to 3·61, as in the experiments previously recorded, which were made with this jet in an inverted position. It may be fairly presumed, therefore, that if the length of the tube or thickness of the plate containing the aperture was still further diminished, the effusive velocity of hydrogen, compared with air, would



be increased, and approximate more nearly to 3.80, the theoretical number.

The tubularity of the opening quickens, on the contrary, the passage of carbonic acid and nitrous oxide in reference to air; for these gases are more transpirable than air, although less effusive; hence their observed time of effusion is always sensibly less than their calculated time.

3. *Effusion of Nitrogen and Oxygen, and of mixtures of these Gases under different pressures, by a second perforated brass plate B.*

This brass plate was of the same thickness as the last ( $\frac{1}{228}$ th of an inch); the aperture was circular and also  $\frac{1}{228}$ th of an inch in diameter, as measured by a micrometer; and the velocity with which air of the usual tension passed into a vacuum by the aperture, one cubic inch in 6.08 seconds. The rate of passage was therefore rather more than twice as quick as by the first perforated plate A.

A two-pint jar was used as the air-pump receiver, or aspirator-jar, as it may be called; and the capacity of the vacuous space into which the gas effuses, including the tubes and channels of the air-pump as well as the jar, was found to be 72.54 cub. in. An exhaustion was always first made of about 29 inches by the gauge barometer of the pump, and then the gas allowed to enter from a counterpoised bell-jar over water (fig. 1, Plate XXXIII). The instant was noted at which the mercury fell to 28 inches, when the observation began, and again at 20 and 12 inches, or after two intervals of 8 inches each; and again at 4 and 2 inches by the gauge barometer. The experiments were made successively on the same day in the order given, with the barometer at 29.34 inches and thermometer at 49°. A small thermometer placed within the aspirator-jar was observed to rise 1° Fahr. very uniformly during the continuance of an experiment. The effusion of air is repeated at the close of the experiments to determine whether or not any change of rate had occurred during their continuance.

TABLE I.—Effusion.

Gauge barometer in inches.	Air.		Nitrogen.		Oxygen.		Mixture of 50 nitrogen + 50 oxygen.	
	I.	II.	I.	II.	I.	II.	I.	II.
28	0	0	0	0	0	0	0	0
20	120	120	119	119	126	126	122	122
12	123	122	120	120	128	130	125	125
8	68	68	67	67	72	72	70	69
4	84	84	83	83	89	88	85	86
2	57	57	55	54	59	59	57	57
	452	451	444	444	474	475	459	459



TABLE II.—Effusion.

Gauge barometer in inches.	25 nitrogen + 75 oxygen.		75 nitrogen + 25 oxygen.		Air.
	I.	II.	I.	II.	
28	0	0	0	0	0
20	122	122	122	121	120
12	125	125	122	122	123
8	70	69	68	68	68
4	85	86	85	85	83
2	57	57	56	56	57
	459	459	453	453	451

The near approach to equality in the times from 28 to 20, and from 20 to 12 inches throughout the whole of these experiments, is very remarkable. Under an average pressure of 24 inches in the former portion of the scale and of 16 in the latter, the gases effuse with nearly equal velocities; which confirms the observation of MM. de Saint-Venant and Wantzel, on the passage of air through a minute aperture, namely, that above two-fifths of an atmosphere, the further increase of the pressure is attended with a very slight increase in the velocity of passage.<sup>1</sup> In the experiments above with an increase of pressure from 16 to 24, or of one-half, the increase in velocity is not in general more than one-sixtieth part.

In the table which follows the average times are given, which the gauge barometer required to fall from 28 to 12 inches, and from 12 to 4 inches, taken from the preceding table, for air, nitrogen, and oxygen, and also the ratio between the times of these gases, that of air being taken as unity, with their relative velocities, also referred to the velocity of air.

Gauge barometer.	Time in seconds.			Time of air = 1.		Velocity of air = 1.	
	Air.	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.
From 28 to 12 in.,	242.5	239	255.0	0.9855	1.0515	1.0146	0.9510
From 12 to 4 in.,	152.0	150	160.5	0.9868	1.0558	1.0133	0.9470

These results do not indicate any material difference between the ratios of effusion of these gases at different pressures. At the low as well as the high pressure, the velocities are in close accordance with the law of effusion; indeed they correspond as closely as the shortness of the time of observation justifies any inference; the small deviations observable being quite within the amount of errors of observation.

<sup>1</sup> *Journal de l'Ecole Royale Polytechnique*, tome xvi., 27 Cabier, 1839, p. 85. This memoir contains a valuable mathematical discussion of the velocities with which air flows into a receiver at different degrees of exhaustion.



The results for the mixtures of oxygen and nitrogen are as follows, for similar divisions of the scale :—

Gauge barometer.	Time in seconds.			Time, air = 1.		
	I. 50 N + 50 O.	II. 25 N + 75 O.	III. 75 N + 25 O.	I. Mixture.	II. Mixture.	III. Mixture.
From 28 to 12 in.,	247	252	243.5	1.0185	1.0391	1.0041
From 12 to 4 in.,	155	157	153	1.0197	1.0329	1.0066

In these instances as well as in the unmixed gases, the results do not justify the inference of any difference in the ratios of effusion at low from the ratios which hold at high pressures.

It appears, on comparing the times observed of the mixtures with the times calculated from the unmixed gases, that they sensibly agree. Thus the mean rate or time of 50 nitrogen + 50 oxygen, or square root of the specific gravity of that mixture, is 1.0191, the observed rate 1.0185; of 25 nitrogen + 75 oxygen, the mean rate is 1.0354, the observed rate 1.0391; of 75 nitrogen + 25 oxygen, the mean rate is 1.0025, the observed time 1.0041, in the range between 28 and 12 inches of the gauge barometer. Lastly, the particular mixture forming atmospheric air has already been seen to have the rate corresponding with its specific gravity or its composition. It may hence be inferred that any mixture of oxygen and nitrogen will possess the average rate of effusion of its constituent gases.

4. *Effusion of Air, Carbonic Oxide, Oxygen, and of a mixture of Carbonic Oxide and Oxygen at different pressures, by Plate B.*

The carbonic oxide was prepared according to Mr. Fownes's process, by heating oil of vitriol upon ferrocyanide of potassium: the gas was collected, as a measure of precaution, over alkali.

The arrangements were similar to the last; barometer at 29.29 inches, thermometer 52°.

TABLE III.—Effusion.

Gauge barometer in inches.	Air.		Carbonic oxide.		Oxygen.		Mixture of 50 car- bonic oxide + 50 oxygen.	
	I.	II.	I.	II.	I.	II.	I.	II.
28	0	0	0	0	0	0	0	0
20	118	119	116	117	125	126	121	121
12	120	120	118	117	126	126	123	122
8	67	66	66	66	71	71	68	68
4	81	82	80	81	86	86	83	83
2	56	56	55	55	60	60	58	58
	442	443	435	436	468	469	453	452



The passage of the gases is somewhat quicker throughout than in the preceding experiments with the same plate, but the ratio between their velocities remains constant.

Comparing again the same portions of the scale, we have—

Gauge barometer.	Time in seconds.				Time, air =1.		
	Air.	Carbonic oxide.	Oxygen.	Mixture.	Carbonic oxide.	Oxygen.	Mixture.
From 28 to 12 in.,	238.5	234	251.5	243	0.9811	1.0545	1.0188
From 12 to 4 in.,	148	146.5	157	151	0.9898	1.0608	1.0202

Taking 0.96779 as the specific gravity of carbonic oxide, the square root is 0.9838, which corresponds closely with the observed time above, being intermediate between the times for the two different portions of the scale.

The time of effusion also of the mixture of carbonic oxide and oxygen in equal volumes is obviously the square root of the density of the mixture of the two gases :

Observed time of mixture,	.	.	.	1.0188
Calculated time of gases, .	.	.	.	1.0182

The observed time of effusion of the mixture being within one thousandth part of the calculated time.

5. *Effusion of Carbonic Acid, Air, and of mixtures of Carbonic Acid and Air, at different pressures, by Plate B.*

The arrangements continued the same as in last experiments; barometer 29.58 in.; thermometer 49°.

TABLE IV.—Effusion.

Gauge barometer in inches.	Air.		Carbonic acid.		First mixture, 75 CO <sub>2</sub> +25 air.		Second mixture, 50 CO <sub>2</sub> +50 air.		Third mixture, 25 CO <sub>2</sub> +75 air.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
28	0	0	0	0	0	0	0	0	0	0
20	121	121	145	146	141	140	135	134	128	128
12	123	123	150	149	143	143	137	137	131	131
8	69	70	83	84	81	80	76	77	74	73
4	85	84	103	103	98	99	95	94	90	90
2	58	59	71	70	68	67	64	64	61	61
	456	457	552	552	531	529	507	506	484	483



Comparing again the times in the two divisions of the scale adopted in the preceding tables :

Time in Seconds.

Gauge barometer.	Air.	Carbonic acid.	Mixture I.	Mixture II.	Mixture III.
From 28 to 12 in., .....	244	295	283.5	271.5	259
From 12 to 4 in., .....	154	187	179	171	163.5

Time of Effusion, time of Air = 1.

Gauge barometer.	Carbonic acid.		Mixture I.		Mixture II.		Mixture III.	
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.
From 28 to 12 in.,	1.2090	1.2365	1.1618	1.1818	1.1127	1.1245	1.0618	1.0647
From 12 to 4 in.,	1.2143	1.2365						

The calculated number for carbonic acid (1.2365) is the theoretical time, or square root of the density of the gas; the calculated times for the mixtures are also the square roots of the respective gravities of those mixtures.

The times of effusion of carbonic acid compared with air do not therefore differ more than the numbers 1.209 and 1.214, in the two divisions of the scale; or 1 part in 242, a deviation which may be considered as within the errors of observation.

The mixtures of carbonic acid and air have also the mean times of the pure gases.

#### 6. *Effusion of mixtures containing Hydrogen.*

<sup>1</sup>[I was induced to examine the effusion of mixtures of hydrogen and other gases very minutely, in order to elucidate if possible certain singular peculiarities which were observed in the transpiration of these mixtures by tubes. A new plate E was employed, composed of thin platinum foil  $\frac{7}{8}$ th of an inch in thickness, with a circular aperture  $\frac{1}{8}$ th of an inch in diameter, as measured by Mr. Powell by means of a micrometer. It was desirable to simplify the experiment at the same time by operating upon a constant volume of gas, measured before effusion, and drawn into an aspirator-jar which was maintained vacuous, or as nearly so as possible, by uninterrupted exhaustion. The gas was measured in a globular jar, to which more particular reference will be made hereafter. It contained 65 cubic inches between two marks, one upon each of its tubular axes, and was supported vertically over the water of a pneumatic trough.

<sup>1</sup> The passages and tables in this paper, which are enclosed in brackets, as the following to p. 103, have been added during the progress of the paper through the press, and the date of the addition is in each case noted at the end of the last paragraph.—S. H. C.



The little brass tube upon which the perforated plate is fixed (*a.* in fig. 5, Plate XXXIII.) was now made to screw upon the end of one of the stop-cocks, namely, L (fig. 1), which is immediately attached to the aspirator-jar, and projected upwards within the block tin tube H. The perforated plate was fixed to the end of its brass tube by means of soft solder.

The results thus obtained I consider superior in value to those already detailed, from the longer periods of observation, the time for air generally amounting to 800 or 900 seconds; from the new plate being thinner and its aperture of a regular circular form; and from the greater simplicity of the conditions of the experiment, namely, the passage of the gases into a sustained vacuum under the whole atmospheric pressure.

The series of experiments is divided into five sections, each containing the experiments of one day, to which the height of the barometer and the temperature are added. Two observations were made of the time of effusion in seconds for each gas, which are given under the columns of experiments I. and II., and the mean of the two experiments is added in a third column. This mean is expressed in the column which follows, with reference to the time of oxygen as 1. The additional column headed "calculated times of mixtures, oxygen = 1," contains times of the mixtures, calculated from their specific gravities, being the square roots of the densities of the respective mixtures. The observed times of the hydrogen mixtures will be seen to correspond very closely with these calculated numbers, the maximum divergences not exceeding that of pure hydrogen itself.

TABLE V.—Effusion into a Sustained Vacuum by Platinum Plate E.

	I.	II.	Mean.	Oxygen=1.	Cal. time, Oxygen=1.	Barometer.	Temp. Fahr.
SECTION I.							
Oxygen, . . . . .	909	909	909	1.0000	...	30.396	68
Air, . . . . .	866	865	865.5	0.9521			
Hydrogen, . . . . .	242	242	242	0.2662			
Carburetted hydrogen, . . . . .	624	622	623	0.6853			
Carbonic oxide, . . . . .	849	850	849.5	0.9345			
Nitrogen, . . . . .	850	851	850.5	0.9356			
Air, . . . . .	864						
Carbonic acid, . . . . .	1053	1051	1052	1.1573			
SECTION II.							
Oxygen, . . . . .	912	912	912	1.0000	...	30.288	66
Air, . . . . .	868	867	867.5	0.9512			
Hydrogen, . . . . .	240	240	240	0.2631			
25H + 75 Air, . . . . .	756	756	756	0.8289	0.8328		
50H + 50 Air, . . . . .	633	633	633	0.6940	0.6951		
75H + 25 Air, . . . . .	483	483	483	0.5296	0.5224		
80H + 20 Air, . . . . .	444	444	444	0.4868	0.4805		
90H + 10 Air, . . . . .	358	358	358	0.3925	0.3830		
95H + 5 Air, . . . . .	309	309	309	0.3388	0.3296		
Air, . . . . .	864						



TABLE V.—*continued.*

	I.	II.	Mean.	Oxygen=1.	Cal. time, Oxygen=1.	Barometer.	Temp. Fahr.
SECTION III.							
Oxygen, . . . .	912	910	911	1.0000	...	30.219	66
Air, . . . . .	867	865	866	0.9506			
Hydrogen, . . .	239	241	240	0.2634			
12.5H + 87.5O, .	853	855	854	0.9374	0.9396		
25 H + 75 O, . .	796	796	796	0.8737	0.8750		
37.5H + 62.5O, .	733	733	733	0.8046	0.7990		
50 H + 50 O, . .	661	661	661	0.7255	0.7289		
62.5H + 37.5O, .	586	586	585.5	0.6427	0.6435		
75 H + 25 O, . .	501	501	501	0.5499	0.5449		
80 H + 20 O, . .	460	461	460.5	0.5055	0.5000		
90 H + 10 O, . .	368	368	368	0.4039	0.3954		
95 H + 5 O, . . .	312	312	312	0.3424	0.3309		
Air, . . . . .	860						
SECTION IV.							
Oxygen, . . . .	914	913	913.5	1.0000	...	29.673	64
Air, . . . . .	870	869	869.5	0.9518			
Carbonic oxide, .	854	853	853.5	0.9343			
Hydrogen, . . .	238	239	238.5	0.2610			
25H + 75CO, . .	749	748	748.5	0.8193	0.8199		
50H + 50CO, . .	626	626	626	0.6852	0.6848		
75H + 25CO, . .	478	478	478	0.5231	0.5155		
80H + 20CO, . .	445	445	445	0.4871	0.4745		
90H + 10CO, . .	360	360	360	0.3940	0.3793		
95H + 5CO, . . .	314	314	314	0.3437	0.3213		
Air, . . . . .	870						
SECTION V.							
Oxygen, . . . .	915	914	914.5	1.0000	...	29.500	63
Air, . . . . .	870	869	869.5	0.9508			
Nitrogen, . . .	855	854	854.5	0.9344			
Hydrogen, . . .	241	241	241	0.2635			
25H + 75N, . . .	753	753	753	0.8234	0.8213		
50H + 50N, . . .	631	631	631	0.6899	0.6859		
75H + 25N, . . .	480	478	479	0.5238	0.5163		
80H + 20N, . . .	442	442	442	0.4833	0.4752		
90H + 10N, . . .	359	359	359	0.3925	0.3797		
95H + 5N, . . . .	309	310	309.5	0.3379	0.3215		
Hydrogen, . . .	241						
Air, . . . . .	869						

The principal results of the preceding table, and also the results of two series of experiments or mixtures of hydrogen with carburetted hydrogen ( $C H_2$ ) and with carbonic acid, are exhibited by means of the curves projected in Plate XXXIV., for the purpose of comparing with them the results of the transpiration of the same mixtures exhibited in Plate XXXV., which I have not yet succeeded in reconciling with any physical law. Feb. 1846.]

The numbers at the top and bottom of the Plate, which apply to the vertical lines, express the times of effusion, the time of oxygen being



taken as 100; while the numbers to the right of the table, and which apply to the horizontal lines, express the volumes of hydrogen in 100 volumes of the mixture. Thus the curves all terminate above in a common point, 26.3, the time of 100 hydrogen; and each terminates below with the proper time of the particular gas which is mixed with hydrogen, the proportion of hydrogen being then 0, and that of the other gas 100; that is, the curve of the carburetted hydrogen mixtures at 72.32; the curve of the nitrogen mixtures at 93.5; that of the air mixtures at 95.1; that of the oxygen mixtures at 100, and that of the carbonic acid mixtures at 116.

7. *Effusion of Air of different Elasticities or Densities, by brass plate B.*

In all the experiments hitherto described, the air or gas effused was under the atmospheric pressure, which varied only within narrow limits. It was desirable to know whether the time remained constant for the passage into a vacuum of equal volumes of air of all densities, which the theory of the passage of fluids into a vacuum requires.

The air was drawn into the receiver of an air-pump (fig. 2, Plate XXXIII.), maintained vacuous by continued pumping, from the globular gas receiver *a*, placed in a deep glass basin half-filled with water and used as a pneumatic trough; this basin and the globular vessel being placed on the plate of a second air-pump under a large bell-jar in which a partial exhaustion could be maintained during the continuance of the experiment. The vessel *a* had tubular openings at top and bottom; its capacity between the marks *b* and *c* in these necks was 65 cubic inches; the lower tube was expanded under the mark *b* into an open funnel; the upper tube was cylindrical with a flange or lip, and had a sound cork fitted into it. A short brass tube *d*, of quill size, soldered to the end of the stopcock *e*, descended into the bell-jar and passed through the cork of *a*, which was perforated. The vessel *a* having thus an air-tight communication with the exhausted receiver *v* of the first air-pump, by the tube *F*, the drying tube *U* and the tube *H*; a measured quantity of air (65 cubic inches) could be drawn from it by observing the time which the water of the trough took to rise from the mark *b* to *c*. The perforated brass plate, through which the gas had to pass, was attached to the stopcock *L*, as before, and was therefore within the tube *H*. It is represented of one-fourth of its linear dimensions in fig. 5, Plate XXXIII.

When the large bell-jar over *a* was not exhausted, the gas in the latter was of the atmospheric tension. With the barometer at 29.28 inches, and thermometer at 54°, the air was withdrawn from the globe *a*, in 388 seconds in one experiment, and in 389 seconds in another.



The pressure upon the air in  $a$  was then reduced to three-fourths of an atmosphere, by exhausting so that the gauge barometer stood at 7.32 inches from the bottom of the scale, which is one-fourth of the whole pressure of 29.28 inches. The globe  $a$  was thus occupied by air of the tension of three-fourths of an atmosphere, or 21.96 inches. It was in this state connected with the vacuous receiver  $v$  of the air-pump, and the time required for the effusion of the constant volume of 65 cubic inches of air, measured in its rarefied state, between the marks  $b$  and  $c$ , observed. The effusion of this volume of air of three-fourths density was effected in two experiments in 389 and 392 seconds.

Again, the air in  $a$  being made of 14.64 inches tension, or half an atmosphere, the constant volume was effused into a vacuum in 411 and 408 seconds.

Lastly, with the air in  $a$  of 7.32 inches tension, or one-fourth of an atmosphere, the time of effusion was 438 and 439 seconds. The results therefore of the effusion of a constant volume are as follows:—

		Time of effusion.	
Air of 1	atmosphere . .	388.5 seconds . .	1.
Air of 0.75	atmosphere . .	390.5 seconds . .	1.0051
Air of 0.5	atmosphere . .	409.5 seconds . .	1.0541
Air of 0.25	atmosphere . .	438.5 seconds . .	1.1287

It thus appears that the effusion of air into a vacuum is very little affected by a moderate change of density; air of 1 atmosphere and of 0.75 atmosphere passing in nearly the same time. The effect therefore of the ordinary changes of the barometer on the effusion of air must be small, if at all sensible. A retardation occurs in the effusion of air of diminished density, which amounts to an excess of  $\frac{1}{200}$ th of the time, on air of 0.75 tension; of  $\frac{1}{20}$ th on air of 0.5 tension, and  $\frac{1}{8}$ th on air of 0.25 tension.

Experiments were also made on the effusion of air of higher density than 1 atmosphere. The air was drawn of any required tension from 1 to 2 atmospheres from a strong globular vessel A (fig. 3, Plate XXXIII.), provided with a gauge barometer and mercury, by which the tension of the compressed air within it was observed. Before its admission into this vessel the air was previously condensed in another vessel D by a syringe, to a higher degree of density than was required in A, and the supply of compressed air, regulated by the adjustment of an intermediate stopcock, so as to keep the gauge of A at a constant elevation, which could easily be done within  $\frac{1}{20}$ th of an inch.

In experiments with compressed air, the latter was allowed to flow into the two-pint jar exhausted on the plate of the air-pump, and the time observed which the gauge barometer required to fall through its range from 28 to 2 inches. During the following experiments the height



of the barometer was 29·3 inches, which is the value of 1 atmosphere, and the thermometer 53°.

TABLE VI.—Effusion of Air of different Densities.

Height of gauge barom. in inches.	Air of 1 atmosphere.		Air of 1·25 atmosphere.		Air of 1·5 atmosphere.		Air of 1·75 atmosphere.		Air of 2 atmospheres.		Air of 1 atmosphere.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	III.	IV.
28	0	0	0	0	0	0	0	0	0	0	0	0
20	116	116	90	91	76	75	65	65	56	55	117	117
12	118	118	92	91	76	76	64	64	56	56	118	118
8	65	65	47	48	38	38	33	33	30	29	66	67
4	79	80	50	50	41	40	33	32	26	28	80	80
2	54	54	26	25	18	18	16	17	14	13	54	53
	432	433	305	305	249	247	211	211	182	181	435	435

In these experiments the depression of the gauge barometer is not produced by a constant volume of the compressed air, but by a volume which is inversely proportional to the density of the compressed air; half a volume of air of 2 atmospheres being equal in the aspirator-jar, on the plate of the air-pump, to a whole volume of air of 1 atmosphere. Correcting the times of the preceding table, we have the passage of *equal volumes* of air of different densities, between the gauge height of 28 and 12 inches, as follows:—

		Time of effusion of equal volumes.	
Air of 1	atmosphere . .	234·5 seconds	. . 1·
Air of 1·25	atmosphere . .	227·5 seconds	. . 0·9701
Air of 1·5	atmosphere . .	227·2 seconds	. . 0·9688
Air of 1·75	atmosphere . .	225·2 seconds	. . 0·9603
Air of 2	atmospheres . .	223 seconds	. . 0·9510

It appears then that air of different densities between 1 and 2 atmospheres is effused in nearly equal times, the time of effusion diminishing slightly, not more than 5 per cent. with air of double tension. Taking the whole range of the preceding and present results, we have air varying in density from 0·25 to 2 atmospheres, or from 1 to 8, while the extreme variation in the time of the effusion of equal volumes is from 0·9510 to 1·1287, or from 1 to 1·1868.

In the lower part of the scale a more sensible inequality is perceived. Thus, with an exhaustion of from 8 to 4 inches in the aspirator-jar, the passage of equal volumes of air of different densities takes place in the following times:—

		Time of effusion of equal volumes.	
Air of 1	atmosphere . .	145 seconds	. . 1·
Air of 1·25	atmosphere . .	121·9 seconds	. . 0·8407
Air of 1·5	atmosphere . .	117·7 seconds	. . 0·8117
Air of 1·75	atmosphere . .	114·6 seconds	. . 0·7903
Air of 2	atmospheres . .	113 seconds	. . 0·7793



Here the time of effusion of air of 2 atmospheres falls about 22 per cent. below that of air of 1 atmosphere, while in the upper part of the scale the difference was only 5 per cent.

[8. *Effusion of Air of different Temperatures, by Plate F.*

This plate was a portion of thin platinum foil, with an aperture of an irregular hatchet form, of which the two greatest cross diameters were  $\frac{1}{8}\frac{1}{50}$ th and  $\frac{1}{8}\frac{1}{10}$ th of an inch. The perforated plate was attached to the end of the little brass cylinder by means of soft solder. A two-pint jar, giving a cavity of 72.54 cubic inches, was used as the aspirator-jar, and the time of the fall of the gauge barometer was observed from 28.5 to 23.5 inches, with the admission of dry air at different temperatures.

1. The temperature of the room being 41° Fahr., and the height of the barometer 29.616 inches, dry air entered the aspirator-jar in three experiments in 533, 532, and 530 seconds, of which the mean is 531.66 seconds. The room being afterwards heated up to 52°, the time of effusion of an equal volume of air was found to be, in three experiments, 525, 527, and 526 seconds, of which the mean is 526 seconds; or, a rise of 11° in temperature has shortened the time of effusion by 5.66 seconds. Taking the density of air at 32° as 1, at 41° it will be 0.9820, of which the square root is 0.9909; and at 52° it will be 0.9609, of which the square root is 0.9802. Now the relative times of effusion observed, namely, 531.66 and 526 seconds, are as 0.9909 to 0.9803, numbers which all but coincide with the square roots of the densities, 0.9909 and 0.9802, at the two different temperatures.

2. With the barometer at 30.186 to 30.150 inches, experiments were again made on the effusion of the same volume of dry air at 38°, 48°, and 58°, four hours elapsing between each set of experiments, which were required to bring up the room and apparatus to a uniform and steady temperature. In three experiments at each temperature,—

The time of effusion at 38° was 526, 527, and 526 seconds: mean 526.33

The time of effusion at 48° was 520, 521, and 520 seconds: mean 520.33

The time of effusion at 58° was 515, 516, and 515 seconds: mean 515.33

Here the first rise of 10° shortens the time of effusion 6 seconds, and the second rise of 10° shortens the time 5 seconds more. The density of dry air being 1 at 32°, it is at 38°, 0.9879; at 48°, 0.9684; and at 58°, 0.9497, of which three last densities the square roots are 0.9939, 0.9841, and 0.9745 respectively. Now the three mean times of effusion observed are in the proportion of the numbers 0.9939, 0.9826, and 0.9731, which correspond more closely with the preceding square



roots than could be expected from the nature of the experiments. It appears then that *the effusion time of air of different temperatures is proportional to the square root of its density at each temperature*. The velocity of the effusion will be inversely as the square root of the air's density. Hence two volumes of air which have not the same temperature, are, in regard to effusion, like different gases possessing the densities of the air at the two temperatures.

As the velocity of the effusion of air does not increase at a rate so rapid as the direct proportion of its expansion by heat, it follows that the flow of air under pressure, through a small aperture, is retarded by heating the air; that is, the same absolute quantity or weight of air will take a longer time to pass, when rarefied by heat, than when in a dense state.

I have made several experiments on the influence of *aqueous vapour* upon the effusion of air. When dry air was effused into an aspirator-jar with the gauge barometer attached, and immediately afterwards air saturated with moisture at the same temperature, the latter passed through in sensibly the same time with comparatively large apertures, but in a shorter time with small apertures, although in general without much uniformity in successive experiments. Thus the time for dry air being constant at 524 seconds with plate F of small aperture, barometer 29.812, and thermometer 49°; with moist air, the time gradually fell, till at last it appeared to settle at 506 seconds, that number being obtained in three successive experiments; the temperature in the meantime having risen to 51°. There is here an acceleration of 18 seconds, of which not more than 2 seconds are accounted for by the diminished density of the moist air, and 1 second more by the rise in temperature. The moist air seemed also to have an extraordinary effect in opening and enlarging fissures, and very soon rendered more than one platinum plate useless, which was fixed by brazing, by that action. Nov. 1847.]

## PART II.—TRANSPIRATION OF GASES.

### 1. *Transpiration of Air of different Densities or Elasticities, by a Glass Capillary Tube E.*

(a.) The same arrangements were adopted as in the effusion of air of different densities, lately described, the capillary tube being interposed in the place of the perforated plate. The apparatus employed is represented in fig. 4, Plate XXXIII.

With barometer 29.28, and thermometer 54°, 65 cubic inches of dry air of the atmospheric density were transpired from the globular vessel *a* (fig. 2), into a good vacuum sustained by continued pumping, through



a capillary glass tube E, twenty feet in length; the same volume of air of 0.75 atmosphere and 0.5 atmosphere, measured at these pressures, were also transpired by the same capillary. The times were as follows:—

	I.	II.	Mean.
Transpiration of air of 1 atmosphere, .	799 <sup>u</sup>	800 <sup>u</sup>	799.5
Transpiration of air of 0.75 atmosphere, .	1049	1051	1050
Transpiration of air of 0.5 atmosphere, .	1545	1542	1543.5

It is obvious that the times approach the inverse ratio of the tensions, as will appear more clearly on comparing the times observed with those calculated on that principle.

	Time observed.	Time calculated.
Transpiration of air of 1 atmosphere, .	1	1
Transpiration of air of 0.75 atmosphere, .	1.3133	1.3333
Transpiration of air of 0.5 atmosphere, .	1.9306	2

With air of higher tension than 1 atmosphere, the same apparatus for compression was also employed as in the effusion experiments (fig. 3). The capillary E communicated with the two-pint aspirator-jar (capacity 72.54 cubic inches), which was fully exhausted on the plate of the air-pump. The air being then allowed to pass into the capillary, the instant of time was noted when the gauge barometer fell to 28 inches, and the other points described below. The external barometer stood at 29.08 inches; thermometer at 53°.

TABLE VII.—Transpiration of Air of different Densities.

Gauge barometer in inches.	Air of 1 atmosphere.		Air of 2 atmospheres.		Air of 1.75 atmosphere.		Air of 1.5 atmosphere.		Air of 1.25 atmosphere.		Air of 1 atmosphere.
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	
28	0 <sup>u</sup>	0 <sup>u</sup>	0 <sup>u</sup>	0 <sup>u</sup>	0 <sup>u</sup>	0 <sup>u</sup>	0 <sup>u</sup>	0 <sup>u</sup>	0 <sup>u</sup>	0 <sup>u</sup>	0 <sup>u</sup>
20	253	254	66	67	85	86	114	114	162	161	255
12	310	310	70	69	91	90	123	124	182	179	311
8	220	220	37	37	49	49	69	70	110	109	221
4	349	352	39	40	53	53	78	77	132	134	346
2	328	328	20	19	29	28	41	41	78	79	229
	1460	1464	232	232	305	306	425	426	664	662	1462

The times of transpiration in the preceding table require to be



corrected, as they represent the passage of equal volumes of air measured after and not before the transpiration. Thus the same depression of the gauge barometer would be produced by half a volume of air of 2 atmospheres, as by a whole volume of air of 1 atmosphere; and it is necessary therefore to double the times observed of air of the former density, to obtain the time of passage of a whole volume. For the transpiration of equal volumes, in the gauge-range from 28 to 20 inches, which is most nearly equivalent to the action of a vacuum, we have—

Equal volumes.	Observed time of transpiration.	Calculated time.
Air of 1 atmosphere.....	254 seconds..... 1	1
Air of 1.25 atmosphere.....	201.9 seconds..... 0.7949	0.8000
Air of 1.5 atmosphere.....	171 seconds..... 0.6732	0.6666
Air of 1.75 atmosphere.....	149.6 seconds..... 0.5890	0.5714
Air of 2 atmospheres .....	133 seconds..... 0.5236	0.5

The calculated times of the last column are the reciprocals of the tension, or number of atmospheres in the first column; they represent the observed times within a sufficient degree of approximation, to prove that *for equal volumes of air of different densities, the times of transpiration are inversely as the densities*. The velocity of transpiration will therefore be directly in proportion to the density of the air,—air of double density being transpired into a vacuum in half time.

This at once separates the action of a capillary tube from that of a minute aperture; for air of all densities, it will be remembered, passes into a vacuum by effusion with equal velocity,

A consequence of this law immediately appears in conducting transpiration experiments, in the marked influence of the height of the barometer on the time of transpiration; the higher the barometer and the denser the air, the more quickly does a constant volume of it pass through a capillary tube into a vacuum.

This appears also to separate transpiration from the ordinary action of friction; for the denser the air, the more should its passage be retarded by friction.

## [2. *Transpiration of Air of different Temperatures.*

Dry air was transpired by a glass capillary tube K, of fine bore, 39.4 inches in length, into a two-pint jar till the gauge barometer fell from 28.5 to 23.5 inches, in 796, 794 and 794 seconds, in three successive experiments, made at the temperature of 41° Fahr., and with the barometer at 30.052 inches. Four hours afterwards, the air and all the apparatus having been for some time at 58°, an equal volume of dry air was transpired twice in 814 seconds. A difference of 17 degrees



of temperature has made a difference of 19 seconds in the time of transpiration, and *the dense cold air is transpired most rapidly*. The times are nearly in the inverse ratio of the square root of the densities of air at the two temperatures.

The transpiration of air in the first experiments which are made in the morning is often observed to be more rapid than in those which follow, owing I believe to the low nocturnal temperature being retained for some time by the glass capillary. January 1847.]

### 3. Preliminary Experiments on the Transpiration of different Gases by Capillary Tubes, A, B, and C.

The times of transpiration of the gases will be expressed in the sequel with reference to the time of oxygen as unity instead of that of air. Assuming what is now almost universally conceded, that the atomic weights of the following elements are exactly expressed by entire numbers, namely, oxygen by 8, nitrogen by 14, carbon by 6, and hydrogen by 1, and that, while the equivalent proportion of the first affords one volume of gas, that of each of the others affords two volumes, we obtain the following theoretical densities for these elements, and several of their gaseous compounds. The experimental determinations which appear to be of most value are subjoined.

TABLE of Specific Gravities of Gases.

	Air=1.		Oxygen=1 and 16.			
	Calculated.	Observed.	Calculated.		Observed.	
Oxygen, . . . .	1·1099*	1·10563 Regnault.	1	16	1	
Nitrogen, . . . .	0·9712	0·97137 Regnault.	0·8750	14	0·8785	Regnault.
Air, . . . . .	1	1	0·9010	14·416	0·9038	Regnault.
Hydrogen, . . . .	0·06937	0·06926 Regnault.	0·0625	1	0·0626	Regnault.
Carbon, . . . . .	0·4162	... ..	0·3750	6		
Carbonic acid, . .	1·5261	1·52901 Regnault.	1·3750	22	1·3830	Regnault.
Nitrous oxide, . .	1·5261	... ..	1·3750	22		
Nitric oxide, . . .	1·0405	... ..	0·9375	15		
Carbonic oxide, . .	0·9712	0·9678 Wrede.	0·8750	14	0·8754	Wrede.
Carburetted hydrogen,	0·5549	0·555 { Thomson and Henry.	0·5000	8	0·5001	{ Thomson and Henry.
Olefiant gas, . . .	0·9712	0·9852 Saussure.	0·8750	14	0·8904	Saussure.
Sulphuretted hydrogen,	1·1793	1·1912 { Gay-Lussac } and Thenard }	1·0625	17	1·0766	{ Gay-Lussac and Thenard.

\* Assigning the theoretical densities of 14 and 16 to nitrogen and oxygen, and assuming air to be composed of 79·2 volumes of the first, and 20·8 volumes of the second, the density of air will be expressed by the intermediate number 14·416; or, with the density of air=1, the density of oxygen becomes 1·1099, and the density of nitrogen 0·9712, both as given above. Hydrogen is calculated in the same column as  $\frac{1}{16}$ th of oxygen (1·1099), carbon as  $\frac{6}{16}$ ths, carbonic acid and nitrous oxide as each  $\frac{22}{16}$ ths; nitric oxide as the mean of nitrogen and oxygen, carbonic oxide and olefiant gas as  $\frac{14}{16}$ ths of oxygen; carburetted hydrogen as  $\frac{8}{16}$ ths, and sulphuretted hydrogen as  $\frac{17}{16}$ ths.



With the exception of the recent valuable determinations of M. Regnault and Baron Wrede, the calculated specific gravities are probably nearer the truth and more to be depended on than the experimental results found in books, which are old, and generally not made with that degree of precision which the science now requires.

*Capillary A.*—This glass tube was thirty inches in length, and of a fine cylindrical bore; it allowed 1 cubic inch of air of the usual tension to pass into a vacuum in about 13 seconds. A pint-jar was exhausted, of which the capacity, including the vacuous spaces of the air-pump, was 41·64 cubic inches. The gas entered into this space, passing through the capillary, and depressed the attached gauge barometer in the times stated in the following Tables :—

TABLE VIII.—Transpiration by Capillary A into a One-Pint Jar.  
Barom. 29·55 in. Temp. 61°.

Gauge barometer in inches.	Air.		Oxygen.		Hydrogen.	
	I.	II.	I.	II.	I.	II.
28	0	0	0	0	0	0
20	150·5	150	166·5	166	71	70·5
12	181·5	182	201	201·5	87	87
4	321	321	354·5	354	156	155
2	...	...	213·5	215·5	94·5	94·5
From 28 to 4 inches . .	653	653				
From 28 to 2 inches . .	...	...	935·5	937	408·5	407

### Mean Results.

Gauge barometer.		Air.	Hydrogen.
From 28 to 20 inches	Time in seconds .....	150·25	70·75
	Time of oxygen=1 .....	0·9037	0·4255
From 20 to 12 inches	Time in seconds .....	181·75	87
	Time of oxygen=1 .....	0·9031	0·4322
From 12 to 4 inches	Time in seconds .....	321	155·5
	Time of oxygen=1 .....	0·9061	0·4389
From 4 to 2 inches	Time in seconds .....	...	94·5
	Time of oxygen=1 .....	...	0·4405
From 28 to 4 inches	Time in seconds .....	653	313·25
	Time of oxygen=1 .....	0·9047	0·4340
From 28 to 2 inches	Time in seconds .....	...	407·75
	Time of oxygen=1 .....	...	0·4355



TABLE IX.—Transpiration by Capillary A into a One-Pint Jar.  
Barom. 29·5. Temp. 58°·5.

Gauge barometer in inches.	Air.		Oxygen.		Carburetted Hydrogen.		Carbonic Acid.	
	I.	II.	I.	II.	I.	II.	I.	II.
28	0	0	0	0	0	0	0	0
20	150	150	166·5	166	94·5	94·5	131	131
12	182·5	182	202	201·5	118·5	119	158	158
4	318·5	318	359·5	357	198·5	198	272	271
2	190·5	192	217	216	119	118	159	159
From 28 to 2 inches	841·5	842	945·5	940·5	530·5	529·5	720	719

### Mean Results.

Gauge barometer.		Air.	Carburetted Hydrogen.	Carbonic Acid.
From 28 to 20 inches	Time in seconds .....	150	94·5	131
	Time of oxygen = 1 .....	0·9022	0·5684	0·7879
From 20 to 12 inches	Time in seconds .....	182·25	118·75	158
	Time of oxygen = 1 .....	0·9033	0·5886	0·7831
From 12 to 4 inches	Time in seconds .....	318·25	198·25	271·5
	Time of oxygen = 1 .....	0·8914	0·5505	0·7600
From 4 to 2 inches	Time in seconds .....	191·25	118·5	159
	Time of oxygen = 1 .....	0·8833	0·5473	0·7344
From 28 to 2 inches	Time in seconds .....	841·75	530·	719·5
	Time of oxygen = 1 .....	0·8928	0·5622	0·7633

It will be observed that the proportion between the times of oxygen and air is subject to a variation at different parts of the scale, but is so small as to be within the errors of observation; while this nearly constant ratio of their times coincides almost with that of their specific gravities (1 to 0·9038 Regnault).

The time or rate of hydrogen varies to the extent of 0·015 at different parts of the scale, the passage of that gas being relatively quicker at high than at low pressures. It is a question how far this variation in the ratio is owing to the action of effusion; the time of effusion of this gas being only 0·25, referred to oxygen as unity, while its time of transpiration is 0·4355. The influence of effusion upon the rate of passage is likely to be most considerable when the pressure is greatest; and that of transpiration, on the contrary, most considerable when the resist-



ance to the passage of the gas is greatest and the pressure least, that is, in the lower part of the scale.

It may be observed that the transpiration time of hydrogen does not differ far from 0.4375, which is one-half of the transpiration time of nitrogen, calculated from the experiment on air, or seven-sixteenths of that of oxygen.

Carbonic acid appears to be much more quickly transpired than oxygen, although denser than that gas in the ratio of 11 to 8; but the effusion time of carbonic acid being slow, any influence of effusion will increase the time of transpiration of this gas, the reverse of what occurs with hydrogen. The transpiration time of carbonic acid varies considerably at different pressures, being slower by 0.0535 at the upper than the lower part of the scale. An approach to 0.75, or twelve-sixteenths of the time of oxygen, may be noted at present in the rate of this gas.

The transpiration rate of carburetted hydrogen appears to be affected by an error of observation in the middle part of the scale; but its rate is slower at the upper part than at the lower, to the extent of 0.0211. This is also in accordance with the assumed influence of effusion, the effusion time of this gas being greater than its transpiration time. The transpiration time of carburetted hydrogen is not in direct proportion to its gravity, which is 0.5, or one-half of that of oxygen: it approaches more nearly to 0.5625, which is nine-sixteenths of the time of oxygen.

*Capillary B.*—This glass tube was 31.5 inches in length, of a round bore, but decidedly conical. It was first placed so that the gas entered the tube by the large and escaped by the small opening. When so arranged this tube allowed 1 cubic inch of air to pass into a vacuum in 34.3 seconds, or the transpiration was nearly three times slower than by A.

TABLE X.—Transpiration by Capillary B into a Half-Pint Jar (21.26 cubic inches). Barom. 29.17. Temp. 68°.

Gauge barometer in inches.	Oxygen.		Nitrogen.			Carburetted hydrogen.	
	I.	II.	I.	II.	I.	I.	II.
28	0	0	0	0	0	0	0
20	235.5	235.5	209	205	205	133	133
12	289	290.5	252	253	...	162.5	163
4	521	521	451.5	453.5	...	290.5	290.5
2	290.5	290.5	258	255.5	...	164	165.5
From 28 to 2 inches ...	1336	1337	1170.5	1167	205	750	752



## Mean Results.

Gauge barometer.		Nitrogen.	Carburetted hydrogen.
From 28 to 20 inches	Time in seconds.....	206·3	133
	Time of oxygen=1 ...	0·8760	0·5647
From 20 to 12 inches	Time in seconds.....	252·5	162·7
	Time of oxygen=1 ...	0·8716	0·5618
From 12 to 4 inches	Time in seconds.....	452·5	290·5
	Time of oxygen=1 ...	0·8685	0·5576
From 4 to 2 inches	Time in seconds.....	256·7	164·7
	Time of oxygen=1 ...	0·8845	0·5677
From 28 to 2 inches	Time in seconds.....	1168·7	751
	Time of oxygen=1 ...	0·8740	0·5619

TABLE XI.—Transpiration by Capillary B into a Half-Pint Jar.  
Barom. 29·2.

Gauge barometer in inches.	Oxygen.			Hydrogen.			Carbonic acid.		
	I.	II.	III.	I.	II.	III.	I.	II.	III.
28	62° 0"	62°·5 0"	64°·5 0"	65° 0"	65° 0"	65°·5 0"	66° 0"	66° 0"	66° 0"
20	234	234	234·5	103	103	103	174·5	174	173
12	285	287·5	288·5	126·5	126	126·5	212	211·5	212
4	516	516	516·5	229·5	228	228	376	379·5	376
2	290	292·5	288·5	129	126	132	...	213	212·5
	62°·5	64°	64°·5	65°	65·5	...	...	66°	66°
From 28 to 2 in.	1325	1330	1328	588	583	589·5	...	978	974

## Mean Results.

Gauge barometer.		Hydrogen.	Carbonic acid.
From 28 to 20 inches	Time in seconds.....	103	173·8
	Time of oxygen=1 ...	0·4398	0·7424
From 20 to 12 inches	Time in seconds.....	126·3	211·8
	Time of oxygen=1 ...	0·4403	0·7385
From 12 to 4 inches	Time in seconds.....	228·5	377·3
	Time of oxygen=1 ...	0·4425	0·7310
From 4 to 2 inches	Time in seconds.....	129	212·75
	Time of oxygen=1 ...	0·4443	0·7327
From 28 to 2 inches	Time in seconds.....	586·8	976
	Time of oxygen=1 ...	0·4413	0·7351

Taking the higher part of the scale, from 28 to 20 inches, which approaches nearest to transpiration into a vacuum, we obtain the fol-



lowing times of transpiration :—Oxygen 1, nitrogen 0·8760, hydrogen 0·4398, carburetted hydrogen 0·5647, carbonic acid 0·7424; which almost coincide with the numbers lately mentioned in relation to these gases, with the exception of carbonic acid, which is 0·7424, instead of 0·75. With the great resistance of this tube, the variation in ratio at different parts of the scale has also become very small, being only 0·0045 for hydrogen and 0·0097 for carbonic acid. The disturbing influence of effusion appears therefore to be in a great measure eliminated. It is also worthy of remark, that the time of passage of carbonic acid into a perfect vacuum would certainly approach still more nearly to 0·75; for the rate of transpiration of that gas appears, in the case of the present capillary, to become slower with the increase of pressure. It will be seen hereafter that the gases deviate very sensibly at low pressures from the empirical coefficients of transpiration which have been named, becoming slower in their passage with reference to oxygen, as is here observed of carbonic acid. This deviation appears to be connected with excessive resistance, whether arising from the smallness of the capillary opening or diminished pressure.

With the view of observing the effect of alterations in the position and dimensions of a capillary, experiments were now made with this tube, (1) in an inverted position, so that the gas entered by the narrow and escaped by the wide end, and (2) after being reduced to half its original length.

*Capillary B reversed.*—The passage of gas through this tube was nearly three times more rapid in the new direction, 1 cubic inch being now transpired into a vacuum in 12·6 seconds. The length of the tube and resistance to passage through it are therefore nearly the same as in capillary A; but while the latter was of uniform bore, the present capillary is highly conical.

TABLE XII.—Transpiration by Capillary B reversed into a One-Pint Jar. Barom. 30·13.

Gauge barometer in inches.	Air.			Oxygen.			Hydrogen.		Carbonic acid.		
	I.	II.	III.	I.	II.	III.	I.	II.	I.	II.	III.
28	59° F. 0''	59° F. 0''	59° F. 0''	61° F. 0''	0''	0''	61°·5 F. 0''	61°·5 F. 0''	62° F. 0''	62° F. 0''	0''
20	149·5	144·5	145	160	160	160	69	69	127	126	126
12	173·5	177·5	178	198	196	196	86	85·5	154	153	152
4	318	318	317	352·5	353·5	353·5	157·5	157·5	268·5	267·5	268·5
2	190	189·5	192·5	216	216·5	215	96	96·5	154·5	155	156·5
From 28 to 12 in.	323	322	323	358	356	356	155	154·5	281	279	278
From 28 to 2 in.	831	829·5	832·5	926·5	926	924·5	408·5	408·5	704	701·5	703



## Mean Results.

Gauge barometer.		Air.	Hydrogen.	Carbonic acid.
From 28 to 12 inches	Time in seconds .....	322	154.75	279.33
	Time of oxygen=1.....	0.9024	0.4338	0.7831
From 12 to 4 inches	Time in seconds .....	317.7	157.5	268.16
	Time of oxygen=1.....	0.8994	0.4459	0.7595
From 4 to 2 inches	Time in seconds .....	190.7	96.25	155.33
	Time of oxygen=1.....	0.8836	0.4459	0.7197
From 28 to 2 inches	Time in seconds .....	831	408.5	702.83
	Time of oxygen=1.....	0.8978	0.4413	0.7594

The coefficients of air and hydrogen, although still corresponding very closely with the numbers 0.9038 and 0.4375, begin to exhibit a sensible variation in different parts of the scale. The variation in carbonic acid is considerable, amounting to 0.0634, and the divergence is on both sides of the empirical number 0.75.

*Capillary B shortened.*—The tube was preserved in its last position, but its length reduced to 14.5 inches. It now allowed 1 cubic inch of air to pass into a vacuum in 6.4 seconds; or twice as rapidly as when entire.

TABLE XIII.—Transpiration by Capillary B (14½ inches long) into a One-Pint Jar. Barom. 30.12.

Gauge barometer in inches.	Air.			Oxygen.			Nitrogen.		Carburetted hydrogen.			Hydrogen.			Carbonic acid.	
	I.	II.	III.	I.	II.	III.	I.	II.	I.	II.	III.	I.	II.	III.	I.	II.
28	0"	0"	0"	62°F.	62°F.	62°F.	63°F.	63°F.	62°F.	61°F.	62°F.	62°F.	62°F.	62°F.	62°F.	62°F.
20	75	75	75.5	82.5	83.5	82	72	72	48	48	48	34.5	34	34	69	69
12	89.5	89.5	89.5	99.5	99.5	100	87.5	88	57	57	57	41.5	41.5	41.5	81	80.5
4	158	157	157.5	175	175.5	174.5	152.5	152.5	98	98	98	75	75	75	137.5	136.5
2	91.5	91	92	102	103	102.5	91	89.5	56	56	55.5	45.5	45.5	45	77	77.5
From 28 to 12 in.	164.5	164.5	164.5	182	183	182	159.5	160	105	105	105	76	75.5	75.5	150	149.5
From 28 to 2 in.	414	412.5	414.5	459	461.5	459	403	402	259	259	258.5	196.5	196	195.5	364	363.5

## Mean Results.

Gauge barometer.		Air.	Nitrogen.	Carburetted hydrogen.	Hydrogen.	Carbonic acid.
From 28 to 12 in.	Time in seconds ..	164.5	159.75	105	75.66	149.7
	Time of oxygen=1	0.9023	0.8763	0.5728	0.4150	0.8211
From 12 to 4 in.	Time in seconds ..	157.5	152.5	98	75	137
	Time of oxygen=1	0.9000	0.8714	0.5600	0.4285	0.7828
From 4 to 2 in.	Time in seconds ..	91.5	90.25	55.83	45.33	77.25
	Time of oxygen=1	0.8926	0.8804	0.5447	0.4325	0.7546
From 28 to 2 in.	Time in seconds ..	413.7	402.5	258.83	196	363.75
	Time of oxygen=1	0.8999	0.8755	0.5632	0.4263	0.7912



The times are now too short for accurate numerical determinations, but it is obvious that while the relative times of air and nitrogen are little changed, particularly from 28 to 4 inches, the times of hydrogen and carbonic acid are sensibly affected by effusion, and most so in the upper part of the scale; the coefficient of hydrogen falling to 0.4150, while that of carbonic acid rises to 0.8211. From 4 to 2 inches, the rates are 0.4325 and 0.7546; numbers which still diverge a little from the empirical coefficients, but both in the direction of the effusion influence.

Reduced to 7 inches in length, and now allowing 1 cubic inch of air to pass into a vacuum in 3.4 seconds, this capillary was found to be still less adapted for transpiration. In a series of observations, which are not of sufficient importance to be particularly detailed, the coefficients of the gases in the range from 28 to 12 inches, were,—air 0.9194, nitrogen 0.8983, carburetted hydrogen 0.6029, carbonic acid 0.9028, and hydrogen 0.3930: numbers which demonstrate an increasing interference of effusion. In the range from 12 to 4 inches, the coefficients were,—air 0.9114, nitrogen 0.8851, carburetted hydrogen 0.5764, carbonic acid 0.8303, hydrogen 0.4180.

Of this last portion of capillary B, 5.5 inches were found to contain 2.78 grains of mercury; which gives the tube a mean diameter of 0.0137, or  $\frac{1}{73}$ d of an inch.

*Capillary C.*—This was a tube of exceedingly fine bore; 8.3 inches of the tube containing only 0.65 grain of mercury; which gives a diameter of 0.00539 inch, or about  $\frac{1}{186}$ th of an inch. Experiments were made with portions of this tube of different lengths; and first with a portion only 1 inch in length, in which it was expected that the influence of effusion would be considerable, from its approach to an aperture in a thin plate.

TABLE XIV.—Transpiration by Capillary C (1 inch long) into a One-Pint Jar. Barom. 28.81. Temp. 60°.

Gauge barometer in inches.	Air.		Oxygen.		Hydrogen.		Carbonic acid.
	I.	II.	I.	II.	I.	II.	I.
28	0	0	0	0	0	0	0
20	248.5	249	273	271.5	108	108	237.5
12	283	281.5	308.5	308.5	126	127	261
8	186.5	185.5	204.5	206	87	87	167
4	284	286	315.5	314	136	137	244
2	270.5	266.5	301	302	133	132	227
From 28 to 2 in.	1272.5	1268.5	1402.5	1402	590	591	1136.5



## Mean Results.

Gauge barometer.		Air.	Hydrogen.	Carbonic acid.
From 28 to 20 in.	{ Time in seconds ...	248.75	108	237.5
	{ Time of oxygen = 1	0.9138	0.3967	0.8725
From 28 to 12 in.	{ Time in seconds ...	531	234.75	498.5
	{ Time of oxygen = 1	0.9139	0.4040	0.8594
From 20 to 12 in.	{ Time in seconds ...	282.25	126.5	261
	{ Time of oxygen = 1	0.9149	0.4100	0.8460
From 12 to 8 in.	{ Time in seconds ...	186	87	167
	{ Time of oxygen = 1	0.9063	0.4238	0.8138
From 8 to 4 in.	{ Time in seconds ...	285	136.5	244
	{ Time of oxygen = 1	0.9054	0.4339	0.7751
From 4 to 2 in.	{ Time in seconds ...	268.5	132.5	227
	{ Time of oxygen = 1	0.8905	0.4374	0.7529
From 28 to 2 in.	{ Time in seconds ...	1270.5	590.5	1136.5
	{ Time of oxygen = 1	0.9060	0.4211	0.8104

TABLE XV.—Transpiration by Capillary C (2 inches long) into a Half-Pint Jar. Barom. 29.32.

Gauge barometer in inches.	Air.		Oxygen.		Hydrogen.	
	I.	II.	I.	II.	I.	II.
28	0	0	0	0	0	0
20	211.5	211.5	234	234	101.5	102
12	254	254	281.5	281	124.5	124
8	176.5	176.5	196	197	88	88
4	280.5	280.5	321.5	320	141.5	138
2	273	272	301	302	141	146
From 28 to 2 in.	1195.5	1196	1334	1334	596.5	598

## Mean Results.

Gauge barometer.		Air.	Hydrogen.
From 28 to 20 inches	{ Time in seconds .....	211.5	101.75
	{ Time of oxygen = 1...	0.9038	0.4348
From 20 to 12 inches	{ Time in seconds .....	254	124.25
	{ Time of oxygen = 1...	0.9031	0.4417
From 12 to 8 inches	{ Time in seconds .....	176.5	88
	{ Time of oxygen = 1...	0.8981	0.4478
From 8 to 4 inches	{ Time in seconds .....	281.25	139.75
	{ Time of oxygen = 1...	0.8768	0.4357
From 4 to 2 inches	{ Time in seconds .....	272.5	143.52
	{ Time of oxygen = 1...	0.9038	0.4759
From 28 to 2 inches	{ Time in seconds .....	1195.75	597.25
	{ Time of oxygen = 1...	0.8964	0.4476



TABLE XVI.—Transpiration by Capillary C (4 inches long) into a Half-Pint Jar.

Gauge barometer in inches.	Air.		Oxygen.
	I.	II.	I.
	65° 0"	65° 0"	65° 0"
28	205	205	228
24	214	212	239
20	234	236	262
16	276	278	313
12	166	163	183
10	195	197	220
8	248	245	273
6	145	151	169
5	177	184	206
4	241	238	265
3	332	330	394
2			
From 28 to 2 inches.....	2433	2439	2752

## Mean Results.

Gauge barometer.		Air.
From 28 to 24 inches	{ Time in seconds ..... Time of oxygen = 1...	205 0·8991
From 28 to 20 inches	{ Time in seconds ..... Time of oxygen = 1...	418 0·8951
From 20 to 12 inches	{ Time in seconds ..... Time of oxygen = 1...	512 0·8904
From 12 to 8 inches	{ Time in seconds .. ... Time of oxygen = 1...	360·5 0·8945
From 8 to 4 inches	{ Time in seconds ..... Time of oxygen = 1...	575 0·8657
From 4 to 2 inches	{ Time in seconds ..... Time of oxygen = 1...	570·5 0·8657
From 28 to 2 inches	{ Time in seconds ..... Time of oxygen = 1...	2436 0·8852

The velocity with which air passed into a vacuum was, by C 1 inch, 1 cubic inch in 21·26 seconds; by C 2 inches, 1 cubic inch in 35·43 seconds; and by C 4 inches, 1 cubic inch in 70 seconds.

C 1 inch exhibits (Table XIV.) great variation in its rate of transpiration at different pressures, as was to be expected. At the head of the scale, the rate of air is 0·9138, of hydrogen 0·3967, and of car-



bonic acid 0.8725; which all indicate a great interference of effusion. At the bottom of the scale, on the other hand, where the pressure is small and the resistance to passage consequently great, the rate of air is 0.8905, of hydrogen 0.4374, and of carbonic acid 0.7529, or nearly normal.

With C 2 inches (Table XV.), the rates of air are pretty uniform at different parts of the scale, and sufficiently normal; the deviation from 8 to 4 inches appears to be an accidental anomaly. The rate of hydrogen also is never distant from 0.4375, except at the very bottom of the scale. This appears to be the length of a tube of so small a bore which gives the most uniform results at different pressures:

For with C 4 inches (Table XVI.), where the resistance is excessive, air has a rate corresponding sufficiently with its specific gravity at the head of the scale, but diverging rapidly in the lower part of the scale, the time of transpiration becoming rapid as compared to that of oxygen. With a tube then like the present, the relation between the times of transpiration is only to be looked for within a limited range, and that at a high degree of pressure approaching to a whole atmosphere.

#### 4. *Transpiration by Capillary Tube H.*

As the existence of any simple numerical relation among the gases, such as the preceding experiments on transpiration render probable, would be a point of fundamental importance in their history, I was induced to try new capillary tubes and to multiply experiments, varying the circumstances in which they were made, and taking additional precautions against the interference of disturbing causes. The arbitrary nature of the coefficients of transpiration indeed produces a more than usual necessity for strong evidence and numerous confirmations, as the numbers themselves have no *a priori* probability in their favour.

It appeared desirable to try capillary tubes of larger diameter than those already employed, and of great length; partly to vary the conditions of the experiment, and partly because extreme shortness of tube appears, in the experiments made with C, to be unfavourable to uniformity of rate at different pressures.

Several portions of capillary tube, of which the bore was as nearly equal as could be judged of by the eye, were accordingly selected and cemented together at the blowpipe, so as to form a continuous tube 22 feet in length, which was bent up into coils for convenience in using it, as represented in figure 4, Plate XXXIII. The extremities of this capillary were connected with the block-tin tubes proceeding from the



drying tube and air-pump jar respectively, by means of thick caoutchouc adopters, which diminished the rigidity of the arrangement and protected the glass tube from the effect of the shocks, which are unavoidable in working the air-pump. This capillary (H) allowed 1 cubic inch of air to pass into a vacuum in 15.64 seconds. Two inches of the tube were found to hold 2.65 grains of mercury, which gives a diameter of 0.0222 inch, or  $\frac{1}{45}$ th of an inch. The tube, however, may have been more contracted at the bendings.

Air-pump jars of greater size were also employed, so as to protract the time of passage, and give larger numbers. Of these vessels, which I have termed aspirator jars, the capacity of the "three-pint jar" was 103.56 cubic inches, and that of the "six-pint jar" 201.78 cubic inches; the vacuous channels of the air-pump and connecting tubes being included in these measurements.

The temperatures recorded are those of the interior of the aspirator jar, observed by a very small mercurial thermometer, containing no more than 50 or 60 grains of mercury, and therefore highly sensitive. It will be remarked that the temperature within the receiver always rises, and in general about half of a degree Fahrenheit during the continuance of an experiment: this is owing to the compression of the gas already in the receiver by that which enters. The change of temperature due to this cause becomes less considerable with large aspirator jars, which are preferable to small jars for this and other reasons.

As it appears that the relation between the coefficients of transpiration is only to be looked for at high pressures, attention should be more directed to the rates of transpiration in the upper than in the lower part of the scale. The inquiry will therefore be directed with the view of solving the question, What are the coefficients of transpiration of the different gases into a vacuum, or under considerable pressures?

TABLE XVII.—Transpiration by Capillary H into a Three-Pint Jar.  
Barom. 30.324.

Gauge barometer in inches.	Air.		Oxygen.		Hydrogen.		Hyd. 95+5 air.		Carbonic acid.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
28	61°.5 0"	61°.5 0"	61°.5 0"	61°.5 0"	61°.5 0"	61°.5 0"	61°.5 0"	61°.5 0"	61°.5 0"	61°.5 0"
24	213	213	236	237	104	104	125	124	178	177
20	227	227	254	253	111	111	132	132	188	188
12	549	549	611	611	268	269	321	321	454	455
8	389	388	435	435	192	192	227	227	321	320
	61°.75	61°.75	61°.75	61°.75	61°.75	61°.75	61°.75	61°.75	61°.75	61°.75
From 28 to 8 inches	1378	1377	1536	1536	675	676	805	804	1141	1140



## Mean Results.

Gauge barometer.		Air.	Hydrogen.	95 Hyd. + 5 air.	Carbonic acid.
From 28 to 24 inches	{ Time in seconds .....	213	104	124.5	177.5
	{ Time of oxygen = 1...	0.9006	0.4397	0.5264	0.7505
From 24 to 20 inches	{ Time in seconds .....	227	111	132	188
	{ Time of oxygen = 1...	0.8954	0.4378	0.5206	0.7416
From 20 to 12 inches	{ Time in seconds .....	549	268.5	321	454.5
	{ Time of oxygen = 1...	0.8985	0.4394	0.5252	0.7438
From 12 to 8 inches	{ Time in seconds .....	388.5	192	227	320.5
	{ Time of oxygen = 1...	0.8931	0.4413	0.5218	0.7368
From 28 to 8 inches	{ Time in seconds .....	1377.5	675.5	864.5	1140.5
	{ Time of oxygen = 1...	0.8968	0.4397	0.5237	0.7425

The numbers for air, hydrogen, and carbonic acid accord well with those obtained by the other capillaries. The small addition of 5 per cent. of air to hydrogen has a surprising effect in retarding the transpiration of that gas. The mean rate of such a mixture, calculated from the rates of air and hydrogen separately, is 0.4625, whereas the actual rate is 0.5264. The rate of the mixture should only be increased by 0.0228, whereas it is really increased by 0.0840. Hence the effect of 5 per cent. of air in retarding the rate of hydrogen is nearly four times greater than it should be by calculation. The experiment shows the effect which a small amount of impurity must have in deranging the transpiration rate of that gas. I shall return again to this point under the subject of the transpiration of mixed gases.

TABLE XVIII.—Transpiration by Capillary H into a Three-Pint Jar.  
Barom. 30.3—30.242.

Gauge barometer in inches.	Oxygen.		Nitrogen.		Carbonic oxide.		Air.	
	I.	II.	I.	II.	I.	II.	I.	II.
28	61° 5'	61° 5'	61° 5'	61° 5'	61° 5'	61° 5'	61° 5'	61° 5'
24	0"	0"	0"	0"	0"	0"	0"	0"
20	238	239	208	208	207	207	214	214
12	253	253	220	221	220	220	229	229
8	614	614	536	533	532	533	552	550
	434	434	378	376	376	377	389	392
	61° 75'	61° 75'	62°	62°	62°	62°	62°	62°
From 28 to 8 inches	1539	1540	1342	1339	1335	1337	1384	1385



## Mean Results.

Gauge barometer.		Nitrogen.	Carbonic oxide.	Air.
From 28 to 24 inches	{ Time in seconds ...	208	207	214
	{ Time of oxygen = 1	0·8721	0·8679	0·8972
From 24 to 20 inches	{ Time in seconds ...	220·5	220	229
	{ Time of oxygen = 1	0·8715	0·8695	0·9051
From 20 to 12 inches	{ Time in seconds ...	534·5	532·5	551
	{ Time of oxygen = 1	0·8705	0·8673	0·8974
From 12 to 8 inches	{ Time in seconds ...	377·5	376·5	390·5
	{ Time of oxygen = 1	0·8698	0·8675	0·8998
From 28 to 8 inches	{ Time in seconds ...	1340·5	1336	1384·5
	{ Time of oxygen = 1	0·8707	0·8678	0·8993

In the preceding table, a comparison is made between two gases, nitrogen and carbonic oxide, of which the theoretical specific gravities are the same, namely, 0·8750, while the mean rate of nitrogen, from 28 to 12 inches, proves to be 0·8707, and that of carbonic oxide 0·8678, which is a pretty close approximation. In several other experiments with these gases, a slight difference in their coefficients of transpiration was observed, carbonic oxide having always the smaller number : the difference generally approached 0·0040. It is not at all impossible, however, that these gases may really differ quite as much in specific gravity; the specific gravity of carbonic oxide found by Wrede being 0·8754, on the oxygen scale, while that of nitrogen by Regnault is 0·8785.

TABLE XIX.—Transpiration by Capillary H into a Three-Pint Jar.  
Barom. 30·232.

Gauge barometer in inches.	Air.		Oxygen.		Carburetted hydrogen.	
	I.	II.	I.	II.	I.	II.
28	65°·25	65°·25	66°	66°	66°	66°
24	0"	0"	0"	0"	0"	0"
20	215	216	239	240	131	131
12	229	230	255	256	141	141
8	555	553	617	616	338	338
	393	393	439	437	240	240
	66°	66°	66°	66°	66°·25	66°·25
From 28 to 8 inches...	1392	1392	1550	1549	850	850



## Mean Results.

Gauge barometer.		Air.	Carburetted hydrogen.
From 28 to 24 inches	Time in seconds .....	215.5	131
	Time of oxygen = 1...	0.8997	0.5474
From 24 to 20 inches	Time in seconds .....	229.5	141
	Time of oxygen = 1...	0.8982	0.5518
From 20 to 12 inches	Time in seconds .....	554	338
	Time of oxygen = 1...	0.8986	0.5482
From 12 to 8 inches	Time in seconds .....	393	240
	Time of oxygen = 1...	0.8972	0.5479
From 28 to 8 inches	Time in seconds .....	1392	850
	Time of oxygen = 1...	0.8983	0.5485

TABLE XX.—Transpiration by Capillary H into a Six-Pint Jar.  
Barom. 30.196—30.174.

Gauge barometer in inches.	Oxygen.		Carburetted hydrogen.		Hydrogen.		Air.	
	I.	II.	I.	II.	I.	II.	I.	II.
28.5	66° 75'	66° 75'	66° 75'	66° 75'	66° 75'	66° 75'	67°	67°
26.5	0"	0"	0"	0"	0"	0"	0"	0"
24.5	228	232	126	128	102	101	207	204
23.5	235	233	130	128	102	104	212	211
	121	121	66	67	54	54	108	110
	67°	67°	67°	67°	67°	67°	67°	67°
From 28.5 to 23.5 inches...	584	586	322	323	258	259	527	525

## Mean Results.

Gauge barometer.		Carburetted hydrogen.	Hydrogen.	Air.
From 28.5 to 23.5 inches	Time in seconds .....	322.5	258.5	526
	Time of oxygen = 1...	0.5512	0.4418	0.8991

Tables XIX. and XX. exhibit the transpiration rates of carburetted hydrogen and hydrogen, the former of which approaches to 0.55, which is certainly a sensible deviation from 0.5625. The number for hydrogen (0.4418), on the other hand, is but very little removed from 0.4375.



TABLE XXI.—Transpiration by Capillary H into a Six-Pint Jar.

Barom. 30·158—30·138.

Gauge barometer in inches.	Oxygen.		Carbonic oxide.			Nitrogen.		Nitrous oxide.		Carbonic acid.	
	I.	II.	I.	II.	III.	I.	II.	I.	II.	I.	II.
28·5	67° 0"	67° 0"	67° 0"	67° 0"	67° 0"	67°·75 0"	67°·75 0"	68° 0"	68° 0"	68° 0"	68° 0"
26·5	230	231	202	200	201	202	202	173	173	173	173
24·5	237	235	202	203	204	205	205	176	175	174	176
23·5	121	121	107	107	106	108	108	91	91	92	92
	67°	67°	67°·25	67°·25	67°·25	68°	68°	68°	68°	68°	68°
From 28·5 to 23·5 in.	588	587	511	510	511	515	515	440	439	439	441

## Mean Results.

Gauge barometer.	Carbonic oxide.	Nitrogen.	Nitrous oxide.	Carbonic acid.
From 28·5 to 23·5 in. { Time in seconds ... { Time of oxygen=1	510·5 0·8689	515· 0·8766	439·5 0·7480	440 0·7455

In the preceding table carbonic oxide and nitrogen are again compared, and also another remarkable pair of gases having the same theoretical density, namely carbonic acid and nitrous oxide. The two latter exhibit an extraordinary parallelism in their rates of transpiration in all experiments which were made upon them, provided due attention was paid to the purity of the nitrous oxide. The solution of nitrate of ammonia should always be *filtered*, and the salt crystallized, as the presence of a very minute quantity of solid matter may cause a change in the mode of decomposition of the salt by heat, and the evolution of a very sensible quantity of free nitrogen.

The carbonic oxide of experiments 1 and 2 was obtained by the action of oil of vitriol on pure oxalic acid; that of experiment 3 was prepared by the process of Mr. Fownes, namely, heating oil of vitriol upon the ferrocyanide of potassium, avoiding a violent reaction by a proper regulation of the temperature. The gas of both processes was washed with alkali, although this precaution is scarcely required with the gas of the last process. The transpiration results are exactly the same with the gas prepared in both ways.



TABLE XXII.—Transpiration by Capillary H (with cupped ends) into a Six-Pint Jar. Barom. 29·39. Temp. 51°.

Gauge barometer in inches.	Nitrogen.		Oxygen.		Olefiant gas.		Air.		Carburetted hydrogen.			
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	III.	IV.
28·5	0	0	0	0	0	0	0	0	0	0	0	0
26·5	203	204	233	235	122	121	211	211	129	129	129	129
24·5	206	207	236	236	122	122	212	212	129	131	130	130
23·5	104	104	121	120	62	63	108	108	67	66	66	66
From 28·5 to 23·5 in.	513	515	590	591	306	306	531	531	325	326	325	325

## Mean Results.

Gauge barometer.	Nitrogen.	Olefiant gas.	Air.	Carburetted hydrogen.
From 28·5 to 23·5 inches { Time in seconds ...	514	306	531	325·25
{ Time of oxygen = 1	0·8704	0·5182	0·9000	0·5512

For the experiments of the preceding table the form of the capillary H was so far altered, that a funnel-form was given to the apertures of the tube. This was done by softening the tube in the blowpipe flame, within an inch of each extremity, and expanding the bore into a small ball of about one-tenth of an inch in diameter; the ball was afterwards cut across the middle, and left the tube of course with a cup-shaped termination. This change in the condition of the capillary seems to have no effect on the comparative rates of transpiration of the different gases.

It was found that the passage of air became a little slower by cupping the end of the tube by which the gas obtains ingress, in the proportion of 509 to 496; but cupping the point of egress occasioned no further change in the rate, the experiments being made within the pressures of 28·5 and 23·5 inches.

The transpiration rate of olefiant gas differs entirely from that of nitrogen and carbonic oxide, of which gases it possesses the theoretical specific gravity, and is a great deal more rapid, the transpiration coefficient being so low as 0·5182. The specific gravity of the gas made use of was found to be 0·9840, and it was absorbed by the perchloride of antimony to the extent of 96·5 per cent. The determination of the true coefficient for this gas is attended with unusual difficulty, from its constant and I believe unavoidable impurity, as prepared by the action of sulphuric acid upon alcohol.



TABLE XXIII.—Transpiration by Capillary H (with cupped ends) into a Six-Pint Jar. Barom. 29.91. Temp. 54°.

Gauge barometer in inches.	Air.		Oxygen.		Hydrogen.		Carburet. hydrogen.		Carbonic oxide.		Carbonic acid.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
28.5	0	0	0	0	0	0	0	0	0	0	0	0
26.5	212	212	234	233	105	105	133	133	206	204	175	176
24.5	212	212	235	236	105	106	134	132	204	205	176	174
23.5	108	107	121	119	53	53	66	67	106	106	90	90
From 28.5 to 23.5 in.	532	531	590	588	263	264	333	332	516	515	441	440

## Mean Results.

Gauge barometer.	Air.	Hydrogen.	Carburet. hydrogen.	Carbonic oxide.	Carbonic acid.
From 28.5 to 23.5 inches { Time in seconds... Time of oxygen = 1	531.5 0.9024	263.5 0.4473	332.5 0.5645	515.5 0.8752	440.5 0.7479

The results of the preceding table are remarkable as approaching more closely to the empirical numbers than any preceding results obtained by the same capillary. The same observation applies to the results of the table which immediately follows. In the one table, the number for carbonic oxide is 0.8732, in the other 0.8752; the numbers for carbonic acid are 0.7479 and 0.7466, and for carburetted hydrogen 0.5645.

TABLE XXIV.—Transpiration by Capillary H into a Six-Pint Jar. Barom. 29.63. Temp. 55°.

Gauge barometer in inches.	Air.		Oxygen.		Carbonic oxide.			Carbonic acid.	
	I.	II.	I.	II.	I.	II.	III.	I.	II.
28.5	0	0	0	0	0	0	0	0	0
26.5	212	212	236	235	214	214	213	175	176
24.5	214	214	237	239	203	205	205	178	177
23.5	110	110	121	120	100	101	101	90	91
From 28.5 to 23.5 inches ...	536	536	594	594	517	520	519	443	444

## Mean Results.

Gauge barometer.	Air.	Carbonic oxide.	Carbonic acid.
From 28.5 to 23.5 inches { Time in seconds ... Time of oxygen = 1	536 0.9023	518.7 0.8732	443.5 0.7466



5. *Transpiration of different Gases by a Capillary Tube of Copper.*

It appeared desirable to have experiments on the passage of gases through tubes of different materials, in order to ascertain how far the coefficients of transpiration observed are peculiar to glass. After some trials, a capillary tube of copper was constructed, of a fine smooth bore, not wider than an ordinary thermometer tube, and indeed less in diameter than the preceding glass capillary H. This tube was formed by first drilling a cylindrical hole in the axis of a solid copper rod, 4 or 5 inches in length, and extending the latter afterwards by drawing it through a wire-plate. An iron wire, or triplet, was placed within the copper tube and drawn through the wire-plate at the same time, in order to keep the interior surface of the copper tube smooth and uniform. It was necessary to pull out the iron wire always after the copper was drawn through the plate, to prevent the former being fixed. The iron wire was then extended somewhat separately, and again introduced into the copper tube, and the operation of drawing out the latter repeated. In this way the copper tube was extended to a length of 11 feet 8 inches. It was found to be perfectly sound and air-tight; and allowed 1 cubic inch of air to pass into a vacuum in 22.12 seconds. Of the iron wire, upon which the copper tube was last drawn, 92.7 inches weighed 18.30 grains; or 1 inch 0.1974 grain. Taking the specific gravity of iron at 7.7, this gives as the diameter of the copper tube 0.0114 inch, or  $\frac{1}{88}$ th of an inch. When used as a transpiration tube it was coiled up into circles of about 10 inches in diameter, and the ends joined by soldering to two block-tin tubes provided with screws by which they could be attached to the aspirator-jar and drying tube.

The experiments were conducted precisely in the same way as with a glass tube, except that oil of vitriol was avoided and chloride of calcium only used in the drying tube. The following series of results were obtained with the copper capillary:

TABLE XXV.—Transpiration by a Copper Capillary Tube into a One-Pint Jar. Barom. 29.97. Temp. 58°.

Gauge barometer in inches.	Air.		Oxygen.		Nitrous oxide.		Carbonic acid.		Air.
	I.	II.	I.	II.	I.	II.	I.	II.	I.
28	0	0	0	0	0	0	0	0	0
20	234	233	260	261	198	198	199	199	234
12	291	292	324	324	244	244	245	245	292
8	206	205	228	228	170	170	171	170	204
4	333	335	372	373	275	277	276	276	336
2	342	344	387	390	283	285	287	288	344
From 28 to 4 in.	1064	1065	1184	1186	887	889	891	890	1066



## Mean Results.

Gauge Barometer.		Air.	Nitrous oxide.	Carbonic acid.
From 28 to 20 inches	Time in seconds .....	233.5	198	199
	Time of oxygen=1...	0.8963	0.7601	0.7639
From 20 to 12 inches	Time in seconds .....	291.5	244	245
	Time of oxygen=1...	0.8997	0.7531	0.7561
From 12 to 8 inches	Time in seconds .....	205.5	170	170.5
	Time of oxygen=1...	0.9000	0.7456	0.7478
From 8 to 4 inches	Time in seconds .....	334	276	276
	Time of oxygen=1...	0.8966	0.7410	0.7410
From 4 to 2 inches	Time in seconds .....	343	284	287
	Time of oxygen=1...	0.8831	0.7310	0.7400
From 28 to 4 inches	Time in seconds .....	1064.5	888	890
	Time of oxygen=1...	0.8983	0.7493	0.7514

It will be observed that the numbers do not differ materially from those obtained with glass tubes, particularly with H. This is a capillary of great resistance, and therefore a deviation from uniformity of ratio may be looked for in the lower part of the scale. A little irregularity in the rate of air, probably accidental, appears in the upper part of the scale; but as with capillary H, the coefficient for air never varies far from 0.9, at least between 28 and 4 inches.

Carbonic acid and nitrous oxide exhibit the usual parallelism of rate; but in the upper part of the scale the excess of the coefficient above 0.75 is rather considerable. Other experiments were made on the transpiration of carbonic acid into different aspirator jars, as the size of the jar and duration of the experiment appeared to have some influence on the ratios.

TABLE XXVI.—Transpiration by Copper Capillary into a One-Pint Jar.  
Barom. 29.07. Temp. 56°.

Gauge barometer in inches.	Oxygen.		Carburetted hydrogen.	
	I.	II.	I.	II.
28	0	0	0	0
20	273	274	151	151
12	338	336	186	186
8	237	236	129	130
4	383	385	210	211
2	391	400	214	213
From 28 to 4 inches..	1231	1231	676	678



## Mean Results.

Gauge barometer.		Carburetted hydrogen.
From 28 to 20 inches	Time in seconds .....	151
	Time of oxygen=1...	0.5521
From 20 to 12 inches	Time in seconds .....	186
	Time of oxygen=1...	0.5519
From 12 to 8 inches	Time in seconds .....	129.5
	Time of oxygen=1...	0.5475
From 8 to 4 inches	Time in seconds .....	210.5
	Time of oxygen=1...	0.5482
From 4 to 2 inches	Time in seconds .....	213.5
	Time of oxygen=1...	0.5398
From 28 to 4 inches	Time in seconds .....	677
	Time of oxygen=1...	0.5500

The coefficient obtained for carburetted hydrogen in the preceding experiments never varies much from 0.55, which is the mean between 28 and 4 inches. The result is similar to that given by glass capillary H for the same gas.

TABLE XXVII.—Transpiration by Copper Capillary into a Two-Pint Jar.  
Barom. 29.49. Temp. 56°5.

Gauge barometer in inches.	Air.		Oxygen.		Nitrogen.		Carbonic oxide.		Air.	Hydrogen.	
	I.	II.	I.	II.	I.	II.	I.	II.	III.	I.	II.
28	0	0	0	0	0	0	0	0	0	0	0
20	421	419	467	466	405	407	405	404	419	206	205
12	515	514	572	574	501	500	496	498	516	255	254
8	360	363	402	404	351	351	348	348	361	179	179
From 28 to 8 in.	1296	1296	1441	1444	1257	1258	1249	1250	1296	640	638

## Mean Results.

Gauge barometer.		Air.	Nitrogen.	Carbonic oxide.	Hydrogen.
From 28 to 20 in.	Time in seconds ...	420	406	404.5	205.5
	Time of oxygen=1	0.9003	0.8703	0.8670	0.4405
From 20 to 12 in.	Time in seconds ...	514.5	500.5	497	254.5
	Time of oxygen=1	0.8979	0.8734	0.8673	0.4441
From 12 to 8 in.	Time in seconds ...	361.5	351	348	179
	Time of oxygen=1	0.8970	0.8709	0.8635	0.4441
From 28 to 8 in.	Time in seconds ...	1296	1257.5	1249.5	639
	Time of oxygen=1	0.8984	0.8717	0.8662	0.4429



The great resemblance which these results bear to those of the last glass capillary is most surprising. The rates of air, nitrogen, carbonic oxide, and hydrogen, may be considered as identical with these two capillaries, although they differ in substance, and also in the time of passage, which is slower in the copper capillary than in H, in the proportion of 22.12 to 15.64. Carbonic oxide, it will be observed, is still sensibly more rapid in its passage than nitrogen.

The experiments in the preceding and all other tables are put down in the order in which they were made. The observation with air is occasionally repeated, to find whether the rate of the capillary remains constant.

TABLE XXVIII.—Transpiration by Copper Capillary into a Three-Pint Jar. Barom. 29.73. Temp. 57°.

Gauge barometer in inches.	Air.		Oxygen.		Nitrogen.		Hydrogen.		Carbonic acid.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
28	0	0	0	0	0	0	0	0	0	0
20	595	595	663	660	575	577	287	287	500	502
12	736	735	818	819	713	713	358	357	616	613
8	516	517	575	577	500	501	251	252	426	428
From 28 to 8 in.	1847	1847	2056	2056	1788	1791	896	896	1542	1543

#### Mean Results.

Gauge barometer.		Air.	Nitrogen.	Hydrogen.	Carbonic acid.
From 28 to 20 in.	Time in seconds.....	595	576	287	501
	Time of oxygen=1	0.8994	0.8707	0.4339	0.7573
From 20 to 12 in.	Time in seconds.....	735.5	713	357.5	614.5
	Time of oxygen=1	0.8986	0.8711	0.4369	0.7507
From 12 to 8 in.	Time in seconds.....	516.5	500.5	251.5	427
	Time of oxygen=1	0.8967	0.8689	0.4366	0.7413
From 28 to 8 in.	Time in seconds.....	1847	1789.5	896	1542.5
	Time of oxygen=1	0.8984	0.8704	0.4358	0.7502

The preceding results with air and nitrogen might be confounded with those obtained with capillary H. The rate of hydrogen is sensibly faster, while that of carbonic acid is decidedly slower; both gases diverging sensibly from their empirical rates 0.375 and 0.75, on the side of effusion, but the former very slightly.



TABLE XXIX.—Transpiration by Copper Capillary into a Six-Pint Jar.  
Barom. 30·14. Temp. 58°.

Gauge barometer in inches.	Air.		Oxygen.		Hydrogen.	
	I.	II.	I.	II.	I.	II.
28	0	0	0	0	0	0
24	...	...	...	614	269	271
20	1139	1139	1268	654	290	290
12	1413	1413	1570	1573	698	699
8	994	993	1109	1110	494	495
From 28 to 8 inches...	3546	3545	3947	3951	1751	1755

## Mean Results.

Gauge barometer.		Air.	Hydrogen.
From 28 to 20 inches	Time in seconds .....	1139	560
	Time of oxygen = 1...	0·8982	0·4416
From 20 to 12 inches	Time in seconds .....	1413	698·5
	Time of oxygen = 1...	0·8991	0·4445
From 12 to 8 inches	Time in seconds .....	993·5	494·5
	Time of oxygen = 1...	0·8955	0·4457
From 28 to 8 inches	Time in seconds .....	3545·5	1753
	Time of oxygen = 1...	0·8978	0·4439

In these experiments with a large aspirator-jar and long times, the rate of air continues very nearly 0·9, and that of hydrogen approaches 0·44. The rates at the upper part of the scale are to be particularly attended to, as most uniform, and as representing pretty nearly transpiration into a vacuum.

TABLE XXX.—Transpiration by Copper Capillary into a Six-Pint Jar.  
Barom. 30·23. Temp. 58°·5.

Gauge barometer in inches.	Air.		Oxygen.		Carbonic acid.	
	I.	II.	I.	II.	I.	II.
28	59° 0"	59° 0"	59°·25 0"	59° 0"	59°·5 0"	59°·75 0"
24	550	550	611	612	469	468
20	590	589	655	655	498	499
12	...	...	1570	1570	1183	1183
8	...	...	1103	1104	824	825
From 28 to 8 inches...	...	...	3939	3941	2974	2975



## Mean Results.

Gauge barometer.		Air.	Carbonic acid.
From 28 to 24 inches	Time in seconds .....	550	468.5
	Time of oxygen = 1...	0.8994	0.7661
From 24 to 20 inches	Time in seconds .....	589.5	498.5
	Time of oxygen = 1...	0.9000	0.7610
From 20 to 12 inches	Time in seconds .....	...	1183
	Time of oxygen = 1...	...	0.7535
From 12 to 8 inches	Time in seconds .....	...	824.5
	Time of oxygen = 1...	...	0.7472
From 28 to 8 inches	Time in seconds .....	...	2974.5
	Time of oxygen = 1...	...	0.7549

The preceding table contains an experiment on carbonic acid transpired into a large jar. The coefficient of that gas still considerably exceeds 0.75 in the upper part of the scale.

It appears then that the rates of transpiration are similar through glass and copper tubes, for air, oxygen, nitrogen, hydrogen, and carburetted hydrogen; whilst the passage of carbonic acid is subject to a retardation in the upper part of the scale of the copper capillary, by which its rate increases so much as from 0.75 to 0.7661, in the last series of experiments. The rate of carbonic acid indeed exhibits a want of steadiness with this capillary, which is not observed in the other gases enumerated. Thus we find it in the upper part of the scale 0.7639 by Table XXV.; 0.7573 by Table XXVIII.; and 0.7661 by the last table. I may add, that in a preliminary experiment which was made with this gas, and also in an experiment made subsequently to those recorded, and after the tube had been some weeks out of use, so high a coefficient was given for carbonic acid as 0.78. It is impossible to say whether this irregularity is properly referable to the material of the tube, or is peculiar to this individual capillary, as it is the only instrument of the same metal which was used.

The copper tube has no advantage over the glass capillary for experiments on transpiration, while it is liable to the objection that it cannot be used at all with certain gases which have a chemical action on copper, and would tarnish the surface of the tube. The experiments made with it, however, have their value in demonstrating that the rates of transpiration of different gases are essential properties of these gases, and not regulated by the material of the transpiring tube. Indeed there is no more reason to suppose that the coefficient of transpiration of a gas would vary with the substance of the tube, than that the specific gravity



of the same gas would be found different according as it was observed in a glass or copper vessel.

6. *Transpiration of different Gases by a Glass Capillary Tube E.*

This was another long capillary glass tube, resembling H, but somewhat shorter. The extreme length of capillary E was 20 feet; it allowed 1 cubic inch of air to pass into a vacuum in 12.03 seconds. One inch of this tube at either end was found to contain 1 grain and 0.94 grain of mercury; the smallest of which admeasurements gives 0.0187 inch as the diameter of the tube; that is, about  $\frac{1}{53.5}$ th of an inch.

The following table contains a series of experiments on various gases, which were made on one occasion, and in the order in which they are given.

TABLE XXXI.—



TABLE XXXI.—Transpiration by Capillary E into a Six-Pint Jar. Barom. 30·340—30·288.

Gauge barometer in inches.	Air.		Oxygen.		Carburetted hydrogen.		Hydrogen.		Carbonic oxide.		Nitrogen.		Nitrous oxide.		Carbonic acid.		Air.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
28·5	72° 0"	72° 0"	72° 0"	72°·25 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"	72°·75 0"
26·5	153	153	172	170	93	93	75	74	150	149	150	149	129	129	130	130	154	154
24·5	156	156	173	175	97	97	75	76	150	151	151	153	133	133	132	132	158	158
23·5	84	84	92	92	52	50	41	40	80	80	81	80	70	70	70	70	84	84
From 28·5 to 23·5 in.	393	393	437	437	242	240	191	190	380	380	382	382	332	332	332	332	396	396

## Mean Results.

Gauge barometer.	Air.		Carburetted hydrogen.		Hydrogen.		Carbonic oxide.		Nitrogen.		Nitrous oxide.		Carbonic acid.		Air.	
From 28·5 { Time in seconds to 23·5 in. } Time of ox. = 1	393	393	241	241	190·5	190·5	380	380	382	382	332	332	332	332	396	396
	0·8993		0·5515		0·4359		0·8696		0·8741		0·7597		0·7597		0·9062	



This table exhibits the transpiration of the gases by E, in the upper part of the scale or into a vacuum nearly, the condition in which the subject is studied with most advantage. The coefficients exhibit a close correspondence with those found by the two preceding capillaries. The number for air is 0·8993 at the beginning, and 0·9062 at the end of the experiments; a variation of rate to which this capillary appeared more liable than the others. The number for nitrogen, 0·8741, again slightly exceeds that for carbonic oxide, 0·8696. Nitrous oxide and carbonic acid have the same number 0·7597, which is in excess compared with 0·75; while the number for hydrogen, 0·4359, is slightly deficient compared with 0·4375. Carburetted hydrogen has the number 0·5515, and is wonderfully constant with all these long capillaries.

As the time of transpiration in these experiments appeared rather short for exact results, a larger aspirator-jar was employed, and the experiment repeated with carbonic acid; air and oxygen being added to give standards of comparison.

TABLE XXXII.—Transpiration by Capillary E into a Nine-Pint Jar.  
Barom. 30·136. Temp. 74°·5.

Gauge barometer in inches.	Air.		Oxygen.		Carbonic acid.	
	I.	II.	I.	II.	I.	II.
28·5	0	0	0	0	0	0
26·5	229	229	254	254	190	191
24·5	233	232	259	258	195	195
23·5	121	121	135	135	104	103
From 28·5 to 23·5 .....	583	582	648	647	489	489

#### Mean Results.

Gauge barometer.	Air.	Carbonic acid.
From 28·5 to 23·5 inches { Time in seconds .....	582·5	489
{ Time of oxygen = 1 ...	0·8996	0·7550

As the result for carbonic acid differed sensibly from the experiment of the preceding table, it was considered desirable to return to the subject on the following day. In the meantime the barometer had fallen considerably, which accounts for the comparative slowness of transpiration in the following repetition of the last experiments.



Repetition of the last Experiments. Barom. 29·616—29·666. Temp. 72°.

Gauge barometer in inches.	Air.		Oxygen.		Carbonic acid.	
	I.	II.	I.	II.	I.	II.
28·5	0	0	0	0	0	0
26·5	237	236	262	262	196	197
24·5	239	239	266	266	199	202
23·5	129	129	141	141	107	106
From 28·5 to 23·5 inches	605	604	669	669	502	505

### Mean Results.

Gauge barometer.	Air.	Carbonic acid.
From 28·5 to 23·5 inches { Time in seconds ..... Time of oxygen = 1 ...	604·5 0·9036	503·5 0·7526

The three results for carbonic acid by this capillary are therefore 0·7597, 0·7550, and 0·7526; of which the mean is 0·7558. The coefficient of capillary E for carbonic acid is therefore not so widely different from 0·75 as it at first appeared.

With these large aspirator jars the rise of temperature within the jar during the experiment becomes very small. In the six-pint jar it did not amount to one-quarter of a degree Fahr., and in the nine-pint jar it was altogether insensible.

I have now detailed the results of the transpiration of gases by all the capillaries used except one,—a tube with which a few preliminary experiments in the inquiry were made, not sufficiently precise to merit being recorded. All of these tubes have given the same coefficient of transpiration to each gas, or coefficients closely approximating, although the tubes themselves have varied considerably in their respective dimensions; namely, in diameter, from  $\frac{1}{4}$ th to  $\frac{1}{18}$ th of an inch; in length from 2 inches to 22 feet; and from 12 to 70 seconds in the time of transmission of one cubic inch of air into a vacuum. It can be said that no selection of the tubes was made; and their dimensions are in a great measure accidental.

From the agreement in results obtained with tubes so different in dimensions, I consider that a glass tube of any diameter whatever will be found suitable for observations on transpiration, provided, a certain length is given to it. If the tube is extremely short, a mere ring, then we know that gases will be transmitted by it into a vacuum according



to the law of effusion; oxygen, hydrogen, and carbonic acid in times expressed by 1, 0.25, and 1.176 respectively. With the slightest elongation of the tube these ratios are disturbed; the number for hydrogen soon increasing to 0.35 or 0.40, and that for carbonic acid falling to 1, or 0.80, referring both to the time of oxygen always taken as unity. The change with the increase of length is very great at first, but soon falls off, and with a certain length of tube seems to cease altogether. The coefficient of hydrogen is then found to have risen to some number approaching closely to 0.4375 or 0.44, and the coefficient of carbonic acid to approach closely to 0.75. The coefficient of nitrogen has fallen at the same time from 0.9373 (its coefficient of effusion, that of oxygen being 1) to nearly 0.875.

With this length of the tube, the influence of effusion upon the transpiration rate of the gas has ceased to be sensible.

The action of the tube attains a certain uniformity, at the same time, in another respect. When the tube is deficient in length, the coefficient of the gas varies greatly with the extent of the exhaustion of the vessel into which the gas is flowing; the rate of transpiration inclining most to the rate of effusion at a high degree of exhaustion of the aspirator jar. But the amount of this variation progressively diminishes as the tube becomes longer, till at last the coefficient of transpiration remains nearly if not perfectly constant, whether the aspiratory jar be entirely vacuum, or contains already gas of the tension of half an atmosphere, three-fourths or even seven-eighths of an atmosphere.

The tube is now of the length most favourable for experiments of transpiration. Farther addition to the tube appears to have no effect in altering the coefficient of transpiration of air, provided the aspirator jar into which the air passes is vacuum or nearly so; or the coefficient of transpiration into a vacuum appears to remain constant for all greater lengths of the tube. But the extent of the barometric range in the aspirator jar to which the vacuum coefficient is found to apply is gradually limited. Instead of extending over seven-eighths of an atmosphere it may be contracted to an eighth of an atmosphere or less, by greatly lengthening the tube.

The coefficients of transpiration which I have endeavoured to ascertain are properly therefore the relative times of passage of the gases into a vacuum, at the mean atmospheric temperature, or near that temperature.

But even with the most favourable length of the tube, when the aspiration is feeble, and does not exceed 2 or 3 inches of mercury, the rate of transpiration is modified from an interference, which is connected with the excessive resistance of the tube to the passage of the gas. I have not been able to undertake an examination of the nature and extent of



this interference, but suppose it to depend upon friction, while the rate of transpiration seems again to depend upon a constitutional difference in the gases themselves.

The theory of the transpirability of gases, which at present appears to me most probable, is that it is a kind of elasticity depending upon the absolute quantity of heat, latent as well as sensible, which different gases contain under the same volume; and therefore that it will be connected more immediately with the specific heat than any other property of the gases.

The only other gases besides those already experimented upon, which could be retained over water, and exposed to the metallic parts of the apparatus without injury, are olefiant gas, nitric oxide and sulphuretted hydrogen; and these were submitted to transpiration with several of the tubes already used. I subjoin the results, although less complete than is desirable, under the head of each gas.

#### 7. *Transpiration of Olefiant Gas.*

TABLE XXXIII.—Transpiration by Capillary H into a Six-Pint Jar.  
Barom. 29·68. Temp. 59°.

Gauge barometer in inches.	Air.		Olefiant gas.	
	I.	II.	I.	II.
28·5	0	0	0	0
26·5	217	218	124	128
24·5	220	220	130	131
23·5	112	113	66	65
From 28·5 to 23·5 inches...	549	551	320	324

#### Transpiration by Capillary H into a One-Pint Jar.

Gauge barometer in inches.	Air.		Olefiant gas.		Air.
	I.	II.	I.	II.	I.
28	0	0	0	0	0
20	184	183	108	108	183
12	227	228	134	134	226
8	163	163	96	96	163
4	265	265	153	151	265
2	260	264	149	149	260
From 28 to 2 inches.....	1099	1103	640	638	1097



	Air.	Olefiant gas.
From 28·5 to 23·5 inches { Time in seconds.....	550	322
{ Time of air=1.....	...	0·5854
{ Time of oxygen=1.....	...	0·5268

	Air.	Olefiant gas.
From 28 to 2 inches ..... { Time in seconds .....	1099·7	639
{ Time of air=1 .....	...	0·5810
{ Time of oxygen=1....	...	0·5229

TABLE XXXIV.—Transpiration by Capillary H (with cupped ends) into a Six-Pint Jar. Barom. 30·2. Temp. 52°.

Gauge barometer in inches.	Air.		Carburetted hydrogen.		Olefiant gas.		Air.	90C <sub>4</sub> H <sub>4</sub> +10CO.		Air.	
	I.	II.	I.	II.	I.	II.	I.	I.	II.	I.	II.
28·5	0	0	0	0	0	0	0	0	0	0	0
26·5	206	207	127	126	120	118	207	126	126	207	207
24·5	208	208	127	128	119	121	208	126	127	209	209
23·5	106	106	64	65	61	61	106	64	64	104	104
From 28·5 to 23·5 inches	520	521	318	319	300	300	521	316	317	520	520

### Mean Results.

Gauge barometer.	Air.	Carburetted hydrogen.	Olefiant gas.	90C <sub>4</sub> H <sub>4</sub> +10CO.	Air.
From 28·5 to 23·5 inches { Time in seconds ...	521·5	318·	300	316·5	
{ Time of air=1 .....	...	0·6118	0·5763	0·6080	
{ Time of oxygen=1	...	0·5506	0·5186	0·5472	

The results for olefiant gas can be considered only as approximative from the circumstance that the gas was always contaminated by a small quantity of carbonic oxide, varying from 3 to 5 per cent., and a sensible trace of the dense gas or vapour, to which allusion has already been made. Both impurities would tend to raise the number for olefiant gas; ten per cent. of carbonic oxide purposely added to that gas, raising its number from 0·5186 to 0·5472. The calculated mean rate of the last mixture is 0·5513, taking the rate of carbonic oxide at 0·8700, and



that of olefiant gas at 0.5186. If the true coefficient for olefiant gas should be a whole number, it may be expected to be 0.5, or exactly one-half of the rate of oxygen.

### 8. *Transpiration of Nitric Oxide.*

TABLE XXXV.—Transpiration by Capillary E into a One-Pint Jar.  
Barom. 30.45. Temp. 52°.

Gauge barometer in inches.	Air.	Nitric oxide.		Oxygen.	Air.
	I.	I.	II.	I.	I.
28	0	0	0	0	0
20	135	135	131	149	135
12	167	162	162	186	169
8	118	115	115	133	118
4	189	183	184	206	188
2	192	184	188	219	195
From 28 to 4 in.	609	595	592	674	610

### Mean Results.

Gauge barometer in inches.	Air.	Nitric oxide.	Air.
From 28 to 4 in. { Time in seconds..... { Time of oxygen = 1	609 0.9035	593.5 0.8805	610 0.9035

TABLE XXXVI.—Transpiration by Capillary E into a Two-Pint Jar.  
Barom. 30.08. Temp. 60°.

Gauge barometer in inches.	Nitrogen.			Nitric oxide.		Oxygen.	
	I.	II.	III.	I.	II.	I.	II.
28	0	0	0	0	0	0	0
20	231	232	...	237	235	266	267
12	286	287	286	288	287	327	328
8	200	200	202	203	206	227	227
4	320	317	320	313	312	363	364
2	314	320	316	311	315	361	361
From 28 to 2 inches...	1351	1356	...	1352	1355	1544	1547



## Mean Results.

Gauge barometer.		Nitrogen.	Nitric oxide.
From 28 to 12 inches	Time in seconds .....	517·83	523·5
	Time of oxygen = 1.....	0·8717	0·8815
From 12 to 4 inches	Time in seconds .....	519·7	517
	Time of oxygen = 1.....	0·8801	0·8755
From 4 to 2 inches	Time in seconds .....	316·7	313
	Time of oxygen = 1.....	0·8772	0·8670
From 28 to 2 inches	Time in seconds .....	1354·2	1353·5
	Time of oxygen = 1.....	0·8768	0·8764

The number for nitric oxide ( $\text{NO}_2$ ) approaches very closely to that of nitrogen, if it does not actually coincide with that number; yet the specific gravities of these two gases are different, that of nitric oxide being 1·0405, air = 1; or 0·9375, oxygen = 1; the mean between the densities of oxygen and nitrogen gases. It would appear from this that the coefficients of transpiration of gases are less various than their specific gravities. In conducting experiments with this gas, the surface of the mercury in the gauge-tube is tarnished, which causes it to adhere to the glass and descend irregularly, so that the observations want the usual uniformity, as seen in both tables. When a few drops of water were placed above the mercury in the gauge barometer, its descent became more regular. This gas acted inconveniently in another way, by forming a solid compound with the oil in the cylinders, and thus clogging the action of the air-pump.

9. *Transpiration of Sulphuretted Hydrogen.*

TABLE XXXVII.—Transpiration by Capillary H into a One-Pint Jar.  
Barom. 29·89. Temp. 59°.

Gauge barometer in inches.	Air.		Sulphuretted hydrogen.			Air.
	I.	II.	I.	II.	III.	I.
28	0	0	0	0	0	0
20	180	180	122	123	121	178
12	226	224	156	153	153	225
8	155	158	108	109	110	156
4	262	257	177	174	173	258
2	253	256	175	173	173	255
From 28 to 2 inches ...	1076	1075	738	732	730	1072



## Mean Results.

Gauge barometer.		Sulphuretted hydrogen.
From 28 to 12 inches	Time in seconds.....	276
	Time of air = 1 ...	0.6814
	Time of oxygen = 1 ...	0.6132
From 12 to 4 inches	Time in seconds.....	283.66
	Time of air = 1 ...	0.6738
	Time of oxygen = 1 ...	0.6060
From 4 to 2 inches	Time in seconds.....	173.66
	Time of air = 1 ...	0.6825
	Time of oxygen = 1 ...	0.6142
From 28 to 2 inches		733.3
		0.6818
		0.6136

TABLE XXXVIII.—Transpiration by Capillary H into a Six-Pint Jar.  
Barom. 29.98. Temp. 59°.

Gauge barometer in inches.	Air.		Sulphuretted hydrogen.				Air.			
	I.	II.	I.	II.	III.	IV.	I.	II.	III.	IV.
28.5	0	0	0	0	0	0	0	0	0	0
26.5	206	203	140	140	140	141	206	203	203	205
24.5	207	209	143	147	146	148	216	214	217	215
23.5	107	109	77	75	77	75	108	109	109	111
From 28.5 to 23.5 inches ...	520	521	360	362	363	364	530	526	529	531

## Mean Results.

Gauge barometer.		Sulphuretted hydrogen.
From 28.5 to 23.5 inches	Time in seconds .....	362.25
	Time of air = 1.....	0.6846
	Time of oxygen = 1.....	0.6161

The experiments with this gas indicate a number above 0.60 for its coefficient of transpiration; 0.625 is 5-8ths of oxygen, while the result of Table XXXVIII., which is the more valuable of the two, is 0.6161. But this gas is likely to vary sensibly in its coefficient with different capillaries, like carbonic acid; and both its physical and chemical properties oppose difficulties to obtaining a correct result. The rate of air following this gas is made very sensibly slower in the last table;



indeed the rate of the capillary appears to be permanently altered, possibly from the deposition of sulphur from the gas.

[I shall add, in an Appendix to this paper, a series of observations on the transpiration of gaseous mixtures, which appear to warrant the following conclusions :—

It appears from Tables XLII. and XLIII. that mixtures of oxygen and nitrogen in all proportions maintain a rate which is sensibly the arithmetical mean rate of the two gases.

From Tables XLIV. and XLV., that the rates of mixtures of oxygen and carbonic oxide are also uniform, but that mixtures of carbonic oxide and hydrogen deviate greatly from the mean, inclining always to that of the heavier gas.

In Tables XLVI. and XLVII., that the mixtures of oxygen and carbonic acid maintain the mean rate; and that mixtures of carburetted hydrogen and hydrogen deviate greatly from the mean, always inclining to the rate of the slower gas.

Tables from XLVIII. to LIII. inclusive exhibit the transpiration of hydrogen mixed with various other gases, particularly nitrogen, oxygen, carbonic acid, nitrous oxide, and nitric oxide; and Tables LIV. and LV. contain the results of the transpiration of mixtures of carburetted hydrogen with oxygen and with hydrogen. It appears that while all the other gases tried appeared to maintain their usual rates of transpiration in a state of mixture, those of carburetted hydrogen and hydrogen are greatly altered; and when the proportion of the latter gas is not more than from 5 to 15 per cent., its rate becomes as slow as the densest gas with which it is mixed; the deviation from the mean in hydrogen mixtures being relatively greatest when one of the gases is present in a small proportion. With an addition of so much as 25 per cent. of hydrogen, carburetted hydrogen, carbonic acid, and nitrous oxide continue to be transpired in sensibly the same times as when pure and unmixed. Hydrogen is then transpired of course as slowly as the other gas with which it is mixed, although the time of hydrogen alone is 0.44, while that of carburetted hydrogen is 0.55, and of carbonic acid and nitrous oxide 0.75. Indeed, small additions of hydrogen, such as 5 or 10 per cent., made to carburetted hydrogen, appear to prolong the time of transpiration; and what is very curious, raise the time of the mixture to the empirical number of pure carburetted hydrogen, namely 0.5625 (Table XLVII.) A slight retardation of the same kind may also be perceived in the similar carbonic acid mixtures. The transpiration-time of equal volumes of hydrogen and carbonic acid is 0.7339, or very little less than that of pure carbonic acid.

Carbonic oxide and nitric oxide, with equal admixtures of hydrogen,



correspond as closely in their times as when pure, as will be seen on comparing together the results of Tables XLV. and LIII. A similar apparent rectification of the time of nitric oxide will be observed, in the last of these tables, to be effected by the addition of 5 per cent. of hydrogen to that gas, as was remarked above of carburetted hydrogen; the time of 100  $\text{NO}_2$  being 0.8661, that of 95  $\text{NO}_2 + 5\text{H}$  is found 0.8788; while the empirical coefficient for nitric oxide is the same as that of nitrogen, namely, 0.8750, or 0.8785, adopting Regnault's density of the latter gas.

It appears that the time of carburetted hydrogen is sensibly increased by the addition of oxygen, at least when the proportion of the latter gas amounts to or exceeds 25 per cent. of the mixture (Table LIV.)

The times of transpiration of the hydrogen mixtures, which have been most minutely observed, namely, those of hydrogen with oxygen, with air, and with carbonic acid, are exhibited by the curves of Plate XXXV. These curves start from a common point 44, the time of pure hydrogen, and terminate respectively with the times of oxygen 100, of air 90, and of carbonic acid 75.

It would be premature to enter at present upon any discussion of these results; for the full elucidation of the transpiration of mixed gases, must await, I believe, the further extension of our knowledge of the laws of gaseous diffusion. Nov. 1846.]



## APPENDIX.

*Tables of the observed Transpiration of Gaseous Mixtures.*

TABLE XLII.—Transpiration by Capillary E into a One-Pint Jar. Barom. 29.55. Temp. 53°.

Gauge barometer in inches.	Air.		Oxygen.		97.5 O+2.5N.		95 O+5N.		90 O+10N.		75 O+25N.		66.6 O+33.3N.		Oxygen.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
28	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
20	142	143	158	158	...	...	157	158	156	157	153	153	151	151	157	157
12	176	175	196	195	353	353	194	194	192	192	190	189	187	187	195	195
8	123	123	137	138	137	137	137	136	136	136	133	134	131	132	137	137
4	197	197	222	220	220	219	220	219	218	216	214	214	211	211	220	220
2	199	197	221	222	222	223	220	221	219	221	218	219	212	212	222	222
From 28 to 2 inches.....	837	835	934	933	932	932	928	928	921	922	908	909	892	893	931	931

## Mean Results.

Gauge barometer.	Air.		97.5 O+2.5N.	95 O+5N.	90 O+10N.	75 O+25N.	66.6 O+33.3N.	Oxygen.
From 28 to 2 inches { Time in seconds ... Time of oxygen = 1 Calculated mean...	836	836	932	928	921.5	908.5	892.5	
	0.8955	0.8955	0.9984	0.9941	0.9871	0.9734	0.9550	
	...	...	0.9969	0.9938	0.9875	0.9688	0.9583	



TABLE XLIII.—Transpiration by Capillary E into a One-Pint Jar. Barom. 29·81. Temp. 54°.

Gauge barometer <sup>scale</sup> in inches.	Air.		50N+50 O.		Oxygen.	66·6N+33·3 O.		75N+25 O.	90N+10 O.		95N+5 O.	97·5N+2·5 O.		Nitrogen.	Air.
	I.	II.	I.	II.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.
28	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0	<sup>h</sup> 0
20	140	141	147	147	157	143	142	139	139	139	139	139	138	138	145
12	174	173	181	181	193	177	176	172	172	170	170	170	169	169	175
8	122	123	128	128	137	125	123	121	121	120	120	120	119	119	124
4	196	196	204	204	219	199	198	193	193	192	192	193	192	192	198
2	197	196	207	207	222	204	201	196	196	196	196	199	194	194	198
From 28 to 2 inches	829	829	868	867	928	848	840	821	821	817	821	821	812	812	840

## Mean Results.

Gauge barometer.	Air.	50N+50 O.	66·6N+33·3 O.	75N+25 O.	90N+10 O.	95N+5 O.	97·5N+2·5 O.	Nitrogen.	Air.
From 28 to 2 in. { Time in seconds ... Time of oxygen = 1 Calculated mean ...	829 0·8933 ...	867·5 0·9348 0·9375	848 0·9138 0·9167	840 0·9051 0·9062	821 0·8847 0·8875	817 0·8804 0·8812	821 0·8847 0·8805	812 0·8750 0·8789	840 0·9052



TABLE XLIV.—Transpiration by Capillary E into a One-Pint Jar. Barom. 29.69. Temp. 54°.

Gauge barometer in inches.	Oxygen.	Carbonic oxide.	97.5CO+2.5 O.	95CO+5 O.	90CO+10 O.	75CO+25 O.	Air.	Oxygen.
	I.	L.	I.	I.	I.	I.	I.	I.
28	" 0	" 0	" 0	" 0	" 0	" 0	0	" 0
20	157	137	139	138	140	142	143	158
12	195	169	169	170	172	176	175	196
8	137	118	120	120	120	124	123	138
4	219	192	191	192	194	198	197	221
2	221	190	192	193	202	202	199	221
From 28 to 4 inches .....	708	616	619	620	626	640	638	713

## Mean Results.

Gauge barometer.	Carbonic oxide.	97.5CO+2.5 O.	95CO+5 O.	90CO+10 O.	75CO+25 O.	Air.	Oxygen.
From 28 to 4 inches { Time in seconds ..... Time of oxygen = 1 Calculated mean .....	616 0.8701 ...	619 0.8743 0.8733	620 0.8757 0.8765	626 0.8842 0.8830	640 0.9040 0.9026	638 0.9011	



TABLE XLV.—Transpiration by Capillary E into a One-Pint Jar. Barom. 30.18. Temp. 52°.

Gauge barometer in inches.	Air.		Carbonic oxide.		66.7CO+33.3 O.		50CO+50 O.		66.7 O+33.3CO.		75 O+25CO.		95CO+5H.		90CO+10H.		75CO+25H.		92.5CO+7.5H.		Air.		Hydro- gen.	
	I.		I.		I.		I.		I.		I.		I.		I.		I.		I.		I.		I.	
28	0		0		0		0		0		0		0		0		0		0		0		0	
20	137		132		140		143		146		148		133		132		128		132		137		78	
12	169		164		172		177		181		183		164		163		159		163		170		84	
8	119		116		122		125		128		130		115		116		113		115		121		59	
4	192		185		195		200		206		205		184		185		181		185		193		95	
2	193		188		201		205		209		204		190		191		181		191		201		100	
From 28 to 4 inches	617		597		629		645		661		666		596		596		581		595		621		316	

## Mean Results.

Gauge barometer.		Air.		Carbonic oxide.		66.7CO+33.3 O.		50CO+50 O.		66.7 O+33.3CO.		75 O+25CO.		95CO+5H.		90CO+10H.		75CO+25H.		92.5CO+7.5H.		Air.		Hydrogen.	
From 28 to 4 inches	Time in seconds	617		597		629		645		661		666		596		596		581		595		621		316	
	Time of ox.=1 ...	0.8905		0.8664		0.9129		0.9361		0.9593		0.9666		0.8650		0.8650		0.8432		0.8635		0.9013		0.4586	
	Calc. mean, A *	.....		.....		0.9109		0.9332		0.9554		0.9666		0.8046		0.8256		0.7644		0.8358					
	Calc. mean, B†	.....		.....		.....		.....		.....		.....		0.8450		0.8237		0.7848		0.8344					

\* Mean with the number for hydrogen actually observed.

† Mean with the number 0.44 as the coefficient of hydrogen. These last results are most to be depended upon, as the rate of the hydrogen alone is often raised by a slight impurity, of which the effect would become much less sensible in the mixtures containing that gas.



TABLE XLVI.—Transpiration by Capillary E into a One-Pint Jar. Barom. 29.94. Temp. 56°.

Gauge barometer in inches.	Air.	Oxygen.	Carbonic acid.	97.5CO <sub>2</sub> +2.5 O.	95CO <sub>2</sub> +5 O.	90CO <sub>2</sub> +10 O.	75CO <sub>2</sub> +25 O.	50CO <sub>2</sub> +50 O.	Carbonic acid.
	I.	I.	I.	I.	I.	I.	I.	I.	I.
28	0	0	0	0	0	0	0	0	0
20	139	155	118	119	...	120	127	136	117
12	172	192	144	145	266	149	156	168	145
8	...	135	101	102	102	104	109	118	102
4	315	218	161	163	163	166	174	188	161
2	198	218	161	162	163	166	175	190	162
From 28 to 2 inches .....	824	918	685	691	694	705	741	800	687

## Mean Results.

Gauge barometer.	Air.	Carbonic acid.	97.5CO <sub>2</sub> +2.5 O.	95CO <sub>2</sub> +5 O.	90CO <sub>2</sub> +10 O.	75CO <sub>2</sub> +25 O.	50CO <sub>2</sub> +50 O.	Carbonic acid.
From 28 to 2 inches { Time in seconds ... Time of oxygen = 1 Calculated mean ...	824 0.8976 ...	685 0.7461 ...	691 0.7538 0.7524	694 0.7559 0.7588	705 0.7679 0.7715	741 0.8071 0.8096	880 0.8714 0.8730	687 0.7467



TABLE XLVII.—Transpiration by Capillary E into a One-Pint Jar. Barom. 29.61. Temp. 54°.

Gauge barometer in inches.	Carbu- retted hydro- gen.	90CH <sub>2</sub> +10H.	95CH <sub>2</sub> +5H.	97.5CH <sub>2</sub> +2.5H.	Hydro- gen.	Oxy- gen.	90 O+10CO <sub>2</sub> .	75 O+25CO <sub>2</sub> .	95 O+5CO <sub>2</sub> .	97.5 O+2.5CO <sub>2</sub> .	Car- bonic acid.	82.5CH <sub>2</sub> +17.5H.
	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.	I.
28	0	0	0	0	0	0	0	0	0	0	0	0
20	87	89	89	87	71	158	154	149	155	156	119	88
12	107	110	109	107	88	194	189	183	192	193	147	109
8	...	76	76	75	61	137	133	128	134	136	102	75
4	195	123	123	120	98	218	214	206	217	218	163	122
2	121	124	123	122	102	224	219	211	222	224	166	123
From 28 to 4 } inches..... }	389	398	397	389	318	707	690	666	698	703	531	394

## Mean Results.

Gauge barometer.	Carburet- ted hydro- gen.	90CH <sub>2</sub> +10H.	95CH <sub>2</sub> +5H.	97.5CH <sub>2</sub> +2.5H.	Hydrogen.	90 O+10CO <sub>2</sub> .	75 O+25CO <sub>2</sub> .	95 O+5CO <sub>2</sub> .	97.5 O+2.5CO <sub>2</sub> .	Carbonic acid.	82.5CH <sub>2</sub> +17.5H.
From 28 to 4 } Time in seconds } Time of ox. = 1 } Calc. mean, A* } Calc. mean, B+ }	389 0.5544 ... ...	398 0.5629 0.5439 0.5429	397 0.5615 0.5266 0.5486	389 0.5502 0.5409 0.5515	318 0.4497 ... ...	690 0.9759 0.9750 ...	666 0.9420 0.9375 ...	698 0.9872 0.9875 ...	703 0.9943 0.9937 ...	531 0.7510 ... ...	394 0.5572 0.5360 0.5343

\* Mean with the number for hydrogen actually observed.

+ Mean with the number 0.44 as the coefficient of hydrogen. These last results are most to be depended upon, as the rate of the hydrogen alone is often raised by a slight impurity, of which the effect would become much less sensible in the mixtures containing that gas.



TABLE XLVIII.—Transpiration by Capillary E into a One-Pint Jar. Barom. 29·63. Temp. 52°.

Gauge barometer in inches.	Air.		Oxygen.		97·5 O+2·5H.		95 O+5H.		90 O+10H.		75 O+25H.		Hydrogen.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
28	"	"	"	"	"	"	"	"	"	"	"	"	"	"
20	141	142	142	158	157	157	157	157	156	156	153	153	70	70
12	177	176	176	195	194	195	195	194	194	194	189	189	87	87
8	122	122	137	136	137	136	136	137	135	136	133	132	62	62
4	197	196	219	219	218	219	218	219	217	217	213	213	99	99
2	195	196	221	221	219	217	223	221	221	221	216	215	100	100
From 28 to 2 inches .....	832	832	928	929	925	924	929	928	923	924	904	902	418	418

## Mean Results.

Gauge barometer.	Air.		97·5 O+2·5H.	95 O+5H.	90 O+10H.	75 O+25H.	Hydrogen.
From 28 to 2 inches { Time in seconds..... Time of oxygen = 1..... Calculated mean, A..... Calculated mean, B.....	833	0·8971	924·5 0·9957 0·9862 0·9860	928·5 1·000 0·9725 0·9720	923·5 0·9946 0·9450 0·9440	903 0·9724 0·8625 0·8600	418 0·4502







TABLE L.—Transpiration by Copper Capillary into a Three-Pint Jar.  
Barom. 30.1. Temp. 61°.

Gauge barometer in inches.	Air.		Hydrogen.		95H+5 Air.		90H+10 Air.	75H+25 Air.	H25+75 Air.
	I.	II.	I.	II.	I.	II.	I.	I.	I.
28	61°.25	61°.25	61°.5	61°.5	61°.75	61°.75	61°.75	61°.75	61°.75
24	0"	0"	0"	0"	0"	0"	0"	0"	0"
20	286	285	139	140	168	165	183	227	280
12	301	302	148	148	178	177	196	241	296
8	729	731	358	360	431	424	474	581	705
	515	512	254	257	306	300	343	412	507
	61°.75	61°.75	62°	62°	62°	62°	62°	62°	62°
From 28 to 8 inches.....	1831	1830	899	905	1083	1066	1196	1461	1788



Transpiration by Copper Capillary into a Three-Pint Jar. Barom. 30.19. Temp. 61.5.

Gauge barometer in inches.	Air.		50H+50 Air.	10H+90 Air.	5H+85 Air.
	I.	II.	I.	I.	I.
28	61°5	61°5	61°5	61°5	61°5
24	0"	0"	0"	0"	0"
20	284	284	258	280	282
12	302	302	274	298	300
8	727	728	662	721	724
	514	515	471	510	514
	62°	62°	62°	62°	62°
From 28 to 8 inches .....	1827	1829	1665	1809	1820

### Mean Results.

Gauge barometer.	Air.	Hydrogen.	95H+5 Air.	90H+10 Air.	75H+25 Air.	25H+75 Air.
From 28 to 8 inches { Time in seconds ..... Time of air = 1 ..... Time of oxygen = 1 ..... Calculated mean .....	1803.5	902	1074.5	1196	1461	1788
	...	0.4927	0.5869	0.6534	0.7987	0.9767
	...	0.4434	0.5282	0.5880	0.7488	0.8790
	...	...	0.4630	0.4860	0.5500	0.7850
From 28 to 8 inches { Time in seconds ..... Time of air = 1 ..... Time of oxygen = 1 ..... Calculated mean .....	Air.	50H+50 Air.	10H+90 Air.	5H+95 Air.		
	1828	1665	1809	1820		
	...	0.9108	0.9876	0.9956		
	...	0.8197	0.8888	0.8960		
	...	0.6700	0.8540	0.8770		



TABLE LI.—Transpiration by Capillary E into a One-Pint Jar. Barom. 29·89. Temp. 54°.

Gauge barometer in inches.	97·5H + 2·5CO <sub>2</sub>	5H + 5CO <sub>2</sub>	90H + 10CO <sub>2</sub>	75H + 25CO <sub>2</sub>	50H + 50CO <sub>2</sub>	Carbonic acid.	Oxygen.	Hydrogen.	Air.
	I.	I.	I.	I.	I.	I.	I.	I.	I.
28	0	0	0	0	0	0	0	0	0
20	77	79	88	105	114	118	156	68	142
12	95	99	110	130	142	145	192	85	173
8	67	69	77	92	99	102	136	60	121
4	109	113	125	148	160	162	217	97	195
2	111	115	127	150	161	161	220	98	201
From 28 to 2 inches	459	475	527	625	676	688	921	398	832

## Mean Results.

Gauge barometer.	97·5H + 2·5CO <sub>2</sub>	95H + 5CO <sub>2</sub>	90H + 10CO <sub>2</sub>	75H + 25CO <sub>2</sub>	50H + 50CO <sub>2</sub>	Carbonic acid.	Hydrogen.	Air.
From 28 to 8 inches	459	475	527	625	676	688	398	832
Time in seconds	0·4983	0·5157	0·5722	0·6786	0·7339	0·7470	0·4321	0·9033
Time of ox. = 1	0·4402	0·4484	0·4648	0·5113	0·5655	0·6185	0·3815	0·8967
Calculated mean								



TABLE LII.—Transpiration by Capillary E into a One-Pint Jar.  
Barom. 30·39. Temp. 52°.

Gauge barometer in inches.	Air.	Oxygen.	Nitrous Oxide.	75NO+25H.	90NO+10H.	Air.
	I.	I.	I.	I.	I.	I.
28	0	0	0	0	0	0
20	136	152	114	114	114	135
12	168	187	141	141	141	168
8	119	132	99	99	98	119
4	189	212	157	159	158	190
2	198	222	159	162	159	196
From 28 to 4 inches ...	612	683	511	513	511	612

Mean Results.

Gauge barometer.	Air.	Nitrous oxide.	75NO+25H.	90NO+10H.	Air.
From 28 to 4 in. { Time in seconds	612	511	513	511	612
{ Time of oxy. = 1	0·8960	0·7481	0·7510	0·7481	0·8960
{ Calc. mean, A....	...	...	0·6757	0·7292	
{ Calc. mean, B....					

TABLE LIII.—Transpiration by Capillary E into a One-Pint Jar.  
Barom. 30·62. Temp. 52°.

Gauge barometer in inches.	Air.	Oxygen.	Hydrogen.	Nitric oxide.		95NO <sub>2</sub> +5H.
	I.	I.	I.	I.	II.	I.
28	0	0	0	0	0	0
20	133	149	66	130	129	130
12	167	184	83	161	158	163
8	117	131	59	114	112	115
4	189	212	95	183	184	186
2	192	214	97	183	181	184
From 28 to 4 inches ...	606	676	303	588	583	594



TABLE LIII.—*Continued.*

Gauge barometer in inches.	90NO + 10H.	75NO <sub>2</sub> + 25H.	50NO <sub>2</sub> + 50H.	25NO <sub>2</sub> + 75H.	Air.
	I.	I.	I.	I.	I.
28	0	0	0	0	0
20	128	125	119	106	134
12	160	157	150	132	168
8	113	112	117	95	120
4	181	180	170	151	192
2	181	185	179	153	193
From 28 to 4 inches ...	582	574	556	484	614

## Mean Results.

Gauge barometer.		Air.	Hydrogen.	Nitric oxide.	95NO <sub>2</sub> + 5H.
From 28 to 4 inches	Time in seconds .....	606	303	585.5	594
	Time of oxygen = 1...	0.8964	0.4482	0.8661	0.8788
	Calc. mean, A.....	...	...	...	0.8452
	Calc. mean, B.....	...	...	...	0.8447
		90NO <sub>2</sub> + 10H.	75NO <sub>2</sub> + 25H.	50NO <sub>2</sub> + 50H.	25NO <sub>2</sub> + 75H.
From 28 to 4 inches	Time in seconds .....	582	574	556	484
	Time of oxygen = 1...	0.8609	0.8491	0.8224	0.7159
	Calc. mean, A.....	0.8243	0.7616	0.6571	0.5527
	Calc. mean, B.....	0.8234	0.7596	0.6530	0.5465
		Air.			
From 28 to 4 inches	Time in seconds .....	614			
	Time of oxygen = 1...	0.9082			

TABLE LIV.—



TABLE LIV.—Transpiration by Capillary E into a One-Pint Jar.  
Barom. 29.71. Temp. 55°.

Gauge barometer in inches.	Oxygen.	Carburetted hydrogen.	97.5CH <sub>2</sub> +2.5 O.	95CH <sub>2</sub> +5 O.	90CH <sub>2</sub> +10 O.	75CH <sub>2</sub> +25 O.	50CH <sub>2</sub> +50 O.	Air.
	I.	I.	I.	I.	I.	I.	I.	I.
28	0	0	0	0	0	0	0	0
20	157	91	91	92	94	109	127	141
12	195	109	112	114	117	134	157	174
8	136	77	79	79	81	94	110	122
4	219	122	126	127	131	151	177	195
2	224	124	127	129	133	153	180	200
From 28 to 4 inches...	707	399	408	412	423	488	571	632

Mean Results.

Gauge barometer.	Carburetted hydrogen.	97.5CH <sub>2</sub> +2.5 O.	95CH <sub>2</sub> +5 O.	90CH <sub>2</sub> +10 O.	75CH <sub>2</sub> +25 O.	50CH <sub>2</sub> +50 O.	Air.
From 28 to 4 inches { Time in seconds.. Time of ox. = 1... Calc. mean .....	399 0.5629 ...	408 0.5770 0.5734	412 0.5827 0.5838	423 0.5983 0.6062	488 0.6902 0.6718	571 0.8076 0.7814	632 0.8939



TABLE LV.—Transpiration by Capillary E into a One-Pint Jar. Barom. 29.43. Temp. 55°.

Gauge barometer in inches.	Air.		Hydrogen.		97.5H + 2.5CH <sub>2</sub> .		95H + 5CH <sub>2</sub> .		90H + 10CH <sub>2</sub> .		75H + 25CH <sub>2</sub> .		50H + 50CH <sub>2</sub> .		Carburetted hydrogen.		Hydrogen.		Oxygen.	
	L.	H.	L.	H.	L.	H.	L.	H.	L.	H.	L.	H.	L.	H.	L.	H.	L.	H.	L.	H.
28	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
20	144	73	75	77	79	84	88	88	88	88	88	88	88	88	88	74	74	160	160	160
12	176	91	93	94	98	105	109	109	109	109	105	105	109	108	108	92	92	197	197	197
8	124	64	65	66	68	73	76	76	76	76	73	73	76	76	76	65	65	138	138	138
4	198	103	105	107	111	119	122	122	122	122	119	119	122	121	121	105	105	222	222	222
2	201	105	107	109	113	120	126	126	126	126	120	120	126	123	123	106	106	225	225	225
From 28 to 4 inches...	642	331	338	344	356	381	395	395	395	395	381	381	395	393	393	336	336	717	717	717

## Mean Results.

Gauge barometer.	Air.	Hydrogen.	97.5H + 2.5CH <sub>2</sub> .		95H + 5CH <sub>2</sub> .	90H + 10CH <sub>2</sub> .		75H + 25CH <sub>2</sub> .		50H + 50CH <sub>2</sub> .		Carburetted hydrogen.	Hydrogen.
From 28 to 4 inches	642	331	338	344	356	381	395	393	336	0.4686			
	0.8955	0.4616	0.4714	0.4797	0.4965	0.5313	0.5596	0.5481					
	...	...	0.4705	0.4725	0.4765	0.4884	0.5083						
	...	...	0.4427	0.4454	0.4508	0.4670	0.4940						



## XV.

ON THE MOTION OF GASES. PART II.<sup>1</sup>

From *Phil. Trans.* 1849, pp. 349-392.

ALL experiments on the velocity with which different gases rush into a vacuum, or pass under pressure through an aperture in a thin plate, are in strict accordance with the physical law that the times of passage for equal volumes are proportional to the square roots of the densities of the various gases. Besides being the law of "Effusion," this is also the law of the Diffusion of one gas into an atmosphere of another gas. The result in both cases is simply and exclusively a consequence of specific gravity.

The velocity with which gases of different nature pass through a tube is necessarily much influenced by the law of their effusion, when the tube is short and approaches in character to an aperture in a thin plate. But if the length of the tube is progressively increased, its diameter or the aperture remaining constant, then while the resistance increases, and the passage for all gases becomes greatly slower, the velocities of the different gases are found rapidly to diverge from those of their effusion. The velocities of different gases appear at last however to attain a particular ratio with a certain length of tube and resistance, and preserve the same relation to each other for greater lengths and resistances. After attaining this constant ratio, the passage of all the gases becomes slower, exactly in proportion to the increased length of the tube, that is, in proportion to the resistance. The different gases are now equally affected by the resistance, and their relative velocities are therefore undisturbed and remain constant. The effect of the law of effusion upon the velocities is no longer sensible, and appears to be eliminated.

As the rates of passage of different gases through a tube appear to depend upon a new and peculiar property of gases, I have spoken of it as the Transpiration or Transpirability of gases. The rates of transpiration appear not to be affected by the material of the tube, as they are found the same for capillary tubes of glass and of copper and for a porous mass of stucco. I may add, that such experiments exhibit a constancy and possess a neatness and precision which is very extraordinary. The experiments of M. Poiseuille indicate an equally remarkable constancy and precision of result in the passage of Liquids through capillary tubes, which has been fully confirmed by M. Regnault.<sup>2</sup>

<sup>1</sup> Received June 21,—Read June 21, 1849.

<sup>2</sup> Rapport sur un Mémoire de M. le Docteur Poiseuille, ayant pour titre, "Recherches expérimentales sur le mouvement des liquides dans les tubes des très-petits diamètres." *Annales de Chimie et de Physique*, 3<sup>me</sup> série, t. vii. p. 50.



The experiments of my former paper afford good grounds for assuming the existence of a relation in the transpirability of different gases, of an equally simple nature as that which is recognised among the specific gravities of gases, or even as the still more simple ratios of their combining volumes. Compared with solids and liquids, matter in the form of gas is susceptible of small variation in physical properties, and exhibits only a few grand features. These differences of property, which are preserved amidst the prevailing uniformity of gases, may well be supposed to be among the most deep-seated and fundamental in their nature with which matter is endowed. It was under such impressions that I have devoted an amount of time and attention to the determination of this class of numerical constants, which might otherwise appear disproportionate to their value and the importance of the subject. As the results, too, were entirely novel, and wholly unprovided for in the received view of the gaseous constitution, of which indeed they prove the incompleteness, it was the more necessary to verify every fact with the greatest care.

Perhaps the most general and simple result which I can offer is, that the transpiration velocity of hydrogen is exactly double that of nitrogen. These gases, it will be remembered, have a less simple relation in density, namely 1 to 14. This was the conclusion respecting the transpiration of these gases in my former paper, and I have obtained since much new evidence in its favour. The transpirability of carbonic oxide, like the specific gravity of that gas, appears also to be identical with that of nitrogen.

The result which I would place next in point of accuracy and importance is, that the transpiration velocity of oxygen is related to that of nitrogen in the inverse ratio of the densities of these gases, that is, as 14 to 16. In equal times it is not equal volumes but equal weights of these two gases that are transpired; the more heavy gas being more slowly transpired in proportion to its greater density. Mixtures of oxygen and nitrogen have the mean velocity of these two gases, and hence the time of air is also found to be proportional to its density when compared with the time of oxygen.

The relation between nitrogen and oxygen is, I believe, equally precise as that between nitrogen and hydrogen. The densities calculated from the atomic weights of oxygen and nitrogen, namely, 16 and 14, being 1 for oxygen, 0.9010 for air and 0.8750 for nitrogen; the observed times of transpiration of equal volumes of the same gases are for oxygen 1, air 0.8970 to 0.9010, and for nitrogen from 0.8680 to 0.8708.

These slight deviations I look upon as of the same character as those which accurate determinations of the densities of the same gases indicate from their calculated or theoretical density; the observed den-



sities of air and nitrogen being 0.9038 and 0.8785 referred to oxygen as unity (Regnault), instead of 0.9010 and 0.8750; or the observed difference in density is sensibly less than it should be by theory. The departure from the law in the transpiration of the same gases is certainly somewhat wider, and it is in the opposite direction; the difference in the observed times of transpiration being greater instead of less than the calculated times.

The points respecting transpiration, which still most demand consideration, are the following:—

1. Determination of the resistance and of the dimensions of the capillary at which the transpiration of gases becomes normal; and the properties of serviceable capillary tubes.
2. New determinations of the transpiration of various gases and vapours.
3. Influence of change of density and elasticity, produced by change of pressure, upon transpiration.
4. Influence of temperature upon transpiration.

#### I. CAPILLARY TUBES FOR TRANSPIRATION.

The transpiration of some gases appears to become sooner normal than others, that is, in capillary tubes which are less elongated or less contracted than is necessary for other gases. This was first observed on breaking down and using portions of the glass capillary tube H of my former paper, which was comparatively wide, being about 0.0222 inch, or  $\frac{1}{45}$ th of an inch in diameter, with the great original length of 22 feet; when it allowed 1 cubic inch of air to pass under the pressure of one atmosphere into a vacuum in 15.64 seconds, or it discharged 3.84 cubic inches of air per minute.

The following table exhibits the times of transpiration of equal volumes of several gases by this capillary reduced in length to a little under 20 feet. The table contains two series of experiments. The first is the transpiration time of a constant volume of the gases drawn from a globular vessel standing over water, into a sustained vacuum. This vessel was terminated above and below by glass tubes, forming hollow axes to the globe. The measure transpired was the capacity of the vessel between a mark on the lower and a mark on the upper tube, and amounted to 56.5 cubic inches. The second series, which consists of carbonic acid gas, with air for comparison, is the transpiration of these gases into a nine-pint jar or receiver upon the plate of an air-pump, beginning the experiment with an exhaustion of 28.5 inches by the attached barometer, and terminating at 23.5 inches. It was necessary to measure the volume of carbonic acid in this manner after transpira-



tion and not before it, to avoid the error which the solution of a portion of this gas in water might introduce. The gases all passed through a drying tube containing asbestos moistened with oil of vitriol, before reaching the capillary.

TABLE I.—Transpiration by Capillary H 237·875 inches in length, and  $\frac{1}{45}$  inch in diameter.

Gas transpired.	Experiment I.	Experiment II.	Mean.	Air=1.	Oxygen=1.	Observations.
Oxygen .....	1146 <sup>u</sup>	1147 <sup>u</sup>	1146·5	...	1·0000	Bar. 29·696. Temp. 67° Fahr.
Air .....	1032	1032	1032·	1·0000	0·9001	
Hydrogen .....	509	510	509·5	...	0·4443	
Protocarb. hyd. (CH <sub>2</sub> )	631	630	630·5	...	0·5499	
Carbonic oxide .....	994	995	994·5	...	0·8674	
Air .....	798	799	798·5	...	...	Bar. 29·602. Temp. 69° Fahr.
Carbonic acid .....	668	668	668·	0·8366	0·7529	

I produce these results principally to show how small the variation is in carefully made experiments, not amounting to more than 1 second in times which exceed 1000 seconds for two of the gases, as well as to afford standard numbers to compare with those obtained for reduced lengths of the same tube.

TABLE II.—Transpiration times of equal volumes by Capillary H of different lengths.

Length of capillary.	Oxygen.	Air.	Carbonic oxide.	Carbonic acid.	Protocarburetted hydrogen.	Hydrogen.
237·875 inches = 1·0000	1	0·9001	0·8674	0·7529	0·5499	0·4443
0·8539	1	0·8983	...	...	...	0·4422
0·6521	1	0·9009	0·8681	0·7585	0·5506	0·4434
0·4513	1	0·9013	0·8743	0·7900	0·5636	0·4424
0·3195	1	0·9131	0·8793	0·8501	0·5826	0·4041
0·2149	1	0·9149	0·8799	0·8849	0·6049	0·3842
0·1234	1	0·9131	0·8790	0·8802	0·5860	0·3924
18·125 inches = 0·0762	1	0·9138	0·8879	1·0395	0·5948	0·3879

The absolute times of transpiration varied with air from 1032 seconds for the greatest to 116 seconds for the shortest length of the capillary.

It will be remarked that the transpiration times of air and hydrogen are preserved with the greatest uniformity, while the length of the capillary is reduced from 1 to 0·4513, air varying only from 0·9001 to 0·9013, and hydrogen from 0·4443 to 0·4424. The variation of the rate



of carbonic oxide is more sensible although still small, namely, from 0.8674 to 0.8743. Protocarburetted hydrogen, however, rises for the same change in the tube from 0.5499 to 0.5636, and carbonic acid still more considerably, namely, from 0.7529 to 0.7900. The resistance of the tube is insufficient for shorter lengths, the influence of effusion becoming manifest, and most conspicuously so in carbonic acid. The times of effusion of equal volumes, to which the gases are now converging, although with unequal degrees of rapidity, are, for oxygen 1, air 0.9507, carbonic oxide 0.9356, carbonic acid 1.1760, protocarburetted hydrogen 0.7071, and hydrogen 0.2502.

An important conclusion to be drawn from these results is, that the transpiration of all gases does not become normal for the same length of tube or amount of resistance, but that a greater length of the tube and consequent resistance is more necessary for some than for others. Carbonic acid in particular, of which the effusion rate differs so widely from its transpiration rate, appears to require a considerably greater resistance than the other gases transpired to bring it to a uniform rate. Indeed the results respecting that gas suggest the inquiry whether the resistance is sufficient with the present capillary in its greatest length, and whether the true transpiration time for this gas may not be less than 0.75, the number provisionally adopted. Let us therefore observe the effect of greatly increased resistances upon the transpiration of this and other gases.

A thermometer tube of the finest flat bore was selected, K, of which  $52\frac{1}{2}$  inches contained only 13.5 grains of mercury. The bore was not quite uniform, 0.6 grain of mercury occupying 2 inches of the cavity at each end of the tube, and 2.3 inches near the middle. Under the pressure of 1 atmosphere, 1 cubic inch of air passed into a vacuum by this capillary in 151.3 seconds, or the discharge of air was not more than 0.4 cubic inch per minute. The resistance was therefore ten times greater than in the capillary H when of its greatest length of 22 feet.

Air and other gases were transpired through K into a two-pint jar placed upon the plate of an air-pump, or into a space amounting to 71.08 cubic inches, till the attached barometer of the air-pump fell from 28.5 to 25.5 inches.

(1.) The time required by air in three experiments was 1075, 1073, and 1074 seconds; and for oxygen in two experiments 1192 and 1192 seconds; the temperature being  $56^{\circ}$  Fahr., and the height of the barometer 30.162 inches. This gives 0.9010 as the transpiration time of air, referred as usual to the time of oxygen as 1, the result accidentally coinciding with the theoretical number for air.

(2.) The time required by hydrogen in two experiments was 552 and 550 seconds, the time of air being 1081, 1079, 1082, and 1080



seconds; thermometer  $57^{\circ}$  degrees, and barometer 29.918 inches. Dividing the mean number for hydrogen 551 by the mean number for air 1080.5, we obtain 0.5099 as the time of hydrogen, that of air being 1. To reduce the time of hydrogen to that of oxygen as 1, we have to multiply 0.5099 by 0.9010, which gives 0.4593 as the transpiration time of hydrogen. This is a considerable departure from the theoretical number 0.4375; but it was found to be due to a small addition of air to the gas, which it obtained from the water over which it stood in the pneumatic trough, and necessarily much longer than usual, from the slow manner in which it was removed by transpiration through the present capillary. In a series of experiments made with hydrogen containing 1, 2, 4, 25, 50, and 75 parts of oxygen in 100 of the mixture, this capillary was found to give the transpiration times 0.4901, 0.5055, 0.5335, 0.7750, 0.9061, and 0.9718. Half a per cent. of air would therefore more than account for the increased time observed with the first hydrogen. In experiments, also, made with other equally fine capillaries, when the hydrogen was preserved in a state of great purity by transmitting it by a bent tube from the generating retort to the upper part of the pneumatic receiver, and in large volumes, so that the gas never passed through water, and was retained only a very short time in contact with the surface of that liquid, the transpiration time then fell, as will afterwards appear, quite as low as the theoretical number.

(3.) The transpiration of carbonic oxide took place in 1051 and 1051 seconds, against 1090 and 1089 seconds for air; thermometer  $58^{\circ}$  Fahr., barometer 29.866. This gives for carbonic oxide the transpiration times 0.9646, air = 1; and 0.8690, oxygen = 1. The transpiration time of the same gas by the former capillary H was 0.8674; while the number corresponding with the theoretical density of the gas is 0.8750.

The capillary K was now shortened to 39.375 inches, and the following experiments were made with it.

(1.) Carbonic acid was transpired in 661 and 659 seconds, thermometer  $58^{\circ}$ , and barometer 30.024. The time of oxygen was 900 and 903 seconds. The means give 0.7321 as the transpiration time of carbonic acid, a number considerably less than 0.75, and confirming my suspicion that the latter number was too high, and that the resistance of H was not sufficiently great to eliminate the whole influence of effusion in this gas. It may be remarked, in passing, that the new number for carbonic acid approaches 0.7272, which is equal to  $\frac{1}{\frac{4}{3}}$ , or is the reciprocal of the density of carbonic acid gas. Such a relation suggests the idea that carbonic acid possesses the time of oxygen (of which gas, carbonic acid contains its own volume), diminished by the carbon present, which gives an additional momentum corresponding to its



weight to the compound gas, and acts thus entirely in increasing its velocity.

In another series of experiments the numbers were 659 and 659 for carbonic acid, against 900 and 902 for oxygen; thermometer  $58^{\circ}$ , and barometer 30.052. This gives 0.7303 as the transpiration time of carbonic acid.

(2.) Without entering into a detail of the experiments, I may add, that the capillary K of its present length gave 0.9034 as the transpiration time of air, and 0.4500 as the transpiration time of hydrogen; the time of the latter gas being undoubtedly elevated by a minute impurity, as in the former case.

The length of capillary K was now reduced to 26.25 inches, and in order to increase the transpiration time, which fell to about 567 seconds for air, the range of the attached barometer observed was increased from 3 to 5 inches, the observations being made at 28.5 and 23.5 inches of the barometer attached to the air-pump.

(1.) The times for air were 946 and 945 seconds; the time for oxygen 1053 seconds, giving 0.8979 as the transpiration time of air; thermometer  $57^{\circ}$ , and barometer 30.096.

(2.) The times for carbonic acid were 773 and 773 seconds, the times for air observed immediately before being 942 and 943 seconds; thermometer  $57^{\circ}$ , and barometer 29.982. This gives 0.8202 as the transpiration time for carbonic acid referred to air, and 0.7361 referred to oxygen.

The length of the capillary K being now reduced to 13.125 inches, air was found to enter so as to depress the attached barometer from 28.5 to 25.5 inches in 284 seconds, and from 28.5 to 23.5 inches in 472 seconds; thermometer  $56^{\circ}$ , and barometer 29.758 inches. To obtain longer times, the two-pint jar, used as the aspirator-jar, was replaced by the six-pint jar, which last gives an available vacuous space estimated at 201.78 cubic inches. The fall of the attached barometer continued to be observed from 28.5 to 23.5 inches.

(1.) The times of air were 1348 and 1353 seconds; the times of oxygen 1498 and 1499 seconds; thermometer  $58^{\circ}$ , and barometer 29.628. The means give 0.9013 as the transpiration time of air.

Observing only through the smaller range of the attached barometer, namely, from 28.5 to 25.5 inches, the following results were obtained:—

- (1.) The time of air was 809, 809 seconds.
- (2.) The time of carbonic oxide was 780 and 779 seconds.
- (3.) The time of hydrogen was 399, 400, and 398 seconds.
- (4.) The time of carbonic acid was 658 and 657 seconds.



The experiments were made successively in the order in which they are stated, with the thermometer at  $59^{\circ}$ , and the barometer from 29.450 to 29.422. The results may be given as follows:—

TABLE III.—Transpiration Times.

	Air=1.	Oxygen=1.
Carbonic oxide .....	0.9635	0.8671
Hydrogen .....	0.4932	0.4438
Carbonic acid .....	0.8127	0.7314

The transpiration times of the second column are obtained by multiplying the times of the first column by 0.9, a number which represents the time of air with sufficient accuracy, the time of oxygen being 1. It will be observed that the number for carbonic oxide remains wonderfully constant for all lengths of K; that the number for hydrogen, 0.4438, now approaches more nearly to 0.4375, probably as nearly as a slight impurity of the gas, resulting from its short contact with water, would admit; and that the number for carbonic acid, 0.7314, is still low, and does not differ much from 0.7272.

In a second series of experiments, which need not be detailed, numbers corresponding closely with the preceding were obtained; namely, 0.9003 for air, 0.8656 for carbonic oxide, and 0.7336 for carbonic acid.

The capillary K was reduced to 8.75 inches, or to one-sixth of its original length, the six-pint jar being retained as the aspirator-jar, and the fall of the attached barometer observed from 28.5 to 23.5 inches.

(1.) The times of air were 933 and 933 seconds; of oxygen 1036, 1036, and 1037 seconds; of carbonic oxide 897, 897 seconds; thermometer from  $59^{\circ}$  to  $60^{\circ}$ , and barometer from 29.1 to 29.134 inches. These experiments give the following transpiration times:—

Oxygen,	.	.	.	1
Air,	.	.	.	0.9003
Carbonic oxide,	.	.	.	0.8656

(2.) The times of air were 920 and 920 seconds; of hydrogen 450 and 451 seconds; of carbonic acid 763, 762 seconds; thermometer  $58^{\circ}$ , barometer 29.346. The resulting transpiration times for hydrogen and carbonic acid are 0.4886 and 0.8288, the time of air being 1; or, multiplying by 0.9 so as to have oxygen 1—

Hydrogen,	.	.	.	0.4398
Carbonic acid,	.	.	.	0.7459

(3.) Experiments on the same gases were repeated at a temperature



lower by  $10^{\circ}$  Fahr. The times of air were 902 and 902 seconds; of hydrogen 442 and 444 seconds, and of carbonic acid 742 and 742 seconds; thermometer  $48^{\circ}$  Fahr., barometer 29.334. These numbers give the transpiration times 1, 0.4911, and 0.8226 for air, hydrogen, and carbonic acid respectively; or, with oxygen as 1—

Hydrogen, . . . .	0.4419
Carbonic acid, . . . .	0.7403

Another series of experiments gave for carbonic acid the transpiration time 0.7432 at  $43^{\circ}$ , and with barometer 29.620. It will be observed that the time for carbonic acid now begins to rise, as if the capillary were too short, and the resistance insufficient to neutralize entirely the effect of effusion in that gas. The times however of air, hydrogen, and carbonic oxide continue normal.

Experiments were made with the same capillary reduced to 6.4375 inches, or to one-eighth of its original length, which are still pretty normal. The times for air were 670 and 670 seconds; for oxygen 746 and 745 seconds; for hydrogen 322 and 322 seconds; for carbonic acid 563 and 562 seconds, with thermometer from  $61^{\circ}$  to  $62^{\circ}$ , and barometer from 29.832 to 29.826. These give the transpiration ratios,—

Oxygen, . . . .	1
Air, . . . .	0.8987
Hydrogen, . . . .	0.4319
Carbonic acid, . . . .	0.7545

For shorter lengths of the capillary K, the deviation from the transpiration rates becomes very notable. I shall supply the results of such experiments, as they illustrate the progress of the deviation from the transpiration rates in a short and narrow capillary, while the results of Table II., page 165, show the progress of this deviation in a long and comparatively wide capillary.

TABLE IV.—Transpiration times of equal volumes, by Capillary K of reduced lengths.

Length of capillary.	Oxygen.	Air.	Hydrogen.	Carbonic acid.
4.3125 inches	1	0.8985	0.4250	0.7770
3.25	1	0.9035	0.4176	0.8059
2.1875	1	0.9121	0.3969	0.8446
1.125	1	0.9199	0.3876	0.9379

The absolute times for air, with the tubes of these four different lengths, were 473, 370, 270, and 178 seconds; the temperature varying from  $61^{\circ}$  to  $63^{\circ}$ , and the barometer from 29.562 to 29.782 inches. These



times, it will be observed, do not become shorter, exactly as the length of the tube is diminished, but less rapidly in a very sensible degree. This is owing to the interference of effusion.

When K was 4.3125 inches in length it allowed 1 cubic inch of air to pass into a vacuum, under the pressure of 1 atmosphere, in 14 seconds; or it discharged 4.3 cubic inches of air per minute. The discharge by the capillary H of its greatest length, 237.875 inches, was 3.84 cubic inches per minute. These two tubes therefore offer a nearly equal resistance to the passage of air under pressure. On comparing the first lines of Tables II. and IV., however, it will be perceived that the transpiration rates of hydrogen and carbonic acid are sensibly more normal for the long than for the short tube, although the difference is not great. Still it appears that contracting the diameter of a tube does not produce an equally available resistance as increasing its length. In other respects the progress of the deviation from the normal transpiration rates of the same gas, and of different gases compared together, in proportion as the resistance diminishes, appears to follow the same law in the short as in the long tube.

While discussing the properties of capillaries of different dimensions, I may allude to results obtained by another capillary M, of the same extreme length, 52.5 inches, and of nearly the same resistance as K, but of which the bore was cylindrical and not flat like that of K. The bore of M was not highly uniform, 0.75 grain of mercury occupying a length of the cavity which varied from 3.3 inches at one end to 2.3 inches at the other end of the tube. It was employed with the two-pint aspirator-jar, and the fall of the attached barometer was observed through the usual range from 28.5 to 23.5 inches.

(1.) This capillary gave the transpiration time of air 0.8997, a highly normal result.

(2.) The times for air in two experiments being 1133 and 1132 seconds, the times of carbonic acid were 913 and 911 seconds; thermometer 68°, and barometer 29.672.

Transpiration time of carbonic acid, . . . 0.7247

In a second series of experiments made upon the same gases, the times of air being 1104 and 1103 seconds, the times of carbonic acid were 892 and 892 seconds; and of hydrogen 534 and 534 seconds; thermometer 58°5, barometer 30.068. These observations give the transpiration time 0.7275 for carbonic acid and 0.4355 for hydrogen.

(3.) The times of air being 1109 and 1109 seconds, the times of carbonic oxide were 1070 and 1070 seconds; thermometer 67°5, barometer 29.808.

Transpiration time of carbonic oxide, . . . 0.8683



(4.) The times of air being 1098 and 1099 seconds, the times of nitrogen were 1064 and 1062 seconds; thermometer  $64^{\circ}$  to  $65^{\circ}$ , barometer 29.904.

Transpiration time of nitrogen, . . . . . 0.8708

(5.) The times of air being 1084 and 1084 seconds, the times of hydrogen were 529 and 529 seconds; thermometer  $69^{\circ}$ , barometer 30.242 inches.

Transpiration time of hydrogen, . . . . . 0.4392

In the present experiments with hydrogen, the precautions formerly referred to for excluding as much as possible the access of a sensible trace of air from the water of the pneumatic trough were put in practice. The times obtained for this and all the other gases, with the present capillary, will be observed to be in the highest degree normal.

(6.) The times of air being 1095 and 1096 seconds, those of olefiant gas were 641, 641, and 641 seconds; thermometer  $69^{\circ}$ , barometer 30.102.

Transpiration time of olefiant gas, . . . . . 0.5265

The time formerly obtained for the same gas by the capillary H of small resistance was 0.5186. This new capillary M was afterwards very fully employed in determining the times of various other gases and vapours, and in examining the influence of pressure and temperature. It is therefore desirable to have the preceding results which this capillary gives with the more familiar gases.

(7.) The times of air being 1120 and 1120 seconds, those of proto-carburetted hydrogen (the gas of the acetates) were 684, 686, and 685 seconds; thermometer  $61^{\circ}5$ , barometer 29.844.

Transpiration time of protocarburetted hydrogen, . . . 0.5504

The time 0.5515 was formerly obtained for this gas by capillary E, which was a long tube of small resistance, very like capillary H.

(8.) The times of air being 1110 and 1111 seconds, those of binoxide of nitrogen ( $\text{NO}_2$ ) were 1070, 1070, and 1070 seconds; thermometer  $60^{\circ}5$ , barometer 29.948 to 29.782 inches.

Transpiration time of binoxide of nitrogen, . . . . . 0.8672

This result is in accordance with the conclusion drawn from my former experiments upon the same gas, made with capillary E, namely, that the time of nitric oxide gas coincides with that of nitrogen and carbonic oxide.

(9.) Observations were made with the same capillary M a little reduced in length, namely, to 50.5 inches, and with a smaller aspirator-jar; the range observed of the attached barometer being still from 28.5 to 23.5 inches.

It now gave for the transpiration time of air 0.8984.



The times for air being 460 and 459 seconds, those of carbonic acid were 381 and 381 seconds, and those of protoxide of nitrogen (NO) 380 and 380 seconds; thermometer  $56^{\circ}$ , barometer 29.674.

Transpiration time of carbonic acid,	.	.	0.7448
Transpiration time of nitrous oxide,	.	.	0.7429

results which illustrate the identity in transpiration rate of these two gases, which have also the same specific gravity, and appear to correspond remarkably in several other physical properties.

The difference of resistance to the passage of a gas offered by the various capillary tubes already used is certainly considerable; the resistance for equal lengths of tube being in round numbers fifty times greater in the new capillaries K and M, than in the old capillaries E and H. But large as is this range, in which a remarkable uniformity of transpiration rate of the gases has been observed, it may still be much extended. The capillaries of extreme resistance to which I shall now refer, have great advantages over the others already described, and form the instruments which I would recommend for the further study of the laws of transpiration.

A thermometer tube of the finest cylindrical bore being selected, a portion of about 8 inches is taken, and being progressively heated and softened at the lamp, is crushed up into a length of 1 inch or less, which can be done without obliterating the cavity. The cylindrical mass is then, while still soft, drawn out into a tube of ten or twelve times its original length. A thin and extremely fine capillary tube is thus obtained, which is much more regular in bore than might be expected from the description of its preparation. It is convenient to divide the rod, which is less in diameter than a fine straw, into lengths of  $4\frac{1}{2}$  inches, and to seal immediately the open extremities of each piece. A transpiration capillary was formed of a bundle of thirty of these little rods, which were placed together within a short glass tube, as a case, of about  $3\frac{1}{2}$  inches in length and half an inch in diameter; so that the ends of the rods projected at both ends of the tube. The rods were fixed within the tube by stucco, which was dried and afterwards, while warm, soaked in melted bees'-wax. These arrangements being entirely completed, and the bundle proved to be impervious to air, the ends of the rods were now broken off, and the tubes thus opened. The transpiration instrument P consisted of a bundle of thirty such capillary tubes, each about 4 inches in length. Each end of the solid cylinder was connected with a block-tin tube of the same diameter by means of a thick vulcanized caoutchouc adapter. One of these tin tubes was connected with the aspirator-jar, or left open to the air, and the other connected with the receiver containing the gas to be transpired.



The mode of conducting the experiment was further changed. Instead of drawing the gas through the capillaries into an exhausted receiver or vacuum, the gas was compressed in a stout metallic receiver or condenser, provided with a mercurial pressure gauge, by which the elasticity of the gas within could be observed.<sup>1</sup> This gauge tube was a barometer about 70 inches in length, with a vacuum above the mercury. The gas was allowed to escape from the condenser through the capillaries into the open atmosphere, or into a space containing air, of which the tension was preserved uniform, and which formed an artificial constant atmosphere, the time being noted which the mercury in the gauge tube of the condenser took to fall through a fixed range of 2, 4, or 10 inches, according to the degree of compression. The available capacity of the condenser was about 72 cubic inches.

The resistance of the fine capillary tube of the present bundle was not less than 400 times greater than the resistance of the finest tubes hitherto used, namely K and M, the comparison being made between equal lengths of the different tubes.

*Experiments with compound Capillary P.*

(1.) Dry oxygen was thrown by a syringe into the condenser till the pressure indicated by the pressure gauge exceeded, by more than 20 inches, the pressure of the external atmosphere. The gas was then allowed to escape from the condenser through the capillaries into the atmosphere, and the times noted which the mercury of the pressure gauge took to fall from 20 to 15, 10, 8, 6, 4, and 2 inches.

TABLE V.—Transpiration of Oxygen.

Pressure by gauge barometer.	Experiment I.	Experiment II.	Experiment III.
Inches.	"	"	"
20	0	0	0
15	241	240	241
10	352	353	352
8	202	202	200
6	266	266	265
4	379	382	378
2	653	650	647
From 20 to 2 inches .....	2093	2093	2083

(2.) A similar series of experiments was made on the transpiration of compressed air, of which the results are as follows :—

<sup>1</sup> *Phil. Trans.* 1846, Plate XXXIII. fig. 3 (see *ante*, p. 105).



TABLE VI.—Transpiration of Air.

Pressure by gauge barometer.	Experiment I.	Experiment II.
Inches.	"	"
20	0	0
15	217	217
10	316	316
8	181	181
6	239	238
4	400	400
2	524	524
From 20 to 2 inches .....	1877	1876

Both these last series and the series which follows on carbonic acid were made with the thermometer at  $66^{\circ}$ , and barometer from 30.144 to 30.112 inches. Means were taken to preserve the temperature constant during this and similar experiments, by immersing the condenser, and also the capillary, in vessels of water of which the temperature was watched by an assistant, and preserved uniform.

The average times of falling from a pressure of 20 to 10 inches are for oxygen and air, 593 and 533 seconds respectively; numbers which are in the proportion of 1 to 0.8988. The average times from 10 to 6 inches are 467 and 419.5 seconds; that is, as 1 to 0.8983: from 6 to 2 inches, 1030 inches and 924 seconds; that is, as 1 to 0.8971. The average whole time of escape, or during the fall from 20 to 2 inches, is 2088 seconds for oxygen and 1876.5 seconds for air, numbers which are in the proportion of 1 to 0.8987.

The transpiration time of air is therefore highly uniform under different pressures, and approaches closely to its theoretical density or time 0.9010.

(3.) The parallel experiments on compressed carbonic acid gas escaping into air are contained in the following Table:—

TABLE VII.—Transpiration of Carbonic Acid.

Pressure by gauge barometer.	Experiment I.	Experiment II.
Inches.	"	"
20	0	0
15	178	178
10	260	260
8	148	148
6	195	195
4	278	279
2	475	474
From 20 to 2 inches.....	1534	1534



Comparing these times with the times of oxygen, we obtain the following results:—

Transpiration times of Carbonic Acid.

From 20 to 10 inches pressure, . . .	0·7384
From 10 to 6 inches pressure, . . .	0·7345
From 6 to 2 inches pressure, . . .	0·7311
<hr/>	
From 20 to 2 inches (average), . . .	0·7346

The times for carbonic acid have not the nearly perfect uniformity of those of air, for different pressures, but still their relation was close, particularly in the lower part of the scale where times are long and can be best observed. The time from 4 to 2 inches is 474·5 seconds with carbonic acid and 650 seconds with oxygen, which give as the transpiration time of carbonic acid 0·7300.

It will be observed how nearly the times for this gas approach 0·7272, the reciprocal of its density.

In a second series of experiments made upon carbonic acid, at the same time as those which follow upon hydrogen, the transpiration times which were obtained for the three portions of the scale already described were 0·7344, 0·7388, and 0·7294, which approach the speculative number for carbonic acid quite as closely as the experiments previously detailed.

(4.) The hydrogen was prepared (as was always the case) from zinc which contained no arsenic, and was passed through a wash bottle containing oxide of lead dissolved in caustic soda, and dried by passing over asbestos moistened with oil of vitriol. The thermometer was 67° and the barometer 29·506 inches.

TABLE VIII.—Transpiration of Air and Hydrogen.

Pressure by gauge barometer.	Air.		Hydrogen.	
	Experiment I.	Experiment II.	Experiment I.	Experiment II.
Inches.	"	"	"	"
20	0	0	0	0
15	221	221	107	107
10	328	328	158	159
8	188	185	92	91
6	251	251	121	121
4	422	423	176	178
2	579	580	310	308
From 20 to 2 inches...	1989	1988	964	964



The results calculated from the means of these experiments are as follows, the transpiration time of air being taken as 0·9 :—

Transpiration times of Hydrogen.

	Air=1.	Oxygen=1.
From 20 to 10 inches...	0·4845	0·4352
From 10 to 6 inches...	0·4866	0·4371
From 6 to 2 inches...	0·4859	0·4364
From 20 to 2 inches...	0·4867	0·4371

The experimental times for hydrogen vary only in the smallest degree at different pressures, and almost coincide with the theoretical time for this gas, 0·4375, which is one-half of the time of nitrogen and 7-16ths of that of oxygen. This result is so important that I shall make no apology for presenting another series of experiments in which hydrogen was compared directly with oxygen.

The temperature during the following experiments was 67°, and the barometer 29·420 to 29·458 inches.

TABLE IX.—Transpiration of Hydrogen and Oxygen.

Pressure by gauge barometer.	Hydrogen.		Oxygen.	
	Experiment I.	Experiment II.	Experiment I.	Experiment II.
Inches.	"	"	"	"
20	0	0	0	0
15	107	107	242	246
10	158	158	263	260
8	91	90	208	208
6	120	120	274	274
4	174	175	396	398
2	298	299	687	687
From 20 to 2 inches.....	948	949	2170	2173

By dividing the means of the hydrogen numbers by the means of the oxygen numbers, as usual, we obtain the following results :—

Transpiration times of Hydrogen.

From 20 to 10 inches,	.	.	0·4380
From 10 to 6 inches,	.	.	0·4367
From 6 to 2 inches,	.	.	0·4363
			<hr/>
From 20 to 2 inches,	.	.	0·4370



These results are therefore in entire concordance with the preceding series, and with 0.4375 as the transpiration time of hydrogen gas.

(5.) A series of experiments were made on the transpiration of carbonic oxide in conjunction with those last related.

TABLE X.—Transpiration of Carbonic Oxide.

Pressure by gauge barometer above 1 atmosphere.	Experiment I.	Experiment II.
Inches.	"	"
20	0	0
15	213	213
10	315	315
8	181	181
6	241	241
4	346	346
From 20 to 4 inches.....	1296	1296

The experiments on this gas are only given from 20 to 4 inches, some error of observation having occurred in taking the times at 2 inches. Comparing them with the last experiments on oxygen, we obtain the following results :—

Transpiration time of Carbonic Oxide.

From 20 to 10 inches,	.	.	0.8727
From 10 to 6 inches,	.	.	0.8755
From 6 to 4 inches,	.	.	0.8715
			<hr/>
From 20 to 4 inches,	.	.	0.8737

The transpiration time of carbonic oxide thus appears to be uniform at different pressures, and to correspond very closely with its theoretical density, 0.8750. The transpiration times of this gas and of nitrogen no doubt correspond with each other as closely as their densities, and are both double the time of hydrogen.

It thus appears that the results obtained by means of the sheaf of capillaries of extreme resistance are the most uniform of all, and that they afford a confirmation of the conclusions drawn from the results of former capillaries of greatly less resistance, which it is difficult to withstand. These conclusions are, that the times of passage through capillary tubes, of equal volumes of different gases under the same pressure, approximate to, and have their limit in, the following numbers :—



## Transpiration times.

Oxygen,	.	.	.	.	1.
Air,	.	.	.	.	0.9010
Nitrogen and carbonic oxide,	.	.	.	.	0.8750
Hydrogen,	.	.	.	.	0.4375
Carbonic acid,	.	.	.	.	0.7272

The times of oxygen, nitrogen, carbonic oxide, and air, are directly as their densities, or equal *weights* of these gases pass in equal times. Hydrogen passes in half the time of nitrogen, or twice as rapidly for equal volumes. The result for carbonic acid appears at first anomalous. It is, that the transpiration time of this gas is inversely proportional to its density, when compared with oxygen. It is to be remembered, however, that carbonic acid is a compound gas, containing an equal volume of oxygen. The second constituent carbon which increases the weight of the gas, appears to give additional velocity to the oxygen in the same manner and to the same extent as increased density from pressure, or from cold (as I believe I shall be able to show), increases the transpiration velocity of pure oxygen itself. A result of this kind shows at once the important chemical bearing of gaseous transpirability, and that it emulates a place in science with the doctrines of gaseous densities and combining volumes.

The circumstance that the transpiration time of hydrogen is one-half of that of nitrogen, indicates that the relations of transpirability are even more simple in their expression than the relations of density among gases. In support of the same assertion may be adduced the additional fact, that binoxide of nitrogen, although differing in density, appears to have the same transpiration time as nitrogen. Protoxide of nitrogen and carbonic acid have one transpiration time, so have nitrogen and carbonic oxide, as each pair has a common density.

## II. TRANSPIRATION OF VARIOUS GASES AND VAPOURS.

1. *Protocarburetted Hydrogen*,  $\text{CH}_2$ .

It is necessary to mention how this gas was prepared, as it is one, like olefiant gas, of which we are never quite certain of the absolute purity. Six hundred grains of dried acetate of soda, the same weight of fused hydrate of potash, and nine hundred grains of unslaked quicklime, all in fine powder, were well mixed in a coated Florence flask used as a retort, and the gas brought off by heat. The last portions of gas were rejected. The hydrate of baryta never, in my hands, gave so pure a gas, when substituted for the hydrate of potash. Free hydrogen, the



usual impurity in this gas, I have formerly shown to have scarcely any effect upon the rate of carburetted hydrogen, when present only to the extent of a few per cent.

The old experiments with the long 20-feet capillaries E and H, of small resistance, agreed remarkably in the transpiration time 0.5515 for this gas. With capillary M, 52.5 inches in length, and transpiring into a vacuum, I obtained 684, 686, 685 seconds as the time for this gas, against 1120 and 1120 seconds for air; thermometer 62°, and barometer 29.844 inches. This gives 0.5504 for carburetted hydrogen for a capillary of great resistance. This gas, in a state of compression, was transpired by the same capillary into air as in the experiments to follow on olefiant gas. The results, without details, were as follows: thermometer 64°, barometer 30.050 to 30.074.

Transpiration of Protocarburetted Hydrogen (into air) by Capillary M,  
52.5 inches in length.

	Air = 1.	Oxygen = 1.
From 20 to 10 inches ...	0.6304	0.5495
From 10 to 6 inches ...	0.6254	0.5490
From 6 to 4 inches ...	0.6269	0.5515
From 4 to 2 inches ...	0.6335	0.5525
From 2 to 1 inch.....	0.6349	0.5607
From 10 to 1 inch .....	0.6321	0.5541

The transpiration of this gas appears highly uniform at different pressures. Excluding the two observations at the extremes of the scale, the mean result is—

Transpiration time of protocarburetted hydrogen, 0.5510

A repetition of the last experiments gave a slightly different series of numbers, namely, 0.5583, 0.5497, 0.5541, 0.5523, 0.5549; showing that the slight departure from uniformity among the results at different pressures before observed is of an accidental nature, and does not follow any fixed law. The mean of the three preferable new observations gives 0.5510, or precisely the same result as the former series.

This number for protocarburetted hydrogen closely approaches 0.5536, which is seven-elevenths, or  $\frac{7}{11}$  of 0.870, the time of nitrogen. The numerical relation may be accidental, but the circumstances that 14, which expresses the density and time of nitrogen, is double the time of hydrogen 7, and that 22 expresses the density of carbonic acid, to which carburetted hydrogen presents a certain chemical analogy in composition, appear to afford some physical basis for it.



The time of protocarburetted hydrogen may also be stated to be one-fourth more than 0.44, the usually observed time of hydrogen itself.

## 2. Olefiant Gas.

The circumstance that olefiant gas has the same theoretical density as nitrogen and carbonic oxide, and yet differs greatly from these gases in transpirability, gives a peculiar interest to the transpiration time of that gas. The olefiant gas used was always prepared in the following manner:—Fifty-four volumes (water ounce measures) of oil of vitriol were mixed with twenty-eight volumes of water and cooled, which gave an acid of specific gravity 1.600. To this twenty-four volumes of alcohol, generally of specific gravity 0.84, were added, and the mixture allowed to stand over night. The gas was evolved by a heat of about 320° Fahr., and transmitted, for the purpose of purifying it, through five wash-bottles, the first containing potash, the second water, the third oil of vitriol, the fourth potash, and the fifth oil of vitriol. The process yielded a good deal of ether, with a large product of gas.

My old experiments, with capillary H of great length but small resistance, gave 0.5186 as the transpiration time of this gas. I subsequently obtained the number 0.5241 with capillary K of 8.75 inches in length, and also of small resistance. With capillary M of 52.5 inches in length, and of considerable resistance, I also obtained the number 0.5265; the gas in all these cases passing into the nearly vacuous jar under the pressure of the atmosphere. But the most complete series of experiments was made upon this gas in a compressed state, in the globular digester of 72 cubic inches in capacity, the gas escaping into air. The capillary M was employed of 50.5 inches in length.

TABLE XI.—Transpiration of Olefiant Gas and Air (into air).

Height of gauge barometer above 1 atmosphere.	Air.		Olefiant gas.	
	Experiment I.	Experiment II.	Experiment I.	Experiment II.
Inches.	"	"	"	"
20	0	0	0	0
15	198	196	116	116
10	285	285	165	165
8	161	161	93	93
6	213	213	120	121
4	307	307	174	174
2	530	530	301	301
1	529	530	299	300

The fall from 20 to 10 inches requires 482 seconds in air and 281



in olefiant gas, numbers which are as 1 to 0·5830. The ratios or transpiration times appear in the following Table :—

Transpiration times of Olefiant Gas.

	Air=1.	Oxygen=1.
From 20 to 10 inches ...	0·5830	0·5212
From 10 to 6 inches ...	0·5709	0·5103
From 6 to 4 inches ...	0·5667	0·5066
From 4 to 2 inches ...	0·5679	0·5085
From 2 to 1 inch.....	0·5656	0·5081

In reducing these results from the scale of air to that of oxygen, the following coefficients were used as the transpiration times of air. They were obtained by experiment. From 20 to 10 inches air = 0·8941; from 10 to 6 inches 0·8939; from 6 to 4 inches 0·8941; from 4 to 2 inches 0·8967; from 2 to 1 inch 0·8967; the air coefficients being all sensibly lower than 0·9.

The transpiration time of this gas appears to vary at different parts of the scale of pressure fully more than carbonic acid does. This may arise, as with carbonic acid, from the extreme difference which exists between the effusion and transpiration rate of the gas.

Hence an unusually great resistance, which is only met in the lower part of the scale, is required to eliminate completely the influence of effusion upon the transpiration rate. The smallest transpiration time observed above for olefiant gas is 0·5066, which certainly does not differ much from 0·5, or half the time of oxygen. But it would be premature to adopt that relation definitively, as a number nearer to 0·51 would be the more legitimate expression of the whole results.

In a second series of experiments conducted precisely in the same manner, with the thermometer at 67° and the barometer 30·020 to 30·034, the results were as follows :—

Transpiration time of Olefiant Gas (into air).

	Air=1.	Oxygen=1.
From 20 to 10 inches ...	0·5855	0·5234
From 8 to 6 inches ...	0·5745	0·5136
From 6 to 4 inches ...	0·5663	0·5062
From 4 to 2 inches ...	0·5642	0·5043
From 2 to 1 inch.....	0·5647	0·5048
From 20 to 1 inch.....	0·5669	0·5068



The same remarks apply to the last as to the immediately preceding series of experiments; the two series agreeing together most closely. The mean of the three times observed in the range of pressure from 6 inches to 1 inch is 0.5051; and the least transpiration time observed for olefiant gas (from 4 to 2 inches pressure) is 0.5043.

To contrast the two different methods of transpiration, that of condensed gas escaping into air, and of gas under the usual pressure of the atmosphere only, or under a less pressure, passing into a vacuum, a third series of experiments was made upon olefiant gas. The same globular condenser being full of olefiant gas, of the tension of the atmosphere at the time, which was 30.034 inches, the gas was allowed to escape through the capillary M into the receiver of an air-pump kept vacuous by constant exhaustion. It was thus transpired into a vacuum, but with constantly diminishing force, for the force with which the gas was sent out would diminish of course in proportion as the globular receiver was emptied. The barometric gauge tube of this receiver, being closed at top and vacuous, gave the necessary means of observing the progress of the escape of the gas as it was transpired into the vacuum. In the following table of observations, the first column of the height of the gauge barometer is its absolute height, and expresses the whole tension or elasticity of the gas. Thermometer 67°.

TABLE XII.—Transpiration of Olefiant Gas.

Height of gauge barometer.	Olefiant gas.		Air.	
	Experiment I.	Experiment II.	Experiment I.	Experiment II.
Inches.	"	"	"	"
30	0	0	0	0
25	191	191	327	327
20	276	276	480	480
18	152	152	267	267
16	187	187	316	315
14	242	242	432	430
12	318	319	558	558
10	446	446	773	771
From 20 to 10	1347	1345	2346	2341

The results are sensibly different in one part of the scale from those obtained by the other method of transpiration, as will be seen by comparing the following statement with the former results.



## Transpiration of Olefiant Gas (into a vacuum).

	Air = 1.	Oxygen = 1.
From 30 to 20 inches ...	0·5791	0·5212
From 20 to 16 inches ...	0·5476	0·4928
From 16 to 14 inches ...	0·5615	0·5054
From 14 to 12 inches ...	0·5717	0·5145
From 12 to 10 inches ...	0·5777	0·5199
From 30 to 10 inches ...	0·5743	0·5169

The time seems to increase as we descend in the scale, or with the resistance, with the exception of the first observation, which probably is made to deviate from the general progression by some accidental cause. It would probably be more correct to take the first and second times together, or the whole fall from 30 to 16 inches, which gives—

	Air = 1.	Oxygen = 1.
Transpiration time of olefiant gas .....	0·5659	0·5093

The times from 30 to 14 inches, 0·5093 and 0·5054, will thus closely approach to the average time obtained by the other method. But under 14 inches of pressure, where the transpiration becomes extremely slow as the resistance is greatly increased, the times rise to 0·5145 and 0·5199. In the present state of our knowledge respecting transpiration, it is difficult to decide upon the comparative value of these results, and to say which represents best the true transpiration time of olefiant gas. An unexplained variation of  $1\frac{1}{2}$  per cent. in the transpiration time of this gas must at present be admitted, which is a much greater latitude in the results than was observed with nitrogen, hydrogen, protocarburetted hydrogen, or even with carbonic acid.

3. *Ammonia.*

This gas is supposed to have certain chemical relations to olefiant gas, although differing very widely from the latter in its physical properties. The theoretical density of ammonia is 8·5, that of oxygen being 16; or 539·6 to oxygen 1000. It is therefore considerably lighter than olefiant gas; it is also liquefied by pressure, and highly soluble in water, which the latter is not.



This gas was always dried by passing over fragments of fused hydrate of potash. The mode of operating with gases like ammonia, which cannot be retained over water, found most convenient was to maintain a continued and copious evolution of the gas during the whole period of the transpiration experiments, conveying the gas into an empty bottle in the first instance, of which the cork was perforated by three tubes. By one of these tubes the gas entered this bottle, by another the portion of gas required for transpiration was conducted to the capillary, and the third, which was bent downwards and its extremity allowed to dip a line or two into a little cup of water, formed a waste-pipe or relief tube, by which the excess of gas evolved escaped into the atmosphere. The same method was equally applicable to hydrogen, carbonic acid, chlorine, etc., and does away with the necessity of collecting these gases over water, and so exposing them to contamination.

(1.) This gas was transpired by capillary K, 8.5 inches in length, into the six-pint aspirator-jar upon the plate of the air-pump, through the usual range of 28.5 to 23.5 inches on the gauge barometer; thermometer  $54^{\circ}$ , barometer 29.772 inches. In two experiments with air the times were 982 and 981 seconds; in three experiments with ammonia 546, 546, and 546 seconds. This gives 0.5563 for the time of ammonia referred to air, or multiplying this number by 0.9 to reduce it to the scale of oxygen = 1, we have,—

Transpiration time of ammonia, . . . . . 0.5007

The conclusion suggested by this result, that the transpiration time of ammonia is one-half that of oxygen, is not supported so strongly by capillary tubes of great resistance.

(2.) Experiments were made with capillary M, 52.5 inches in length; thermometer  $61^{\circ}$ , barometer 29.900 to 29.908 inches. The time of air being 1110, 1111, and 1111 seconds, that of ammonia was 632, 632, and 632 seconds; as 1 to 0.5688. Referred to oxygen, the result becomes—

Transpiration time of ammonia, . . . . . 0.5119

A second series of experiments with the same capillary, thermometer  $61^{\circ}.5$  and barometer 29.800 to 29.810, gave a very similar result, namely, 1121 and 1123 seconds for air, and 640 and 640 seconds for ammonia; numbers which are as 1 to 0.5704, and give,—

Transpiration time of ammonia, . . . . . 0.5134

(3.) A third series of experiments was made upon this gas under pressure in the globular digester, and escaping into air by the sheaf of thirty capillary tubes P. The thermometer was at  $60^{\circ}$ , and the barometer from 29.888 to 29.918 inches during the experiments.



TABLE XIII.—Transpiration of Ammonia (into air).

Height of gauge barometer above 1 atmosphere.	Air.		Ammonia.	
	Experiment I.	Experiment II.	Experiment I.	Experiment II.
Inches.	"	"	"	"
20	0	0	0	0
15	218	217	124	124
10	319	321	182	182
8	186	186	107	106
6	243	243	138	139
4	354	355	201	201
2	621	621	350	357
1	635	645	352	350
From 20 inches to 1.....	2576	2588	1454	1459

The observation at 1 inch, or even at 2 inches, does not admit of the same precision as in the higher parts of the scale, owing to the slowness with which the mercury descends, leaving a doubtful period of 3 or 4 seconds which the mercury is in passing the mark. The experiments at different parts of the scale, it will be seen, concur in giving nearly the same result, except for the last inch, where this uncertainty appears to have occasioned a sensible error.

Transpiration times of Ammonia at different pressures.

	Air = 1.	Oxygen = 1.
From 20 to 10 inches ...	0·5693	0·5112
From 10 to 6 inches ...	0·5711	0·5128
From 6 to 2 inches ...	0·5684	0·5104
From 2 to 1 inch.....	0·5484	0·4936

The common multiplier by which the numbers of the oxygen scale have been derived from the air scale is 0·898. Excluding the last result we have, on the oxygen scale,—

The mean transpiration time of ammonia, . 0·5115

This time for ammonia corresponds very closely with the results previously obtained by the long single capillary M, namely, 0·5119 and 0·5134. The coincidence in the rates of M with those of the compound capillary, for a liquefiable gas like ammonia, is a circumstance of considerable importance, as a large proportion of the experiments which I have to detail on gases of this class were made with the first-named only of these capillaries. The number for ammonia certainly approaches to 0·5076 and 0·5093, the mean transpiration times of olefiant gas, but



cannot be said to coincide with them, and is of course somewhat more distant from 0.5.

#### 4. *Cyanogen.*

This gas was prepared from well-crystallized and perfectly dry cyanide of mercury. To secure its purity the gas was besides passed over red oxide of mercury and chloride of calcium. The gas was conveyed to the capillary in the same manner as ammonia. The capillary employed was the long tube M, of 52.5 inches, the gas under the pressure of the atmosphere being drawn into the two-pint aspirator-jar, exhausted as usual upon the plate of an air-pump. Thermometer  $60^{\circ}$ , barometer from 29.910 to 29.864 inches.

The experiments were made in the following order:—air 1113, 1114 seconds; cyanogen, 626, 628, 627, and 627 seconds; air, 1117, 1117 seconds. The slight increase of the air-time in the last-made experiments is undoubtedly owing to the fall of the barometer. The ratio of the cyanogen to the first air-time is 0.5631, and to the second air-time 0.5613; or 0.5068 and 0.5052, with oxygen = 1. The mean of the two results gives—

Transpiration time of cyanogen, . . . . . 0.5060

The transpiration time of cyanogen may therefore be confounded with that of olefiant gas, 0.5076, transpired in the same manner, although the densities of these two gases differ so widely as 14 to 26 (oxygen = 16).

#### 5. *Hydrocyanic Acid.*

A considerable quantity of the absolute acid was prepared by distilling 15 ounces of crystallized ferrocyanide of potassium with 9 ounces of oil of vitriol diluted by an equal weight of water. The liquid acid was afterwards dried by digesting it over pounded chloride of calcium.

As hydrocyanic acid is liquid at the usual temperature, air or hydrogen saturated with the vapour of the acid was transpired instead of the pure substance itself. The air or hydrogen was made to stream through the liquid acid contained in a wash-bottle to a depth of 2 inches, and surrounded with water to which a slight heat was applied, so as to maintain the water and wash-bottle at the fixed temperature of the experiment, and to compensate for the cold of evaporation. The tension of the hydrocyanic acid vapour at  $59^{\circ}$ , the temperature of the experiments, was found to be 18.8 inches. The composition of the mixed vapour operated upon was—

	Volumes.
Air or hydrogen, . . . . .	10.8 or 36.48
Hydrocyanic acid, . . . . .	18.8 or 63.52
	<hr/> 29.6 100.00



The vapour was transpired under the pressure of the atmosphere by the capillary M, 52.5 inches in length, into the two-pint aspirator-jar, through the usual range (28.5 to 23.5 inches) of the attached barometer. Thermometer  $59^{\circ}$ , barometer 29.518 to 29.644 inches.

The transpiration time of air was 1138 and 1138 seconds in two experiments. The time of air impregnated with hydrocyanic acid was 807, 809, 808, 808 seconds, in four experiments; which gives to the latter the ratio of 0.7100. Multiplying by 0.9 we obtain—

Transpiration time of air saturated with hydrocyanic acid vapour at  $59^{\circ}$ , 0.6390.

It is obvious therefore that hydrocyanic acid vapour is greatly more transpirable than air. The theoretical density of hydrocyanic acid vapour is 13.5, the density of oxygen being 16.

Hydrogen gas equally impregnated with hydrocyanic acid vapour was transpired in the times 579 and 579 seconds, which gives the ratio to air of 0.5088. Multiplying by 0.9 we obtain—

Transpiration time of hydrogen saturated with hydrocyanic acid vapour at  $59^{\circ}$ , 0.4579.

Judging from our former results on mixtures of hydrogen with denser gases, in which it appeared that the rate of the mixture never deviated far from that of the dense gas in a state of purity, unless the proportion of hydrogen exceeded 50 per cent., it may be inferred that the transpiration time of pure hydrocyanic acid vapour is between 0.4375, the time of hydrogen, and 0.4579, the observed time, but much nearer to the latter than to the former. For the transpiration of gaseous mixtures of more nearly equal density, it is known, on the contrary, that the transpiration time does not deviate far from the mean time of the constituents when transpired separately. Taking the transpiration time of air as 0.9, and that of hydrocyanic acid vapour as 0.46, then 36.48 volumes of the first and 63.52 volumes of the second would give a mean time of 0.6205.

The time observed of a mixture in these proportions was 0.6390.

Hydrocyanic acid is composed of equal volumes of cyanogen and hydrogen united without condensation. The transpiration time of the compound gas is intermediate between the times of its constituents.

#### 6. *Hydrosulphuric Acid.*

This gas was evolved by the action of hydrochloric acid upon the sulphide of antimony; it was washed with water, and afterwards dried by passing over chloride of calcium.

(1.) Hydrosulphuric acid was first transpired by a short length of



capillary M, of 8.75 inches, into the six-pint aspirator-jar, through the usual range of 28.5 to 23.5 inches of the attached barometer: thermometer  $62^{\circ}$ , barometer 29.674 to 29.652 inches. The following observations were made in the order in which they are related:—times of air, 999 and 1001 seconds; of hydrosulphuric acid, 692, 692 seconds; of hydrosulphuric acid gas saturated with the vapour of bisulphide of carbon, 682, 680 seconds; and lastly, of hydrosulphuric acid again, 685, 685 seconds.

The ratio of the first hydrosulphuric acid to air is 0.691, and of the second 0.685; the ratio of the hydrosulphuric acid saturated with the vapour of bisulphide of carbon is 0.681, or differs little from that of hydrosulphuric acid itself; showing that these two sulphur compounds nearly coincide in transpirability. Multiplying these results by 0.9, we have—

Transpiration time of hydrosulphuric acid (1),	. . .	0.6219
Transpiration time of hydrosulphuric acid (2),	. . .	0.6165
Mean transpiration time,		<hr/> 0.6192

This gas proved less uniform in its rate in different experiments than I have generally observed for other gases, at least with the present capillary.

In a repetition of the preceding experiments, thermometer  $60^{\circ}$ , barometer 29.860 to 29.858, the times observed were for air, 982, 983, and 981 seconds; for hydrosulphuric acid saturated with bisulphide of carbon, 659, 659, 659 seconds; and for hydrosulphuric acid alone, 663, 664 seconds; which give the ratios to air of 0.6711 and 0.6746. And multiplying by 0.9, we have—

Transpiration time of hydrosulphuric acid,	. . .	0.6071
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(2.) Hydrosulphuric acid gas was also transpired by means of the long capillary M, 52.5 inches in length, into the two-pint aspirator-jar. It was then supplied from a wash-bottle with a relief tube as in the experiments upon cyanogen and ammonia, without being retained over water. Thermometer  $59^{\circ}.5$  Fahr., barometer 29.550 to 29.292.

The times of air were 1134, 1134 seconds; of hydrosulphuric acid, 782, 780 seconds; of hydrosulphuric acid carried through a column of bisulphide of carbon  $2\frac{1}{2}$  inches in depth and kept at the fixed temperature of  $59^{\circ}.5$ , 773, 771, 772 seconds. These give the ratios to air, of 0.6887 for hydrosulphuric acid, and 0.6808 for hydrosulphuric acid saturated with the vapour of bisulphide of carbon at  $59^{\circ}.5$ . Also, multiplying by 0.9,—

Transpiration time of hydrosulphuric acid,	. . .	0.6198
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This last result almost coincides with the first determinations with the short capillary M, namely 0.6192. The mean of the two results is,—

Transpiration time of hydrosulphuric acid, . . . 0.6195

The mercury in the gauge tube of the air-pump was soiled by these experiments, and the tube required to be cleaned after them.

### 7. Bisulphide of Carbon.

At the temperature of  $63^{\circ}$ , the tension of the vapour of bisulphide of carbon was observed to be 10.462 inches. Experiments were made with air, oxygen, hydrogen, and carbonic acid gases, all saturated with the vapour of bisulphide of carbon at  $63^{\circ}$ , and with barometer from 29.874 to 29.850 inches. The short capillary K, 8.75 inches in length, was made use of, and the gas was transpired into the six-pint aspirator jar. The gases were impregnated by the vapour in passing through a large U-shaped tube filled with cotton-wick which was moistened by the liquid bisulphide of carbon.

Air alone was transpired in 982 and 981 seconds; air saturated with bisulphide of carbon vapour in 837 and 838 seconds; oxygen saturated with bisulphide of carbon vapour in 895 and 896 seconds; hydrogen saturated with bisulphide of carbon vapour in 662 and 661 seconds; carbonic acid saturated with bisulphide of carbon vapour in 763 and 762 seconds. The ratios appear in the following Table :—

Transpiration times of different Gases saturated with  $\text{CS}_2$  at  $63^{\circ}$ .

	Air=1.	Oxygen=1.
Oxygen .....	0.9124	0.8212
Air .....	0.8533	0.7679
Carbonic acid.....	0.7769	0.6992
Hydrogen .....	0.6739	0.6065

It may be safely concluded that the transpiration time of bisulphide of carbon is not less than 0.6065, but probably sensibly greater. It must, according to former observations, approach very closely to, if it does not actually coincide with, 0.6195, the transpiration time of hydrosulphuric acid gas.

### 8. Sulphurous Acid.

This gas was evolved by the action of copper upon sulphuric acid, was washed with water, and conveyed in a continuous manner to a bottle



with a relief tube from which the capillary was supplied, as in the experiments with ammonia and cyanogen. The gas was dried by passing over pumice soaked in oil of vitriol before reaching the capillary.

(1.) With short capillary K, 8.75 inches in length, the six-pint aspirator-jar, and usual range from 2.85 to 23.5 inches: thermometer  $53^{\circ}$ , barometer 29.964 to 29.942 inches.

The time of air was 970, 970 seconds; of sulphurous acid, 714 and 711 seconds; ratio of latter to air, 0.7345. Multiplying by 0.9, we obtain—

Transpiration time of sulphurous acid, . . . 0.6610

(2.) With the long capillary M, 52.5 inches in length, this gas was transpired into the two-pint jar: thermometer  $60^{\circ}.5$ , barometer 29.880 to 29.878 inches.

The time of air was 1120, 1120, and 1120 seconds; the time of sulphurous acid 814, 811, and 812 seconds. Using the two last observations only for sulphurous acid, we obtain the transpiration time 0.7245 for that gas, air being 1; or multiplying by 0.9,—

Transpiration time of sulphurous acid, . . . 0.6520

In a second series of experiments with the same capillary, thermometer  $58^{\circ}$  and barometer from 29.880 to 29.886, the following observations were made. Time of air, 1105, 1111, 1105, and 1111 seconds; time of sulphurous acid, 798, 797, and 798 seconds, and ratio to air 0.7199. This gives—

Transpiration time of sulphurous acid, . . . 0.6479

The mean of the two results by this capillary gives—

Transpiration time of sulphurous acid, . . . 0.6500

### 9. *Sulphuric Acid.*

Both air and oxygen gas saturated with the vapour of anhydrous sulphuric acid were transpired under the pressure of the atmosphere into an air-pump vacuum, by the short capillary K, 8.75 inches in length. Certain new arrangements of the apparatus, however, were required in operating upon so highly corrosive a vapour as that of sulphuric acid. Two ounces of the solid sulphuric acid were melted by heat in a U-tube stuffed with asbestos, and having while liquid impregnated the asbestos, were allowed to cool and become solid again before the air or other gas to be saturated with sulphuric acid vapour was conducted through the U-tube. For the tin conducting-tubes of the former arrangements, glass tubes were substituted, and the air-pump was employed to exhaust a stout globular glass globe of six pints in capacity and provided with three openings, which was employed as the



aspirator cavity. Two of the openings of the globular receiver were in the sides, and one at the bottom of the receiver; by one of the former openings the globular receiver was connected with the transpiring capillary and by the other with the air-pump; a tube containing carbonate of potash being interposed between the receiver and the air-pump, to arrest the acid vapours and prevent them from reaching the air-pump, when the latter was used for exhausting the globular receiver. The third and lower opening communicated with a gauge barometer, by which the tension of the gas or vapour within the globular receiver was observed. The mercury in this barometer was found to adhere slightly to the glass, and not to descend with an entirely level surface in the transpiration experiments, owing to a slight chemical action of the acid vapour upon the mercury. This circumstance prevents the times being observed with the same precision as in other gases.

With the thermometer from  $72^{\circ}$  to  $74^{\circ}$ , and barometer from 30.076 to 30.028 inches, the times of descent of the gauge barometer from 28.5 to 23.5 inches were, with air, 865 and 863 seconds; with air saturated with sulphuric acid vapour at  $73^{\circ}$  Fahr., 960, 961, and 958 seconds. The ratio of the last times to air is 1.1106; and multiplying by 0.9, we obtain,—

Transpiration time of air saturated with vapour of  $\text{SO}_3$  at  $73^{\circ}$ , 0.9993

The tension of the vapour of anhydrous sulphuric acid at  $73^{\circ}$  was observed to be 11.50 inches.

The experiments on sulphuric acid vapour were repeated: thermometer  $67^{\circ}5$ , barometer 29.914 to 29.908 inches; the range of the gauge barometer now observed, however, being only from 28.5 to 24.5 inches.

The time for air was 695 and 694 seconds; for oxygen saturated with the vapour of sulphuric acid at  $67^{\circ}5$ , 786 and 782 seconds; for oxygen alone at  $68^{\circ}$ , 774 seconds; and for air alone again 692 seconds. The result to be deduced is,—

Transpiration time of oxygen saturated with vapour of  $\text{SO}_3$  at  $67^{\circ}5$ , 1.0130

The sensible equality of the times of air observed at the beginning and end of the experiments proves that the working of the apparatus was not deranged by the sulphuric acid vapour. It is evident that the time of pure sulphuric acid vapour itself cannot deviate far from that of oxygen gas. Sulphuric acid appears to be one of the very few gases, the transpirability of which, if not really coincident with, is slightly inferior to, or slower than, that of oxygen.

#### 10. Chlorine.

The transpiration time of chlorine has a peculiar interest as that of



an elementary substance. The same arrangements were had recourse to with this corrosive gas as with sulphuric acid. It was found necessary, in addition, to preserve a small column of water above the mercury in the gauge barometer, to defend the metal from the action of the chlorine, or at least to prevent the surface of the metal from becoming foul and adhesive. This gas immediately reached the capillary, like ammonia, from a bottle with a relief tube, to permit the escape of the redundant supply. It was dried by means of chloride of calcium.

(1.) The transpiration was made by capillary K, 8.75 inches in length, into the six-pint globular receiver as aspirator, from 28.5 to 23.5 inches by the gauge barometer attached to the latter: thermometer  $70^{\circ}$  to  $71^{\circ}$ , barometer 30.222 to 30.208 inches.

The times of air in two experiments were 865 and 866 seconds; the times of chlorine 670 and 672 seconds; giving the ratio to air of 0.7753. Multiplying the latter number by 0.9, we have—

Transpiration time of chlorine, . . . . . 0.6978

(2.) In a second series of experiments with the same capillary, the following observations were made; the thermometer being  $72^{\circ}$  to  $74^{\circ}$ , and barometer 30.248 to 30.218 inches.

The times of air were 858, 860, and 859 seconds; the times of carbonic acid 711 and 712 seconds; the times of chlorine 670, 670, 670, and 670 seconds; the time of air again 866 and 867 seconds. A slight increase in the air-time is observed, after the chlorine experiments, but I would refer this increase more to the rise of two degrees in temperature between the first and last observations, than to any derangement in the apparatus. Taking the last observed air as the standard of comparison for the chlorine, and the first observed air for the carbonic acid, we find—

	Air = 1.	Oxygen = 1.
Transpiration time of chlorine, .....	0.7732	0.6959
Transpiration time of carbonic acid, ...	0.8282	0.7454

But the true transpiration time of chlorine gas is probably less than 0.6959, for the true time of carbonic acid is certainly less than 0.7454, the time obtained above for the latter gas. The present capillary, it has been already remarked, is one of too small resistance to bring out the true transpiration time of a gas whose effusion rate differs very widely from its transpiration rate. The present experiment indeed is not inconsistent with the true transpiration time of chlorine, being 2 or 3



per cent. lower than that observed, or falling as low as 0.66, that is, two-thirds of the time of oxygen.

(3.) The transpiration of chlorine was also observed by means of the long capillary M, 52.5 inches in length, with the same six-pint glass globular receiver as aspirator-jar. The fall observed by the gauge barometer was only 3 inches, or from 28.5 to 25.5 inches. Thermometer  $58^{\circ}$ , barometer 29.742 inches.

The time of air was 1907 and 1911 seconds; of chlorine 1432 and 1395 seconds. The difference of 37 seconds in the two observed times of chlorine, which is so considerable, arose from the action of chlorine upon the mercury; for notwithstanding that the latter was covered with water, its surface became so uneven that the observations could not be made with any great nicety. The first observation of chlorine gives the time of that gas 0.7501 referred to air, and 0.6751 referred to oxygen; the second observation gives the time of chlorine 0.7307 referred to air, and 0.6576 referred to oxygen. Calculating from 1413.5 seconds, the mean of the two observed times for chlorine, we obtain—

	Air = 1.	Oxygen = 1.
Transpiration time of chlorine, .....	0.7404	0.6664

The transpiration time of chlorine appears therefore to be about two-thirds of the time of oxygen; or, chlorine passes through a tube with  $1\frac{1}{2}$  time the velocity of oxygen.

#### 11. *Bromine and Hydrochloric Acid.*

The only observations which I possess upon the transpiration of these two substances were made by means of the short capillary K, of 8.75 inches in length, the six-pint globular receiver being the aspirator, and the fall being as usual from 28.5 to 23.5 inches of the gauge barometer. For both the bromine and hydrochloric acid the bottle and relief tube were employed also as before, to regulate the supply of gas to the capillary. Chloride of calcium was employed to dry the gases.

The time of air was 846, 848 seconds; of hydrochloric acid, 693, 693 seconds; of air saturated with the vapour of bromine at  $75^{\circ}$ , 889, 889, and 889 seconds; of hydrogen saturated with the vapour of bromine, 760, 760 seconds: thermometer from  $73^{\circ}$  to  $75^{\circ}$ , barometer 30.230 to 30.178 inches. In an observation which was made at the same time upon the tension of bromine vapour, it was found that liquid bromine placed in an air-pump vacuum depressed the mercurial gauge 9.19



inches at  $75^{\circ}$ , which may therefore be taken as the tension of the vapour of bromine in the present experiments. The results are as follows:—

	Air = 1.	Oxygen = 1.
Transpiration time of hydrochloric acid gas.....	0.8181	0.7363
Transpiration time of 9.2 vol. bromine and 21.0 vol. air ...	1.0496	0.9446
Transpiration time of 9.2 vol. bromine and 21.0 vol. hydrogen	0.8973	0.8076

It appears that the transpiration time of hydrochloric acid observed, 0.7363, is greater than that of chlorine, 0.66, while that of hydrocyanic acid was found less, on the contrary, than that of cyanogen.

Bromine vapour increases the transpiration time of air, and is therefore less transpirable. This vapour, however, does not appear to be greatly more transpirable than sulphuric acid vapour or oxygen gas.

## 12. *Ether (Oxide of Ethyl, $C_4H_5O$ ).*

The ether employed was carefully washed with water, to deprive it of alcohol, and afterwards dried by agitation with pounded chloride of calcium. Dry hydrogen and other gases were impregnated with the vapour of this substance in the same manner as with bromine.

(1.) The first experiments were made with the short capillary K, 8.75 inches in length; the gas being transpired as usual under the pressure of the atmosphere into the exhausted six-pint aspirator jar, through the range from 28.5 to 23.5 inches of the gauge barometer of the air-pump: thermometer  $56^{\circ}$ , barometer 29.670 to 29.708 inches. The tension of the ether vapour at  $56^{\circ}$  being found 12.85 inches, the mixture transpired may be represented as composed of 12.85 volumes ether vapour and 16.85 volumes gas; or of 43.26 ether vapour and 56.74 gas in 100 volumes.

The time of air was 988, 988 seconds; of hydrogen 474, 473 seconds; of hydrogen gas saturated with ether vapour at  $56^{\circ}$ , 498, 500 seconds; of oxygen gas saturated with ether vapour at the same temperature, 696 and 695 seconds. The transpiration times deducible from these observations are,—

	Air = 1.	Oxygen = 1.
Transpiration time of hydrogen.....	0.4792	0.4312
Transpiration time of ether vapour and hydrogen.....	0.5051	0.4546
Transpiration time of ether vapour and oxygen.....	0.7040	0.6336



It thus appears that the transpiration time of hydrogen, 0.4312, is only increased to 0.4546 by 43.26 per cent. of ether vapour. As the influence of hydrogen upon the rate of transpiration of the dense gases and vapours is scarcely sensible, this may be held as proving that the time of ether vapour does not sensibly exceed the time of the hydrogen mixture, 0.4546. But as the experiment has been made with a capillary of small resistance, it is not impossible that the normal time of ether vapour may be still sensibly less.

(2.) The capillary M, 52.5 inches in length, with the two-pint aspirator, was now used, the other arrangements remaining as before: thermometer  $68^{\circ}.5$  to  $69^{\circ}$ , barometer 30.242 to 30.264 inches.

The time of air was 1084, 1084 seconds; of air saturated with ether at  $68^{\circ}.5$  (59.5 ether vapour to 40.5 air), 675, 676 and 673 seconds; of hydrogen saturated with ether vapour at  $68^{\circ}.5$  (59.5 ether vapour to 40.5 hydrogen), 533, 529 and 531 seconds; of oxygen saturated with ether vapour at  $68^{\circ}.5$  (59.5 ether vapour to 40.5 oxygen), 728, 725 and 727 seconds; of hydrogen alone, 529, 529 seconds. The tension of ether vapour was observed at the time to be 17.95 inches at  $69^{\circ}$ . The results deduced from these experiments are as follows:—

	Air = 1.	Oxygen = 1.
Transpiration time of ether vapour and air.....	0.6224	0.5601
Transpiration time of 59.5 ether vapour and 40.5 hydrogen	0.4898	0.4408
Transpiration time of 59.5 ether vapour and 40.5 oxygen...	0.6771	0.6039
Transpiration time of hydrogen.....	0.4880	0.4392

In this capillary of great resistance, the time of hydrogen is therefore not sensibly affected by nearly one and a half times its volume of ether vapour, from which it may be inferred that the transpiration time of ether vapour itself does not diverge sensibly from that of hydrogen. The near if not perfect coincidence in transpirability in these two substances is very remarkable, considering their great dissimilarity in physical characters, particularly in weight, the densities of hydrogen and ether vapour being as 1 to 37.

Although hydrogen and ether may have the same transpirability, still the influence which each of these gases exerts upon the transpiration of other gases with which it is mixed, is widely different. It will be seen by the experiments above on ether and air, or ether and oxygen, that the transpiration time inclines most to the ether rate, while in hydrogen mixtures the time also deviates from the mean of the mixed gases, but greatly in the direction of the rate of the other gas, and not towards the hydrogen rate. The density of a gas is no doubt an important element in this influence.



In an experiment with the short capillary K, the time of olefiant gas was reduced from 0.5246 to 0.4816, by saturation with ether vapour at 60°.5.

The rates of hydrogen and ether appear to diverge from each other in experiments made at a high temperature. The water in the copper trough in which the long capillary M was always placed, with the view of commanding a constant temperature, was heated to 203° (95° Centig.), and preserved at that temperature during the continuance of the following experiments. Thermometer in air 60°.5, barometer 29.956 to 29.982 inches.

Time of air 1634 and 1637 seconds; of hydrogen, 798 and 797 seconds; of hydrogen saturated with ether vapour at 60°.5, 863, 863 seconds. As the gas transpired was measured at 60°.5 instead of 203°, the temperature at which it passed through the capillary, these times fall to be diminished in the proportion of the volume of air at 203° and at 60°.5 respectively. We thus obtain as the three mean times in which equal volumes were transpired at 203°,—air 1282.4 seconds, hydrogen 625.9 seconds, and hydrogen saturated with ether vapour at 60°.5, 677.3 seconds.

	Air = 1.	Oxygen = 1.
Transpiration time at 203° Fahr. of hydrogen .....	0.4880	0.4392
Transpiration time at 203° of hydrogen saturated at 60°.5 with ether vapour .....	0.5281	0.4753

While air and hydrogen preserve, at 203°, their usual ratio of transpirability, ether vapour appears therefore to become sensibly less transpirable at the high temperature.

### 13. *Methylic Ether* (*Oxide of Methyl*, $C_2H_3O$ ).

This vapour was evolved in a continuous manner in proportion as required for transpiration, with the arrangements necessary for gases soluble in water. The vapour was passed over both hydrate of potash and chloride of calcium. The experiments were made with the short capillary K, 8.75 inches in length, like the first experiments with common ether. Thermometer 56°, barometer 29.650.

Time of air 993 and 991 seconds; of methylic ether, 532 and 532 seconds; of methylic ether saturated with the vapour of common ether at 56°, 508, 506, and 507 seconds.



## Transpiration times.

	Air = 1.	Oxygen = 1.
Methylic ether.....	0.5363	0.4826
Methylic ether saturated with ether vapour at 56°.....	0.5111	0.4600

The time of methylic ether, 0.4826, is decidedly longer than that of common ether, 0.4546, as the latter was formerly observed by the same capillary; and consequently an addition of ether vapour shortens the methylic ether time, as appears in the second experiment, where the transpiration time of such a mixture falls to 0.4600.

14. *Hydrochloric Ether (Chloride of Ethyl, C<sub>4</sub>H<sub>5</sub>Cl).*

The experiments were made with the same short capillary K, 8.75 inches in length, and with the other arrangements as for the two preceding ethers. Thermometer 56°, barometer from 29.794 to 29.758 inches.

The time of air was 980 and 981 seconds; of hydrochloric ether, 548, 544, and 543 seconds.

	Air = 1.	Oxygen = 1.
Transpiration time of hydrochloric ether .....	0.5543	0.4988

It would be unsafe to draw any conclusion from a single experiment upon this ether and that experiment made with a capillary of inferior resistance, but it may be remarked that the time of this ether approaches to half the time of oxygen, while the density of the vapour is little more than double that of this gas; the theoretical density of hydrochloric ether vapour being 32.25 to hydrogen 1 and oxygen 16.

15. *Hydrochloric Methylic Ether (Chloride of Methyl, C<sub>2</sub>H<sub>3</sub>Cl).*

This ether, which like the two last is entirely vaporous at the temperature of the experiments, was prepared by distilling together half a pound of wood-spirit, one and a half pounds of oil of vitriol, and one pound of common salt. The gas was exposed to a large quantity of dilute caustic soda in two wash-bottles, and dried afterwards by chloride of calcium. The same capillary and arrangements were employed as in the immediately preceding experiments. Thermometer 54°, barometer 29.862 to 29.856 inches.



The time of air was 973, 973 seconds; of chloride of methyl, 592, 587, and 582 seconds; of chloride of methyl again, after changing the solution of caustic soda in the wash-bottles, 592, and 592 seconds. Calculating from the last observed time of chloride of methyl, we have—

	Air = 1.	Oxygen = 1.
Transpiration time of chloride of methyl .....	0.6084	0.5475

It thus appears that the chloride of methyl has a longer time, or is more slowly transpired than the corresponding chloride of ethyl; as the oxide of methyl was also found to be less transpirable than the oxide of ethyl. Indeed the difference between the two oxides and between the two chlorides appears to be the same, or about 0.045 in both cases. This is in accordance with the general observation, that transpiration is promoted by increase of density. The theoretical density of chloride of methyl is 25.25 to hydrogen 1 and oxygen 16.

#### 16. *Water.*

Although great care was always taken to dry air when transpired, as well as other gases, in all experiments, still it does not appear that the rate of air is much affected by the presence of aqueous vapour unless the latter is present in considerable proportion.

The times observed by capillary K, 8.75 inches in length, into a vacuum, were for air dried by chloride of calcium 1008 seconds, and for air drawn afterwards directly from the atmosphere, of which the temperature was 60°, and the dew-point 32°, 1006 and 1006 seconds. So small a difference may be due to accidental causes.

With dry air at 60°, the times with the same capillary were, upon another occasion, 1021 and 1021 seconds; and with air of 60° temperature, but containing aqueous vapour with the dew-point at 38°, 1018 and 1017 seconds.

In other experiments, the presence of aqueous vapour appeared to occasion a sensible retardation in the time of air. The transpiration was made into a vacuum by the capillary M, 52.5 inches in length; the temperature of the capillary being maintained at 58° 5, and the barometer varying from 29.798 to 29.832 inches. The air was charged with vapour by passing through a tube filled with cotton wick, which had been previously moistened with dilute sulphuric acid of different strengths. The time of dry air was 1115, 1115 seconds; of air carried over the fourth hydrate of sulphuric acid ( $\text{HO} \cdot \text{SO}_3 + 3\text{HO}$ ), 1117, 1117 seconds;



of air passed over the eighth hydrate ( $\text{HO} \cdot \text{SO}_3 + 7\text{HO}$ ), 1120 and 1121 seconds; of air passed over the eighteenth hydrate ( $\text{HO} \cdot \text{SO}_3 + 17\text{HO}$ ), 1122, 1122, and 1121 seconds. Here we observe in the dampest air a slight but sensible increase of the air time, not exceeding 7 seconds. But on repeating the experiment immediately afterwards with dry air, the time was 1120 and 1119 seconds, or within two seconds of the immediately preceding observations with moist air. Indeed the transpiration of moist air appears to produce a slight but sensible retardation of a persistent character, probably from the condensation of a film of moisture on the inner surface of the capillary, which is not immediately removed by the subsequent passage of dry air.

With the same capillary, thermometer  $57^\circ$  and barometer 30.136 to 30.078 inches, dry air was transpired in 1089, 1089 seconds; dry hydrogen in 532 and 532 seconds; air saturated with aqueous vapour at  $57^\circ.5$  in 1098, 1098 seconds; hydrogen saturated with aqueous vapour at the same temperature, in 548 and 548 seconds; and lastly, dry air, first in 1106 seconds, and afterwards in 1084 and 1085 seconds. Here the damp air is less transpirable, volume for volume, than dry air by 9 seconds. Also, dry air immediately following the damp air does not recover its usual transpirability in the first experiment.

These experiments upon damp and dry air seem to indicate that the transpiration time of aqueous vapour does not differ greatly from that of air itself. The influence of aqueous vapour upon the time of hydrogen, however, is considerably less than that of air upon the same gas, and therefore suggests a more rapid transpiration.

#### 17. *Alcohol.*

Air was impregnated with the vapour of alcohol of specific gravity 0.835 at  $60^\circ$ , barometer 29.358. The tension of the vapour of alcohol of specific gravity 0.813 at  $60^\circ$  is estimated at 1.23 inch. The capillary K, 8.75 inches in length, was made use of, with an air-pump vacuum, as in all these experiments.

The time of dry air was 1013 and 1014 seconds; of air containing alcohol vapour, 1011 and 1012 seconds. The rate of air is scarcely affected, and consequently the time of alcohol vapour must approximate to that of air.

#### 18. *Naphtha and Coal-Gas.*

In experiments made with air saturated with the vapour of coal-tar naphtha at  $62^\circ$ , the capillary K being employed, the times obtained for air alone were 978 and 979 seconds; for air saturated with naphtha vapour, 949 and 949 seconds. The transpiration time of air is diminished



30 seconds, showing that the volatile hydrocarbons of naphtha are highly transpirable, like ether vapour. The time of coal-gas, taken from the service-pipes of a London company, and observed in the same circumstances, was 621 and 622 seconds; of the same coal-gas impregnated with naphtha vapour, 621 and 621 seconds, or the naphtha vapour produced no sensible change in the transpirability of the gas; showing a near coincidence in their transpirabilities. The transpiration time of the coal-gas, reduced to the oxygen scale, is 0.5716, or a little more than protocarburetted hydrogen, 0.5510.

That a considerable quantity of naphtha vapour was taken up by the coal-gas, notwithstanding that its transpiration was unaffected, appears in certain experiments which were made with a particular object upon the effusion of the same gases. The capillary was removed and replaced by a plate of platinum foil, G of former paper, having an extremely minute aperture, the other arrangements remaining the same. The gases were all moistened with water. For the passage of equal volumes into an air-pump vacuum (the six-pint aspirator-jar, through the usual range from 28.5 to 23.5 inches of the attached barometer), the times were, at 61°, for air, 434 and 434 seconds; for hydrogen, 139 and 139 seconds; for coal-gas, 314 and 314 seconds; for coal-gas saturated with naphtha vapour at 61°, 331 and 331 seconds; for hydrogen and naphtha vapour, 194 and 193 seconds; and for air with naphtha vapour, 503 and 503 seconds. It is to be remembered that the densities of the gases effused are in the proportion of the squares of these times, and may be deduced from the latter. The time of coal-gas is increased by the addition of naphtha vapour, but to a much less extent, than hydrogen and air are, no doubt from the former being from the first partially saturated with naphtha vapour.

A good deal of light could be obtained, I believe, upon the composition and value of coal-gas by a combination of effusion and transpiration experiments. Great density, which would be indicated by slow effusion, is always valuable, unless when occasioned by air, carbonic oxide or carbonic acid, which gases exclusively make the transpiration slow; so that slow effusion with rapid transpiration would mark the coal-gas of superior quality.

### III. TRANSPARATION OF AIR OF DIFFERENT DENSITIES OR ELASTICITIES.

A series of observations on air varying in density from 0.5 to 2 atmospheres, made with the long 20-feet capillary E in my former paper, appeared to establish the conclusion that "for equal volumes of air of different densities, the times of transpiration are inversely as the



densities." The law of Effusion, or flow of air into a vacuum by an aperture in a plate, is entirely different; equal volumes of air of all densities passing in equal times.

With the short capillary K, 8.75 inches in length, the result was now found to be materially different. Air in three different states of rarefaction was drawn into a sustained vacuum from a globular receiver of which the capacity was 56.5 cubic inches, standing over water. To command the desired density of the air in the globular receiver, the little system of the latter and the basin of water in which it stood was retained within a large air-pump receiver, the atmosphere of which was adjusted to the requisite pressure. Thermometer  $62^{\circ}$ , external barometer from 29.984 to 29.936 inches.

#### Transpiration of equal volumes of Air.

Density or Elasticity.	Time in seconds.	
	Experiment I.	Experiment II.
1 atmosphere.....	2172	2173
0.75 atmosphere.....	2948	2946
0.5 atmosphere.....	5292	5288

It will be observed that the time 5292 seconds for air of 0.5 density is considerably more than double 2172 seconds, the time for air of 1 density.

With compressed air, varying in density from 1 to 2.5 atmospheres, the deviation from the law was equally conspicuous; the times of transpiration of equal volumes at 1, 1.25, 1.5, 1.75, 2, and 2.5 atmospheres, being in the ratio of 1, 0.8625, 0.7553, 0.6834, and 0.5519, instead of 1, 0.8, 0.6666, 0.5714, 0.5, and 0.4.

On operating, however, with the long capillary M, 52.5 inches in length, and of great resistance, results were again obtained in strict accordance with the law. The air was drawn from a metallic digester provided with a gauge barometer, in which it was preserved of a constant elasticity; this digester itself being supplied from a second similar digester, in which the air was in a state of still higher compression. The air was transpired into the two-pint aspirator-jar (capacity about 72 cubic inches) upon the plate of the air-pump, for the usual range of the gauge barometer from 28.5 to 23.5 inches. Thermometer  $66^{\circ}$ , external barometer 30.122 to 30.086 inches.



## Transpiration of equal volumes of Air.

Density or elasticity.	Time in seconds.		Reduced time of means.	Calculated or theoretical times.
	Experiment I.	Experiment II.		
1 atmosphere .....	1095	1096	1095.5	1095.5
1.25 atmosphere .....	707	707	883.1	884.8
1.5 atmosphere .....	493	493	739.5	737.3
1.75 atmosphere .....	359	359	628.25	632
2 atmospheres .....	277	276	553	553
2.25 atmospheres .....	218	217	489.4	491.5
2.5 atmospheres .....	176	176	440	442

The column of "Time in seconds," contains the times of the fall of the air-pump barometer from 28.5 to 23.5 inches actually observed, and which are produced by the admission to the aspirator-jar of an equal volume of air of constant density. These times must therefore be multiplied by the density in atmospheres of the air transpired, to obtain the reduced times of the following column. It will be observed that these reduced times are in perfect harmony with the "Calculated times" of the last column. Indeed nothing could illustrate more strongly the great precision of which transpiration experiments are susceptible, than these results.

The conclusion to be drawn from the present observations with the capillary M, and the old observations with E, as compared with the observations made with the short capillary K, is that to bring out the normal effect of densities on transpiration, a greater resistance and length of tube are necessary than are required for the observations of the normal relations in the transpiration times of such gases as oxygen, nitrogen, and hydrogen; for the short capillary K, which fails so much in the law of densities, exhibits the other relations nearly with as much accuracy as the long capillary M. The marked superiority also of the 20-foot tube E over the 8-inch tube K, although the power of resistance of these two capillaries is nearly equal, suggests again the idea that resistance produced by elongation of the capillary acts differently from an equal resistance produced by contracting the diameter of the capillary, and more advantageously in transpiration experiments.

#### IV. TRANSPIRATION OF AIR AND OTHER GASES AT DIFFERENT TEMPERATURES.

The experiments which I have made upon the transpiration of air and also of other gases at different temperatures are very numerous, but



not altogether satisfactory. Looking upon the experiments as only preliminary, I shall confine myself at present to a statement of results without detail, and endeavour to return to the subject at some future opportunity.

The transpiration of equal volumes becomes slower as the temperature rises. The experiments which follow upon air, carbonic acid, and hydrogen, were made upon different days with slightly different barometric pressures, so that the absolute times of one gas cannot be compared with another; but this is unnecessary for our present purpose. The capillary employed was M, 52·5 inches in length, and of great resistance.

TABLE XIV.—Transpiration of equal volumes at different temperatures.

Temperature.	Time in seconds.		
	Air.	Carbonic acid.	Hydrogen.
32 Fahr.	1054·1	857·9	545·4
59	1092·8	897·4	557·8
86	1133·4	931·5	577·7
113	1175·7	969·4	598·8
140	1211	993·9	615·9

The difference of time of transpiration at the two extreme temperatures, 32° and 140°, is 157·9 seconds for air, 136 seconds for carbonic acid, and 70·5 seconds for hydrogen. The differences, calculated in the proportion of the transpiration times of the same gases at the temperatures usually observed (56° to 74°), namely air 0·9, carbonic acid 0·73, and hydrogen 0·44, are for carbonic acid 128·1 seconds instead of 136, and for hydrogen 73·2 seconds instead of 70·5. It would be unsafe to conclude from these small deviations that the transpiration of the three gases in question is unequally affected by heat in the range of temperature from 32° to 140°; for at temperatures distant from the temperature of the atmosphere, the unavoidable errors of observation increase in magnitude. The increment upon the time of air was 156·2 seconds, and upon hydrogen 62·8 seconds, at 140°, in a repetition of the same experiments.

My most unexceptionable experiments all concur in showing that no sensible change takes place in the transpiration ratios of hydrogen, nitrogen, and carbonic oxide, at temperatures so high as 347° Fahr. Thus the observed transpiration times of a mixture of equal volumes of hydrogen and carbonic oxide at 60° and 347°, were 0·8870 and 0·8853;



the transpiration times of air observed at the same temperatures being taken as unity. The transpiration times of a mixture of equal volumes of hydrogen and nitrogen, referred to the times of air in the same manner, were at  $65^{\circ}$ , 0.8939; at  $347^{\circ}$ , 0.8924; again, at  $64^{\circ}5$ , 0.8930; and at  $347^{\circ}$ , 0.8872. The transpiration ratios are thus as nearly as possible constant at these widely distant temperatures.

The transpiration times of air and hydrogen alone, at  $203^{\circ}$ , were found on two different occasions as 1 to 0.4841, and 1 to 0.4880. Multiplying these hydrogen times by 0.9 to bring them to the scale of oxygen, we have for the transpiration times of hydrogen at  $203^{\circ}$ , 0.4357 and 0.4392, numbers which might have been obtained at atmospheric temperatures.

Carbonic acid, however, appears to present a sensible deviation from this uniformity of rate. In a series of observations made upon this gas at  $60^{\circ}$ ,  $203^{\circ}$ ,  $299^{\circ}$ , and  $347^{\circ}$ , its transpiration time referred to air at the same temperatures was 0.8291, 0.8551, 0.8777, and 0.8907; and referred to oxygen, 0.7448, 0.7541, 0.7741, and 0.7855. The transpiration time of carbonic acid at  $347^{\circ}$  varied in other experiments from 0.7729 to 0.7905, the time of oxygen being 1. The protoxide of nitrogen gave the number 0.7969 at the same high temperature.

The time of oxygen appears also to become relatively slower at high temperatures, although much less considerably than carbonic acid. It gave the numbers 0.8877 and 0.8860 for air at  $347^{\circ}$ , instead of 0.8984, the number at low temperatures. As we may assume from its uniform relation to hydrogen that the nitrogen remains constant, it follows that the oxygen has become relatively slower in transpiration at the high temperature.

If oxygen deviates from a supposed normal rate at high temperatures, it cannot necessarily coincide with that rate at any lower temperature, which is accidental, such as that of the atmosphere. But this influence of heat upon the transpiration time of oxygen is, I believe, still sensible at the low temperature in question.

By increasing the time of oxygen, this influence of heat may be the cause of that slight deviation, so uniform in its amount, of the observed times of air and nitrogen from their theoretical times, which was always remarked. I am disposed then to look upon the slight inconstancy of transpiration rate observed in some gases at different temperatures, as a fact of the same class as the deviations from their theoretical specific gravities observed in a greater or less degree in the same substances, and to those other points in which all the gaseous bodies we have to operate upon depart in some measure from the mechanical idea of a perfect gas.

The normal effect of temperature upon transpiration, as observed in



air, varies I find with the resistance of the capillary in a much higher degree than any other property of transpiration; the retardation from the same change of temperature being much greater in a capillary of great than small resistance. The resistance of a capillary such as M, which exhibits so exactly the law of densities, is insufficient to bring out the full effect of temperature. With the fine tubes of the compound capillary, on the other hand, the limit to the retarding influence of heat seems to be reached. The retardation then appears to be simply in proportion to the expansion; and rarefaction by heat, therefore, to have the same effect upon transpiration as expansion from diminished pressure.

In illustration of this inequality of action upon heated air, I may refer to results obtained by two capillary tubes of small and of intermediate resistance, before stating the normal results of capillaries of extreme resistance.

With the copper capillary tube described in my former paper, and which admitted 1 cubic inch of air into a vacuum in 22 seconds, the time of passage of a constant volume of air into a vacuum was 853 seconds at  $60^{\circ}$ , 899 seconds at  $116^{\circ}$ , and 924.5 seconds at  $152^{\circ}$ . The theoretical times, or those corresponding to the rarefaction by heat at these temperatures, are 853, 945, and 1004 seconds. Here the observed times at  $116^{\circ}$  and  $152^{\circ}$ , are 46 and 79.5 seconds shorter respectively than the times obtained by calculation; and the difference in transpirability observed at the high and low temperatures only amounts to about one-half of what it should be.

With capillary M, of which the resistance is seven times greater than the last capillary, the observed times of air at  $59^{\circ}$  ( $15^{\circ}$  Centig.), and at  $203^{\circ}$  ( $95^{\circ}$  Centig.), were 1106.5 and 1286.4 seconds. The time at the higher temperature is 1400 seconds by calculation, and the observed time is therefore 113.6 seconds deficient. The difference at the high and low temperatures amounts to nearly two-thirds of the difference which theory requires. The deviation is therefore less than with the preceding capillary.

Air compressed in the globular digester with pressure gauge, of which the capacity was reduced to about 10 cubic inches by the introduction of mercury, was transpired by a small capillary V, 3 inches in length, into the atmosphere, from a pressure beginning at 17 inches above that of the barometer. Thermometer  $50^{\circ}$ , barometer 29.546 to 29.590.

The resistance of this capillary is excessive. Under a pressure of 17 inches of mercury, 1 cubic inch of air is transpired in 2329 seconds, or the volume transpired is 0.0258 cubic inch per minute.



TABLE XV.—Transpiration of Air under pressure (into air) at different temperatures.

Pressure by gauge barometer.	Time in seconds.		Ratio at 203°, Time at 50° = 1.
	Thermometer 50° Fahr.	Thermometer 203° Fahr.	
Inches.	"	"	
17	0	0	
16	1370	2329	1.7000
15	1445	2442	1.6900
14	1541	2601	1.6880
From 17 to 14 inches.....	4356	7372	1.6924

Now the volume of air at 32° being = 1, at 50° it is 1.0366, and at 203°, 1.3480. But it must be remembered that the volume actually transpired in the experiment was greater at 203° than that at 50°, in proportion as the volume of air is expanded at the higher of these two temperatures, that is as 1.3480 to 1.0366 (volume at 32° = 1). It is therefore necessary to reduce the observed times of the table at 203° in that proportion. The time from 17 inches to 16 is thus reduced from 2329 to 1792.5 seconds, which last is the true time of the passage of the same volume at 203° as passed at 50°. The law requires that the times of equal volumes should be inversely as the densities of air at these temperatures, or as 1.0366 to 1.3480. Thus calculated from 1370 seconds, the time at 50°, the time at 203° is 1780.9 seconds; the time actually observed was 1792.5 or 11.6 seconds more, a close approximation considering the difficulties of the experiment.

But the resistance does not require to be so excessive as in capillary V to bring out the law of temperature. It appeared equally distinct in a capillary tube, having only one-ninth of the resistance of V for equal lengths. This tube however was used in lengths of 4½ inches (instead of 3 inches), so that its resistance is properly stated at one-sixth of V. A sheaf was put together of thirty lengths of the new tube, forming the compound capillary Q. The digester was employed of its full capacity, of 72 cubic inches, to contain the compressed air, which was allowed to escape by the channels of Q into the atmosphere. The range of pressure was from 20 inches to 8. The observed times at 49° and 203° without reduction were 802, 799, and 798 seconds at the low temperature, and 1350 and 1347 seconds at the high temperature. Taking the means 800 and 1349 seconds, and reducing as in the experiments with V, we have 1036.1 seconds for the high temperature. Now the calculated time for that temperature is 1041.6 seconds, or only 5.5 seconds above



the observed time. The barometer during these experiments marked from 30.044 to 30.058 inches.

In another series of experiments, the time observed at  $49^{\circ}$  being 797 seconds, the times observed after reduction, at certain intermediate temperatures, were as follows:—

TABLE XVI.—Times of transpiration of Air (into air) in seconds.

Temperature.	Observed time.	Calculated time.	Error of observation.
$49^{\circ}$ Fahr.	797	797	
96	879.3	870.4	+ 8.9
141	950.1	935.8	+ 14.3
203	1020.8	1032.1	- 11.3

The deviations of the observed from the calculated times, from 8.9 to 14.3 seconds, are small considering the difficulty of maintaining the temperature constant in the experiments. Nor are they always in the same direction. This appears in a third series of experiments, conducted in the same manner as the last, of which I subjoin the results.

TABLE XVII.—Times of transpiration of Air (into air) in seconds.

Temperature.	Observed time.	Calculated time.	Error of observation.
$49^{\circ}$ Fahr.	797	797	
96	897.3	870.4	+ 8.9
141	932.3	940.8	- 8.5

These observations leave little doubt that the transpiration of air at different temperatures takes place according to the law by which the times above have been calculated. In one experiment which was made upon oxygen at  $49^{\circ}$  and  $203^{\circ}$ , the increase upon the time at the higher temperature corresponded within 0.7 per cent. of the increase upon the time of air, and evidently followed the same ratio. I may add that the transpiration times of air and oxygen, as determined by a single observation in each case, were 0.9058 to 1 for the compound capillary Q, and 0.9020 to 1 for the single capillary V of extreme resistance.

In conclusion I may sum up the general results hitherto obtained in this inquiry.

1. The velocities with which different gases pass through capillary tubes bear a constant relation to each other, and appear to constitute a peculiar and fundamental property of the gaseous form of matter, which I have termed transpirability. The constancy of these relations,



or of the transpiration times, has been observed for several of the gases for tube resistances varying in amount from 1 to 1000. These relations, there is reason to believe, are more simple in their expression than the densities of the gases. The following relations are particularly remarkable :—

The velocity of hydrogen is exactly double that of nitrogen and carbonic oxide.

The velocities of nitrogen and oxygen are inversely as the specific gravities of these gases.

The velocity of binoxide of nitrogen is the same as that of nitrogen and carbonic oxide.

The velocities of carbonic acid and protoxide of nitrogen are equal, and directly proportional to their specific gravities, when compared with oxygen.

The velocity of protocarburetted hydrogen is 0·8, that of hydrogen being 1.

The velocity of chlorine appears to be  $1\frac{1}{2}$  that of oxygen ; of bromine vapour and sulphuric acid vapour the same as that of oxygen.

Ether vapour appears to have the same velocity as hydrogen gas.

Olefiant gas, ammonia, and cyanogen to have equal or nearly equal velocities, which approach closely to double the velocity of oxygen.

Hydrosulphuric acid gas and bisulphide of carbon vapour appear to have equal or nearly equal velocities.

The compounds of methyl appear to have a less velocity than the corresponding compounds of ethyl, but to be connected by a certain constant relation.

2. The resistance of a capillary tube of uniform bore to the passage of any gas is directly proportional to the length of the tube.

3. The velocity of passage of equal volumes of air of the same temperature but of different densities or elasticities, is directly proportional to the density.

4. Rarefaction by heat has a similar and precisely equal effect in diminishing the velocity of the transpiration of equal volumes of air, as the loss of density and elasticity by diminished pressure has.

5. A greater resistance in the capillary is required to bring out the third result, or the law of densities, than appears necessary for the first and second results ; and a resistance still further increased, and the highest of all, to bring out the fourth result or the law of temperatures.

6. Finally, it will be remarked throughout, that transpiration is promoted by density, and equally whether the increased density is due to compression, to cold, or to the addition of an element in combination, as the velocity of oxygen is increased, by combining it with carbon without change of volume, in carbonic acid gas.



It was no part of my plan to investigate the passage of gases through tubes of great diameter, and to solve pneumatic problems of actual occurrence, such as those offered in the distribution of coal-gas by pipes. But I may state that the results must be similar, with truly elastic gases such as air and carburetted hydrogen, whether the tubes are capillary or many inches in diameter, provided the length of the tube is not less than 4000 times its diameter, as in the long glass capillaries of my early experiments. The small propulsive pressure applied to coal-gas is also favourable to transpiration, as well as the great length of the mains; and I should therefore expect the distribution of coal-gas in cities to exemplify approximately the laws of gaseous transpiration. The velocity of coal-gas should be 1.575, that of air being 1, under the same pressure (p. 201). And with a constant propulsive pressure in the gasometer, the flow of gas should increase in volume with a rise of the barometer or with a fall in temperature, directly in proportion to the increase of its density from either of these causes.

## XVI.

ON THE MOLECULAR MOBILITY OF GASES.<sup>1</sup>

From *Phil. Trans.* 1863, pp. 385-405. [*Chemical News*, viii. 1863, pp. 79-81; *Paris Comptes Rendus*, lvii. 1863, pp. 181-192; *Pharmaceut. Journ.*, v. 1864, pp. 166-171; *Poggendorf, Annal.* cxx. 1863, pp. 415-425.]

THE molecular mobility of gases will be considered at present chiefly in reference to the passage of gases, under pressure, through a thin porous plate or septum, and to the partial separation of mixed gases which can be effected, as will be shown, by such means. The investigation arose out of a renewed and somewhat protracted inquiry regarding the diffusion of gases (which depends upon the same molecular mobility), and has afforded certain new results which may prove to be of interest in a theoretical as well as in a practical point of view.

In the Diffusiometer, as first constructed, a plain cylindrical glass tube, about 10 inches in length and rather less than an inch in diameter, was simply closed at one end by a porous plate of plaster of Paris, about one-third of an inch in thickness, and was thus converted into a gas-receiver.<sup>2</sup> A superior material for the porous plate has since been found in the artificially compressed graphite of Mr. Brockedon, of the

<sup>1</sup> Received (i.e. by the Royal Society) May 7,—Read June 18, 1863.

<sup>2</sup> "On the Law of the Diffusion of Gases," *ante*, pp. 44-70 (*Trans. of the Royal Society of Edinburgh*, vol. xii. p. 222; or *Phil. Mag.* 1834, vol. ii. pp. 175, 269, 351).



quality used for making writing-pencils. This material is sold in London in small cubic masses about 2 inches square. A cube may easily be cut into slices of a millimetre or two in thickness by means of a saw of steel spring. By rubbing the surface of the slice without wetting it upon a flat sand-stone, the thickness may be further reduced to about one-half of a millimetre. A circular disc of this graphite, which is like a wafer in thickness but possesses considerable tenacity, is attached by resinous cement to one end of the glass tube above described, so as to close it and form a diffusimeter (fig. 1). The tube is filled with hydrogen gas over a mercurial trough, the porosity of the graphite plate being counteracted for the time by covering it tightly with a thin sheet of gutta percha (fig. 2). On afterwards removing the latter, gaseous diffusion immediately takes place through the pores of the graphite. The whole hydrogen will leave the tube in forty minutes or an hour, and is replaced by a much smaller proportion of atmospheric air (about one-fourth), as is to be expected from the law of the diffusion of gases. During the process, the mercury will rise in the tube, if allowed, forming a column of several inches in height—a fact which illustrates strikingly the intensity of the force with which the interpenetration of different gases is effected. Native graphite is of a lamellar structure, and appears to have little or no porosity. It cannot be substituted for the artificial graphite as a diffusion-septum. Unglazed earthenware comes next in value to graphite for that purpose.

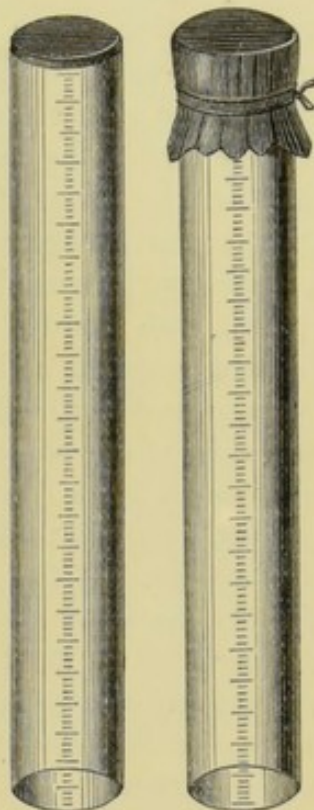
The pores of artificial graphite appear to be really so minute, that a gas *in mass* cannot penetrate the plate at all. It seems that molecules only can pass; and they may be supposed to pass wholly unimpeded by friction, for the smallest pores that can be imagined to exist in the graphite must be tunnels in magnitude to the ultimate atoms of a gaseous body. The sole motive agency appears to be that intestine movement of molecules which is now generally recognised as an essential property of the gaseous condition of matter.

According to the physical hypothesis now generally received,<sup>1</sup> a gas

<sup>1</sup> D. Bernoulli, J. Herapath, Joule, Krönig, Clausius, Clerk Maxwell, and Cazin. The merit of reviving this hypothesis in recent times, and first applying it to the facts of gaseous diffusion, is fairly due to Mr. Herapath. See *Mathematical Physics*, in two volumes, by John Herapath, Esq. (1847).

FIG. 1.

FIG. 2.





is represented as consisting of solid and perfectly elastic spherical particles or atoms, which move in all directions, and are animated with different degrees of velocity in different gases. Confined in a vessel, the moving particles are constantly impinging against its sides and occasionally against each other, and this contact takes place without any loss of motion, owing to the perfect elasticity of the particles. If the containing vessel be porous, like a diffusimeter, then gas is projected through the open channels, by the atomic motion described, and escapes. Simultaneously the external air is carried inwards in the same manner, and takes the place of the gas which leaves the vessel. To this atomic or molecular movement is due the elastic force, with the power to resist compression, possessed by gases. The molecular movement is accelerated by heat and retarded by cold, the tension of the gas being increased in the first instance and diminished in the second. Even when the same gas is present both within and without the vessel, or is in contact with both sides of our porous plate, the movement is sustained without abatement—molecules continuing to enter and to leave the vessel in equal number, although nothing of the kind is indicated by change of volume or otherwise. If the gases in communication be different but possess sensibly the same specific gravity and molecular velocity, as nitrogen and carbonic oxide do, an interchange of molecules also takes place without any change in volume. With gases opposed of unequal density and molecular velocity, the permeation ceases of course to be equal in both directions.

These observations are preliminary to the consideration of the passage through a graphite plate, in one direction only, of gas under pressure, or under the influence of its own elastic force. We are to suppose a vacuum to be maintained on one side of the porous septum, and air or any other gas, under a constant pressure, to be in contact with the other side. Now a gas may pass into a vacuum in three different modes, or in two other modes besides that immediately before us.

1. The gas may enter the vacuum by passing through a minute aperture in a thin plate, such as a puncture in platinum foil made by a fine steel point. The rate of passage of different gases is then regulated by their specific gravities, according to a pneumatic law which was deduced by Professor John Robison from Torricelli's well-known theorem of the velocity of efflux of fluids. A gas rushes into a vacuum with the velocity which a heavy body would acquire by falling from the height of an atmosphere composed of the gas in question, and supposed to be of uniform density throughout. The height of the uniform atmosphere would be inversely as the density of the gas, the atmosphere of hydrogen, for instance, sixteen times higher than that of oxygen. But as the velocity acquired by a heavy body in falling is not directly



as the height, but as the square root of the height, the rate of flow of different gases into a vacuum will be inversely as the square root of their respective densities. The velocity of oxygen being 1, that of hydrogen will be 4, the square root of 16. This law has been experimentally verified.<sup>1</sup> The relative times of the effusion of gases, as I have spoken of it, are similar to those of molecular diffusion; but it is important to observe that the phenomena of effusion and diffusion are distinct and essentially different in their nature. The effusion movement affects masses of gas, the diffusion movement affects molecules; and a gas is usually carried by the former kind of impulse with a velocity many thousand times as great as is demonstrable by the latter.

2. If the aperture of efflux be in a plate of increased thickness, and so becomes a tube, the effusion-rates are disturbed. The rates of flow of different gases, however, assume again a constant ratio to each other when the capillary tube is considerably elongated, when the length exceeds the diameter by at least 4000 times. These new proportions of efflux are the rates of the "Capillary Transpiration" of gases.<sup>2</sup> The rates are found to be the same in a capillary tube composed of copper as they are in glass, and appear to be independent of the material of the capillary. A film of gas no doubt adheres to the surface of the tube, and the friction is really that of gas upon gas, and is consequently unaffected by the tube-substance. The rates of transpiration are not governed by specific gravity, and are indeed singularly unlike the rates of effusion.

The transpiration-velocity of oxygen being 1, that of chlorine is 1.5, that of hydrogen 2.26, of ether vapour the same or nearly the same as that of hydrogen, of nitrogen and carbonic oxide half that of hydrogen, of olefiant gas, ammonia, and cyanogen 2 (double or nearly double that of oxygen), of carbonic acid 1.376, and of the gas of marshes 1.815. In the same gas the velocity of transpiration increases with increased density, whether occasioned by cold or pressure.

The transpiration-ratios of gases appear to be in direct relation with no other known property of the same gases, and they form a class of phenomena remarkably isolated from all else at present known of gases.

There is one property of transpiration immediately bearing upon permeation of the graphite plate by gases. The capillary offers to the passage of gas a resistance analogous to that of friction, proportional to the surface, and consequently increasing as the tube or tubes are multiplied in number and diminished in diameter, with the area of discharge preserved constant. The resistance to the passage of liquid through a capillary was observed by Poiseuille to be nearly as the fourth power of

<sup>1</sup> "On the Motion of Gases," *ante*, p. 88 (*Phil. Trans.* 1846, p. 573).

<sup>2</sup> *Ante*, p. 108; also p. 162 (*Phil. Trans.* 1849, p. 349).



the diameter of the tube. In gases the resistance also rapidly increases; but in what ratio, has not been observed. The consequence, however, is certain, that as the diameter of the capillaries may be diminished beyond any assignable limit, so the flow may be retarded indefinitely, and caused at last to become too small to be sensible. We may then have a mass of capillaries of which the passages form a large aggregate, but are individually too small to allow a sensible flow of gas under pressure. A porous solid mass may possess the same reduced permeability as the congeries of capillary tubes. Indeed, the state of porosity described appears to be more or less closely approached by all loosely aggregated mineral masses, such as lime-plaster, stucco, chalk, baked clay, non-crystalline earthy powders like hydrate of lime or magnesia compacted by pressure, and in the highest degree perhaps by artificial graphite.

3. A plate of artificial graphite, although it appears to be practically impermeable to gas by either of the two modes of passage previously described, is readily penetrated by the agency of the molecular or diffusive movement of gases. This appears on comparing the time required for the passage through the plate of equal volumes of different gases under a constant pressure. Of the three gases, oxygen, hydrogen, and carbonic acid, the time required for the passage of an equal volume of each through a capillary glass tube, in similar circumstances as to pressure and temperature, was formerly observed to be as follows:—

	Time of capillary transpiration of equal volumes.
Oxygen, . . . . .	1
Hydrogen, . . . . .	0·44
Carbonic acid, . . . . .	0·72

Now through a plate of graphite, half a millimetre in thickness, the same gases were observed to pass, under a constant pressure of a column of mercury of 100 millimetres in height, in times which are as follows:—

	Time of molecular passage.	Square root of density (oxygen 1).
Oxygen, . . . . .	1	1
Hydrogen, . . . . .	0·2472	0·2502
Carbonic acid, . . . . .	1·1886	1·1760

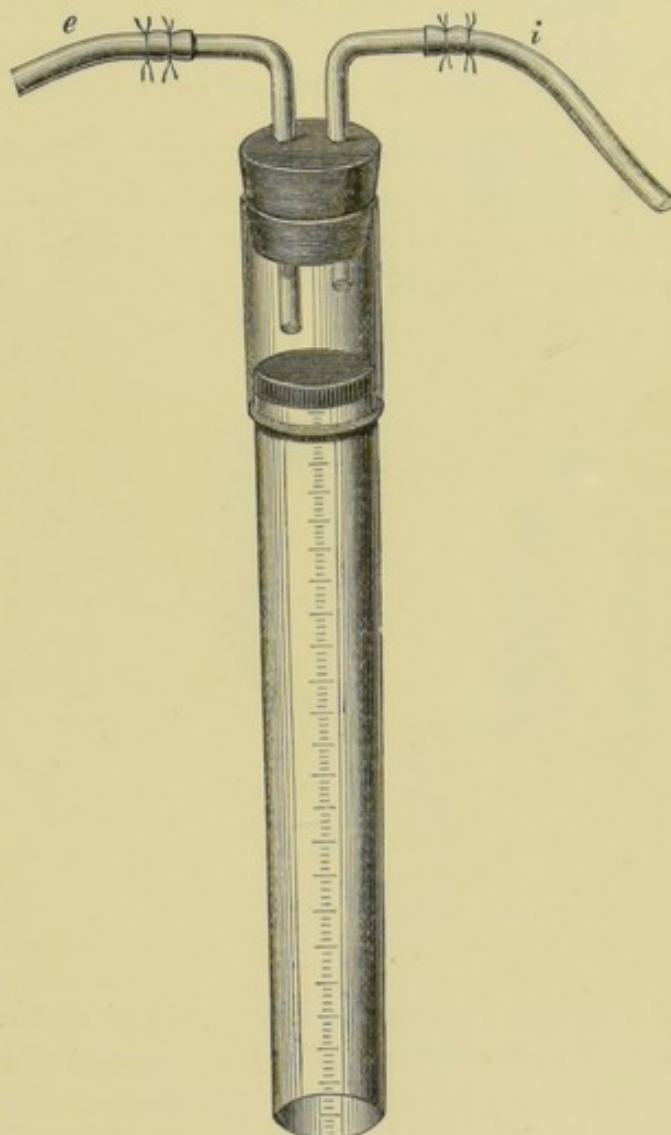
It appears that the times of passage through the graphite plate have no relation to the capillary transpiration-times of the same gases as first quoted. The new times in question, however, show a close relation to the square roots of the densities of the respective gases, as is seen in the last Table; and they so far agree with theoretical *times of diffusion* usually ascribed to the same gases.

These results were obtained by means of the graphite diffusiometer,



already referred to, which was a plain glass tube about 22 millimetres in diameter, closed at one end by the graphite plate. In order to conduct gas to the upper surface of the graphite plate, a little chamber was formed above the plate, to which the gas was conveyed in a moderate stream by the entrance-tube *e* (fig. 3); while the gas brought in

FIG. 3.



excess was constantly escaping into the air by the open issue-tube *i*. The chamber was formed of a short piece of glass tube, about two inches in length, cemented over the upper end of the diffusiometer. The upper opening of this short tube was closed by a cork perforated for the entrance and exit tubes. It will be observed that by this arrangement the upper surface of the graphite plate was constantly swept by a stream of gas, which was under no additional pressure beyond that of the atmosphere, a free escape being allowed by the exit-tube. The gas also was always dried before reaching the chamber. The diffusiometer stood over mercury, and was raised or lowered by the

lever movement introduced by Professor Bunsen in his very exact experiments upon gaseous diffusion.<sup>1</sup> To obtain the pressure of 100 millimetres of mercury, the diffusiometer was first entirely filled with mercury and then raised in the trough. Gas gradually entered till the column of mercury in the tube fell to 100 millimetres. The mercury was then maintained at this height, but gradually raising the tube in proportion as gas continued to enter and the mercury to fall, so as to maintain a constant difference of level of 100 millimetres, as observed by the graduation

<sup>1</sup> Bunsen's *Gasometry*, by Roscoe.



inscribed upon the tube itself, between the level of the mercury in the tube and trough. The experiment consisted in observing the time in seconds which the mercury took to fall 10 millimetre divisions with each gas. The constant volume of gas which entered was 2.2 cubic centimetres (0.1342 cubic inch). Two experiments were made with each gas.

Oxygen entered in 898 and 894 seconds; mean 896 seconds.

Hydrogen in 222 and 221 seconds; mean 221.5 seconds.

Carbonic acid in 1070 and 1060 seconds; mean 1065 seconds.

In such experiments the same gas exists on both sides, and also occupies the pores of the diaphragm. But the molecular movement within the pores in a downward direction is not fully balanced by the molecular movement in an upward direction, owing to the less tension, by 100 millimetres, of the gas below the diaphragm and within the tube

FIG. 4.

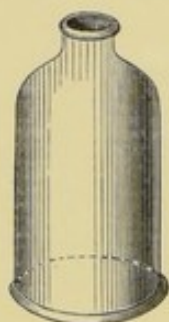
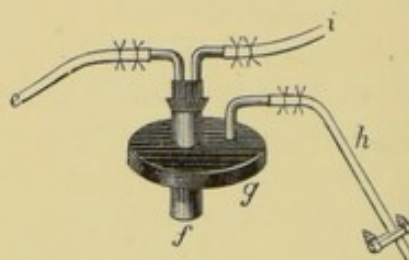


FIG. 5.



FIG. 6.



than the gas above and without. The influx of gas indicates the difference of molecular movement in opposite directions. Taking the full tension of the gas above the diaphragm at 760 millimetres, that below would be 660 millimetres, and the movement downwards and that upwards are represented by these numbers respectively.

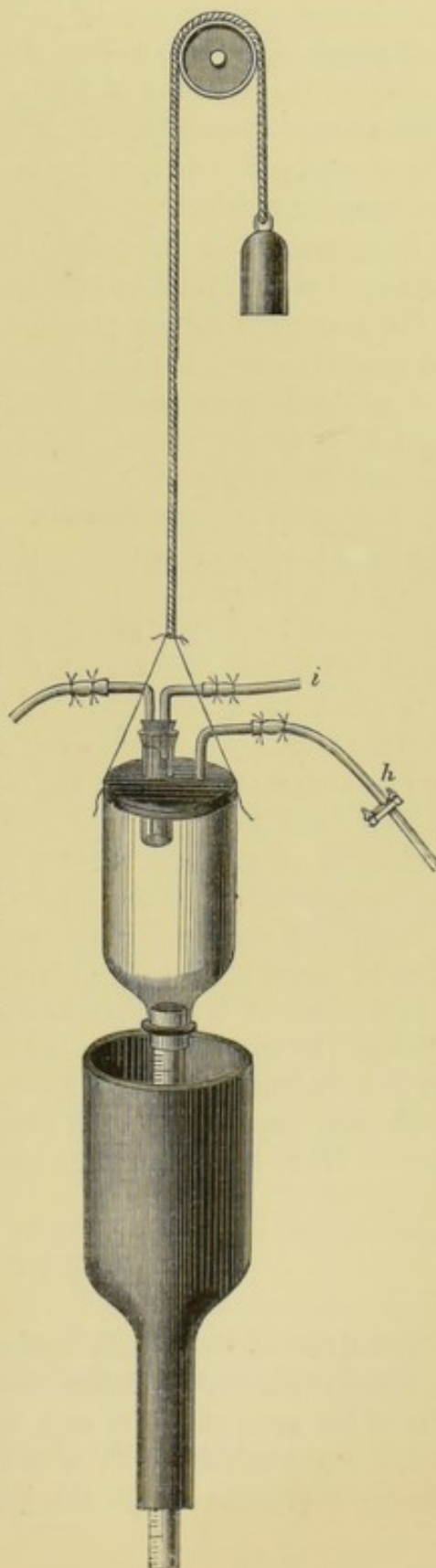
To increase the inequality of tension and favour the passage of gas through the graphite plate, a diffusion-tube was now used, 48 inches in length, or of the dimensions of a barometer-tube, by which a Torricellian vacuum could be commanded. The pneumatic trough in which this gas-tube was suspended consisted of a pipe of gutta percha of equal length, closed at the bottom by a cork, and widening into a funnel-form at the top. In one modification of the instrument it was found convenient to cement a capillary glass tube to the side of the glass diffusio-



meter, within about 15 millimetres of the upper end of the tube. An opening into the upper part of the glass tube was thus obtained, by means of which the gas contained in the diffusiometer could escape when the latter was depressed in the mercurial trough. A flexible tube with clip was attached to the capillary tube referred to, so that the latter could be closed. From the same opening a specimen of the gas contained in the diffusiometer could be drawn when required for examination.

In another and more serviceable modification of this barometrical diffusiometer a large space was obtained above the mercurial column by surmounting the long glass tube, unprovided with a graphite plate by a glass jar about half a litre in capacity. This jar was more correctly a small bell jar (fig. 4) open at top. It was fitted in an inverted position, as in fig. 5, to the open end of the long glass tube *d*, by means of a cork and cement. The large upper opening was closed by a circular plate of gutta percha (fig. 5), about 10 millimetres, or nearly half an inch, in thickness. This disc of gutta percha had two perforations at *f* and *g* (fig. 6), the former of which was fitted above with a wide glass tube. The tube *f* was closed below by the plate of graphite, and above with a perforated cork carrying a quill tube, *e*. This quill tube was the entrance-tube for gas, and was accompanied by the usual issue-tube, *i*. The other aperture in the gutta percha cover was fitted with a plain quill tube, *h*, which did not descend below the level of the gutta percha, and formed

FIG. 7.





a tube of exit. No difficulty was found in making all these junctions air-tight, by applying the heated blade of a knife to fuse the gutta percha in contact with the glass. Gutta percha is indeed of no ordinary value in the construction of pneumatic apparatus. The graphite plate itself required to be not less than 1 millimetre in thickness, in order to support the pressure of a whole atmosphere, to which it is exposed in the present apparatus. This barometrical diffusiometer is supported from above by a cord passing over a pulley, and is duly counterpoised by a hanging weight.

In operating, the first point is to expel the air from the barometer-tube and upper chamber. The instrument (fig. 7, p. 217) is sunk completely in the mercurial trough previously described, till the whole is filled, and mercury enters the quill tube of exit, *h*. The caoutchouc extension of this tube is then closed by a pinch. The diffusiometer is now elevated 30 or 40 inches, when the mercury sinks in the glass tube till it comes to stand at the barometric height for the time, leaving the upper chamber entirely vacuous. The gas to be tried has in the meantime been made to stream over the upper surface of the graphite plate, exactly as in the experiment with the former diffusiometer. The graphite is permeated by the gas, and the mercury in the diffusiometer-tube begins to fall, but it now falls slowly, owing to the considerable vacuous space to be filled. It is allowed to fall about half an inch, and the exact time is then noted, by a watch, when the mercury passes a certain point in the graduation of the tube, and again when the mercury descends to another fixed point an inch or two below the former. The time of permeation of a certain volume of gas is thus ascertained in seconds. The experiment is immediately repeated with two or more gases in succession, in similar circumstances as to pressure, and with great care taken to insure uniformity of temperature during the whole period.

In a series of four experiments made with hydrogen, the mercury fell from 758 to 685 millims. (29.9 inches to 27 inches) in 252, 256, 254, and 256 seconds; mean 254.5 seconds.

In three experiments with oxygen the mercury fell through the same space in 1019, 1025, and 1024 seconds; mean 1022.7 seconds:—

$$\frac{1022.7}{254.5} = 4.018.$$

The times of these gases appear therefore to be as 1 to 4.018, while the times calculated as being inversely as the square root of the densities of the same gases are as 1 to 4.

On another day, with a different height of the barometer, four gases were passed through the graphite plate in succession through a



somewhat shorter range, namely, from 754 to 685 millims. (29·7 to 27 inches).

The time of permeation of air was 884 and 885 seconds; mean 884·5 seconds.

The time of carbonic acid was 1100 and 1106 seconds; mean 1103 seconds.

The time of oxygen was 936, 924, and 930 seconds; mean 930 seconds.

The time of hydrogen was 229, 235, and 335 seconds; mean 233 seconds.

These times of permeation are in the following proportion :—

Times of the permeation of equal volumes of gas through graphite.					
Oxygen,	.	.	.	.	1
Air,	.	.	.	.	0·9501
Carbonic acid,	.	.	.	.	1·1860
Hydrogen,	.	.	.	.	0·2505

These numbers approach so closely to the square roots of the density, or the theoretical diffusion-times of the same gases, namely, oxygen 1, air 0·9507, carbonic acid 1·176, and hydrogen 0·2502, that they may be held to indicate the prevalence of a common law. They exclude the idea of capillary transpiration, which gives to the same gases entirely different numbers.

The movement of gases through the graphite plate appears to be solely due to their own proper molecular motion, quite unaided by transpiration. It seems to be the simplest possible exhibition of the molecular or diffusive movement of gases. This pure result is to be ascribed to the wonderfully fine (minute) porosity of the graphite. The interstitial spaces appear to be sufficiently small to extinguish capillary transpiration entirely. The graphite plate is a pneumatic sieve which stops all gaseous matter in mass, and permits molecules only to pass.

It is worth observing what result a plate of more open structure, such as stucco, will give in comparison with graphite. For the graphite plate, a cylinder of stucco, 12 millims. in thickness, was accordingly substituted, and gas allowed to percolate at both low and high pressures, as in the former experiments with graphite.

1. Under a constant pressure of 100 millims. of mercury, gas was allowed to enter through 100 millim. divisions of the diffusiometer.

With air, the time in two experiments was 515, and again 515 seconds.

With hydrogen 178 seconds, and again 178 seconds :

$$\frac{515}{178} = 2·894.$$



2. Under a pressure beginning with 710 millims. (28 inches) and ending with 660 millims. (26 inches), the time with air was 374 and 375 seconds; mean 374.5 seconds. The time with hydrogen was 129 and 130 seconds; mean 129.5 seconds:

$$\frac{374.5}{129.5} = 2.891.$$

The stucco cylinder of the preceding experiments had been dried over sulphuric acid, without the application of heat. It was further desiccated at 60° C. for twenty-four hours, in order to find whether the porosity would be altered. The ratio of the time of hydrogen to that of air now became 1 to 2.788 at the lower degree of pressure, and 1 to 2.744 at the higher degree of pressure.

It will be observed that the theoretical diffusion-ratio of hydrogen to air, which is 1 to 3.80, is greatly departed from in these experiments with stucco. The ratio appears to be tending to the proportion of the transpiration-times of the same gases, namely, 1 to 2.04. In an experiment recorded by Bunsen, the ratio observed between the times of hydrogen and oxygen in passing, under a small degree of pressure, through stucco dried by heat, was so low as 1 to 2.73, the stucco being probably less dense than in the experiments before us.

With stucco the permeation of gases *under pressure* appears to be a mixed phenomenon—to some extent molecular diffusion into a vacuum, such as holds with the plate of graphite, but principally capillary transpiration of gas in mass.

The diffusimeter was now closed by a plate of white biscuitware, 2.2 millims. in thickness. The time of fall at the constant pressure of 100 millims., through a range of forty divisions of the diffusimeter, was, for air 1210 seconds, for hydrogen 321 seconds.

$$\begin{array}{rcl} \text{Air,} & . & 1210 \\ \text{Hydrogen,} & . & 321 \end{array} = 3.769.$$

The time, again, from 736 to 685 millims. (29 to 27 inches) was, for air 685 and 684 seconds; mean 684.5 seconds; and for hydrogen 183, 183, and 184 seconds; mean 183.3 seconds.

$$\begin{array}{rcl} \text{Air,} & . & 684.5 \\ \text{Hydrogen,} & . & 183.5 \end{array} = 3.754.$$

The stoneware was evidently of a much closer texture than stucco, and the ratio appears again less influenced by capillary transpiration. In fact the molecular ratio of 1 to 3.80 is approached within 1 per cent. Biscuitware therefore appears to be but little inferior to graphite for such experiments, a circumstance which is important, as the latter is



not easily procured, and cannot be converted into tubes and other convenient forms like plastic clay.

Further, the rate of passage of gas through the plate of graphite appears to be closely proportional to the pressure. The resistance was increased by augmenting the thickness of the plate to 2 millims.; and with air and hydrogen at a pressure maintained constant at 50 and 100 millims., the time was observed that the gas took to enter 10 linear millimetre divisions of the tube.

	Seconds.	Ratio.
Air under pressure of 100 millims.,	1925	1
Air under pressure of 50 millims.,	3880	2.015
Hydrogen under pressure of 100 millims.,	497	1
Hydrogen under pressure of 50 millims.,	1022	2.056

By halving the pressure the time of passage is doubled or increased somewhat more. Greater pressures might probably give a rate of passage corresponding more exactly with the pressure.

The ratio between the comparative times of the two gases in the last experiments may also be noticed, the observations having been made in similar circumstances as to pressure and temperature.

Barom. 760 millims. ; Therm. 12° 9 C.	At pressure of 50 millims.
Air, . . . . .	3880
Hydrogen, . . . . .	1022
	$\frac{3880}{1022} = 3.796.$
Barom. 760 millims. ; Therm. 12° 9 C.	At pressure of 100 millims.
Air, . . . . .	1925
Hydrogen, . . . . .	497
	$\frac{1925}{497} = 3.873.$

The observation was repeated at the pressure of 100 millims. with barometer at 754 millims. and thermometer at 10° C.

Air, . . . . .	1920
Hydrogen, . . . . .	498
	$\frac{1920}{498} = 3.855.$

The velocity of hydrogen appears, as usual, to be nearly 3.8 times that of air ;  $\frac{1}{\sqrt{0.6926}} = 3.7994.$

An experiment was made at the same time as the former series upon a mixture of 95 hydrogen and 5 air, which gave an unlooked-for result that led to a great deal of inquiry. It is known that such a mixture is effused through an aperture in a fine plate in a time which is as the square root of the density of the mixture, and therefore nearly the arithmetical mean of the two gases effused separately. But in transpiration by a capillary, a mixture of 95 hydrogen and 5 air requires a considerably longer time than the gases transpired separately. In fact 5 per cent. of



air retards the transpiration of hydrogen nearly as much as 20 per cent. of air would retard the effusion of hydrogen.<sup>1</sup> Now the mixture in question permeates the graphite plate in 527.5 seconds, while the calculated mean of the times of the two gases is 562.1 seconds.

The mixture has therefore passed neither in the effusion time, nor in a longer time, as it would do by capillary transpiration, but, singular to say, in a time considerably shorter than either. The gas that came through was found by analysis to be *altered in composition*. It contained more hydrogen and less air than the original mixture. Hence it passed through with increased rapidity. On consideration it appeared that such a separation of the mixed gases must follow as a consequence of the movement being molecular. Each gas is impelled by its own peculiar molecular force, which, as has been seen, is capable of causing hydrogen to permeate the graphite plate about 3.8 times as rapidly as air.

Each gas may permeate a graphite plate into a vacuum with the same relative velocity as it diffuses into another gaseous atmosphere, but it remains a question whether the velocities of permeation and diffusion are absolutely as well as relatively the same. To illustrate this point, hydrogen and air were first allowed to permeate into a vacuum, and then to diffuse into each other, through the same graphite plate, which was 1 millim. in thickness. The plate was a circular disc of 22 millims. in diameter.

The mercurial column in the barometrical diffusiometer fell from 762 to 685 millims. (30 inches to 27) with air in 878 seconds, and with hydrogen in 233 seconds.

$$\begin{array}{rcl} \text{Air,} & . & . & 878 \\ \text{Hydrogen,} & . & . & 233 \end{array} = 3.768.$$

The volume of gas which produced this effect was found by the calibration of the tube to be 8.85 cub. centims. Hence 1.22 cub. centim. of the hydrogen entered the diffusiometer in 60 seconds, or one minute. But the pressure under which the hydrogen gas entered was the mean of 762 to 685 millims., or 723.5 millims.; while a whole atmosphere (the height of the barometer at the time) was 765 millims. The volume of the gas has therefore to be increased as 723.5 to 765 to give the full action of a vacuum. The volume becomes 1.289 cub. centim. in one minute.

When the diffusiometer was filled with hydrogen and the gas allowed to diffuse into air, the rise of the mercury was pretty uniform for the first five minutes, being 15.5 millim. divisions in the first two minutes, 7 in the third minute, 7.5 in the fourth minute, and 7 in the fifth

<sup>1</sup> *Ante*, pp. 155, 156 : Table L. (*Philosophical Transactions*, 1846, p. 628).



minute, making 37 divisions in five minutes. But as in diffusion 1 air may be supposed to enter the tube for 3·8 hydrogen which escape, the hydrogen which diffused was more than 37 divisions, by  $\frac{1}{3\cdot8}$ , that is, by about 10 divisions. Hence 47 divisions of hydrogen have diffused into air in five minutes. These divisions measured, by the calibration of the tube, 6·215 cub. centims. One-fifth of this amount, that is, 1·243 cub. centim., diffused in one minute. The result of the whole is that in one minute there passed of hydrogen through the graphite plate,

1·289 cub. centim. by permeation into a vacuum,

1·243 cub. centim. by diffusion into air.

The numbers indicate a close approach to equality in the velocities of permeation into a vacuum and of diffusion into another gas, through the same porous diaphragm. The diffusion appears the slower of the two by a small amount; but this is as it should be, our estimate of the diffusion-velocity being certainly underrated; for the initial-diffusion, or even the diffusion in the first minute, must obviously be somewhat greater than the average of the first five minutes, which we have taken to represent it—the hydrogen necessarily diffusing out in a diminishing progression, or more slowly in proportion as air has entered the diffusometer. It is strictly the initial velocity of diffusion (that of the first second if it could be obtained) that ought to be compared with the percolation into a vacuum.

In fine, there can be little doubt left on the mind that the permeation through the graphite plate into a vacuum and the diffusion into a gaseous atmosphere, through the same plate, are due to the same inherent mobility of the gaseous molecule. They are the exhibition of this movement in different circumstances. In interdiffusion we have two gases moved simultaneously through the passages in opposite directions, each gas under the influence of its own inherent force; while with gas on one side of the plate and a vacuum on the other side, we have a single gas moving in one direction only. The latter case may be assimilated to the former if the vacuum be supposed to represent an infinitely light gas. It will not involve any error, therefore, to speak of both movements as gaseous diffusion,—the diffusion of gas into gas (double diffusion) in one case, and the diffusion of gas into a vacuum (single diffusion) in the other. The inherent molecular mobility may also be justly spoken of as the diffusibility or diffusive force of gases.

The diffusive mobility of the gaseous molecule is a property of matter fundamental in its nature, and the source of many others. The rate of diffusibility of any gas has been said to be regulated by its specific gravity, the velocity of diffusion having been observed to vary inversely as the square root of the density of the gas. This is true, but not in the



sense of the diffusibility being determined or *caused* by specific gravity. The physical basis is the molecular mobility. The degree of motion which the molecule possesses regulates the volume which the gas assumes, and is obviously one, if not the only, determining cause of the peculiar specific gravity which the gas enjoys. If it were possible to increase in a permanent manner the molecular motion of a gas, its specific gravity would be altered, and it would become a lighter gas. With the density is also associated the equivalent weight of a gaseous element, according to the doctrine of equal combining volumes.

*Diffusion of mixed gases into a vacuum, with partial separation*  
—*Atmolysis.*

*Oxygen and hydrogen.*—A diffusiometer of the same construction as that described (fig. 3, p. 215), with a graphite plate of 1 millim. in thickness, was now employed. The upper surface of the plate was swept by a current of the mixed gas proceeding from a gas-holder, the excess of gas being allowed to escape into the atmosphere, as usual, by an open exit-tube. The gas was drawn through the graphite by elevating the diffusiometer containing a column of mercury, from its well, so as to command a partial vacuum in the upper part of the tube. Care is taken that any gas left in the upper part of the diffusiometer-tube before the experiment begins, should be of the same composition as the gas to be allowed afterwards to enter, so that, on starting, the gas may be uniform in composition on both sides of the graphite plate. The height of the mercurial column, which measures the aspirating force of the diffusiometer, is preserved uniform by gradually raising the tube in the mercurial trough in proportion as gas enters and the mercury falls. The diffusiometer is suspended from the roof of the apartment by a cord passing over a pulley and properly weighted, as in former experiments.

The mixture to be diffused consisted of nearly equal volumes of oxygen and hydrogen. The effect of different degrees of pressure on the amount of separation produced was first observed. It will be seen that as the pressure or aspirating force is increased the amount of separation becomes greater. Barom. 0·759 millim.; therm. 18°·3 C.

Diffusion into a partial vacuum.

	Oxygen.	Hydrogen.
Composition of original mixture in 100 parts, . . .	49·3	50·7
Diffused by pressure of 100 millims., . . .	47·0	53·0
Diffused by pressure of 400 millims., . . .	37·5	62·5
Diffused by pressure of 673 millims. (mean of 635-710),	26·4	73·6
Diffused by pressure of 747 millims. (mean of 736-759),	22·8	77·2

In the last observation, or that with the greatest pressure (747 millims.), the oxygen is reduced to 22·8 per cent. and the hydrogen



increased to 77.2 per cent. of the diffused mixture, showing a considerable separation. The mixed gases appear to make their way through the graphite plate independently, each following its own peculiar rate of diffusion.

But it is only under the aspiration of a complete vacuum that the separation can attain its maximum, and reach the full difference that may exist between the special diffusibilities of the two gases. The reason is that while we have the original mixture on both sides of the plate, and of equal tension, the gases are not at rest, but diffusion is proceeding as actively through the plate in opposite directions, as if the gases were different or the tension unequal on the two sides. This is a condition of the molecular mobility of gases (p. 212). The tension therefore being supposed to differ by 100 millims. only, as when the gas above the plate was of 759 millims. tension, and below of 659 millims. (in the first experiment of the last series), then 100 volumes only out of 759 of the mixture are subject to separation. But while these 100 volumes press through they are accompanied by 659 volumes of unchanged mixture. The latter 659 volumes are replaced by an equal bulk of unchanged mixture diffused from below, so that the volumes are not disturbed by this portion of the molecular interchange.

The amount of separation, then, attainable by transmitting a mixed gas through a porous diaphragm by pressure will be in proportion to the pressure—that is, to the inequality of tension on different sides of the diaphragm.

*Oxygen and Nitrogen.*—The separation of the gases of the atmosphere by transmission through the graphite plate has a peculiar interest.

In an experiment resembling those last described, atmospheric air was swept over the upper surface of a graphite plate having a thickness of 2 millims. The gas that penetrated into the vacuum contained, as was to be expected, the lighter and more diffusible constituent in excess. It gave by the pyrogallic acid and potash process of Liebig,

Oxygen,	.	.	.	.	.	20
Nitrogen,	.	.	.	.	.	80

This was an increase in the nitrogen of quite 1 per cent.; for air, analysed for comparison at the same time and in the same manner, gave oxygen 21.03 and nitrogen 78.97.

It may be legitimately inferred from the last experiment, that if pure hydrogen in a diffusiometer were allowed to diffuse into the atmosphere through a porous plate, the portion of air which then enters the diffusiometer should also have its composition disturbed. A diffusion of hydrogen through a graphite plate was interrupted before completion. The air which had entered was found to consist of



Oxygen,	.	.	.	.	19.77
Nitrogen,	.	.	.	.	80.23
					<hr/> 100.00

The increase of nitrogen is 1.23 per cent.

While the nitrogen is increased and the oxygen diminished in the air which makes its way under pressure through the graphite, the converse effect must be produced on the air left behind. But the latter result of atmolysis cannot be made apparent without a change in the mode of experimenting.

With the view of effecting an increase in the proportion of oxygen, a volume of air, confined in a jar suspended over mercury, was allowed to communicate through a graphite plate of 2 millims. in thickness, with a vacuum sustained by means of an air-pump, the gauge being about 1 inch only below the height of the barometer during the whole time of experimenting.

The jar containing the air to be atmolysed was formed of a plain glass cylinder, open at both ends, and about 400 millims. in height (15.75 inches). The upper end was closed by a thick plate of gutta percha cemented on. This plate was itself penetrated by a wide glass tube, descending about an inch into the jar. The last tube carried the graphite disc, which was 27 millims. (1.04 inch) in diameter, sufficient to close the lower end of the tube upon which it was cemented. The other or upper end of the same tube was fitted with a cork and quill tube, and was put into communication with a large bell jar upon the plate of the air-pump.

The permeation was slow, owing to the unusual thickness of the graphite plate, occupying three hours to drain away one-half of the original volume of air in the jar. The air remaining behind in the jar was examined in a series of experiments, in which the original volume was reduced to one-half, one-fourth, one-eighth, and one-sixteenth.

The residual air, reduced to one-half, gave in two experiments 21.4 and 21.57 per cent. of oxygen, the air of the atmosphere being by the same analytical process 21 per cent.

Reduced to one-fourth of its volume, the residual air gave, in two experiments, 21.95 and 22.01 per cent. of oxygen.

Reduced to one-eighth of its volume, the air gave 22.54 per cent. of oxygen.

Reduced to one-sixteenth of its volume, the air gave 23.02 per cent. of oxygen. The proportion of oxygen had therefore increased about one-tenth in the last experiment, where the effect is greatest.

When the numbers are compared, it appears that by a reduction to half its volume the air gains about one-half per cent. of oxygen; when



this last air is reduced to one-half again, another half per cent. of oxygen is gained, and so on—the gain in the proportion of oxygen increasing in an arithmetical ratio, while the volume of air is diminished in a geometrical ratio, or as the powers of the number 2.

Reduction of 1 volume of air.		Proportion of oxygen per cent.	Increase of oxygen.
To 1	volume.....	21	0
To 0.5	volume.....	21.48	0.48
To 0.25	volume.....	21.98	0.98
To 0.125	volume.....	22.54	1.54
To 0.0625	volume.....	23.02	2.02

The densities of oxygen and nitrogen approach too nearly to admit of any considerable separation being effected by this method. The density of oxygen being taken as 1, that of nitrogen is 0.8785. The square roots of these numbers are 1 and 0.9373, which are inversely as the diffusive velocity of the two gases.

	Diffusive velocity.
Oxygen, . . . . .	1
Nitrogen, . . . . .	1.0669

The velocity of nitrogen therefore exceeds that of oxygen by about 6.7 per cent. Hence by a simple diffusion of a whole volume of air the oxygen could only be increased 6.7 per cent., according to theory. In experiments such as the preceding only one-half of the volume of the air is diffused, and consequently only one-half of the stated amount of concentration of oxygen could possibly be produced at each step. About three-fourths of the theoretical separation is actually obtained, although the apparatus works at an obvious disadvantage from the air within the jar being at rest.

This diffusive method of separation recalls the original observation of Döbereiner on the escape of hydrogen gas from a fissured jar standing over water, which will always hold its place in scientific history as the starting-point of the experimental study of gaseous diffusion. That observation proved to be an instance of double diffusion, air entering the jar by the fissure at the same time that hydrogen escaped by it—although, as Döbereiner looked upon the phenomenon, it was more akin to single diffusion or the passage of gas in one direction only.<sup>1</sup>

The atmolytic power of other diffusing plates was tested, besides the artificial graphite.

The barometrical diffusiometer already described was closed by a

<sup>1</sup> *Annales de Chimie*, 1825.



plate of *red unglazed earthenware* 4 millims. in thickness, which was attached to the glass by resinous cement.

Dry air was swept over the upper surface, as in operating with the graphite plate. With a mercurial column of 340 millims. falling to 200 millims., the air which entered was found to contain 79.45 per cent. of nitrogen, instead of 79. With a column of mercury, maintained at 508 millims. in the tube, the air entering contained 79.72 nitrogen, and with a column beginning at 761 millims., the full barometrical height, and falling to 679 millims. in seven minutes, the air entering contained 80.21 nitrogen. This is a full degree of separation, exceeding 1 per cent., while the time was greatly shorter than with graphite. Thermometer  $19^{\circ}5$  C.

With a diffusing plate of gypsum (stucco) 10 millims. in thickness, the proportion of nitrogen was also increased, although less considerably than with biscuitware. The standard proportion of nitrogen observed in atmospheric air being 78.99 per cent., the air drawn into the diffusio-meter was as follows:—

	Proportion of nitrogen per cent.
In air entering over column of 330—200 millims. mercury, . . . .	79.26
In air entering over column 508 millims., . . . .	79.32
In air entering over column 761—685 millims., . . . .	79.53
In air entering over column 761—685 millims., . . . .	79.69

The separation is sufficiently decided, and is certainly remarkable considering the comparatively loose texture of the stucco plate. The gas entered in the two last experiments in about one minute, which appears too rapid a passage, and not to be attended with increased separation, compared with the immediately preceding experiment, in which the pressure was less and the passage of the gas proportionally slower. In all such highly porous plates, we have always to apprehend the passage of a large proportion of the gas in the manner of capillary transpiration, where no separation takes place.

It may be concluded that all porous masses, however loose their texture, will have some effect in separating mixed gases moving through them under pressure. The air entering a room by percolating through a wall of brick or a coat of plaster will thus become richer in nitrogen, in a certain small measure, than the external atmosphere.

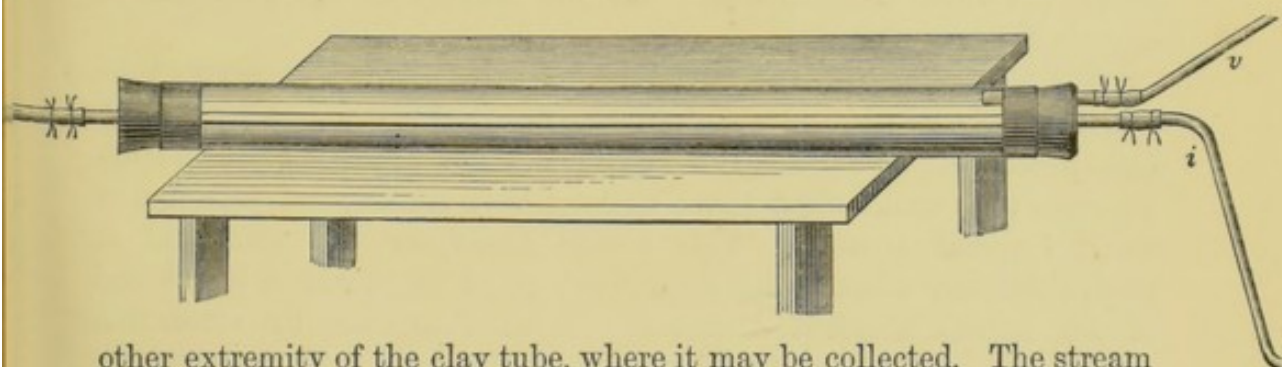
#### *The Tube Atmolyser.*

In the application of diffusion through a porous septum to separate mixed gases, as a practical analytical method, it is desirable that the process should be more rapid than it can be made with the use of graphite and other diffusing-plates of small size, and also that the process should if possible be a continuous one. Both objects are



attained in a considerable degree by adapting a tube of porous earthenware to the purpose. Nothing has been found to answer better than the long stalk of a Dutch tobacco-pipe used as the porous tube. A tube of this description, about two feet long and having an internal diameter of 2.5 millims., is fixed by means of perforated corks within a glass or metallic tube, a few inches less in length and about  $1\frac{1}{2}$  inch in diameter (*e, i* fig. 8), as in the construction of a Liebig condenser. A second quill tube (*v*) is inserted in one of the end corks, and affords the means of communication between the annular space and the vacuum of an air-pump. The external surface of the corks, and of those portions of the pipe-stalk which project beyond the enclosing tube, should be coated with a resinous varnish, to render them impermeable to air. Now, a good vacuum being obtained within the outer tube, and sustained by the action of an air-pump, the mixed gas is made to enter and traverse the clay tube. More or less of gas is drained off through the porous walls and pumped away, while a portion courses on and escapes by the

FIG. 8.



other extremity of the clay tube, where it may be collected. The stream of gas diminishes as it proceeds, like a river flowing over a pervious bed. The lighter and more diffusive constituent of the mixed gases is drawn most largely into the vacuum, leaving the denser constituent, in a more concentrated condition, to escape by the exit end of the clay tube. The more slowly the mixed gas is moved through that tube, the larger the proportion of light gas that is drained off into the vacuum, and the more concentrated does the heavy gas become. The rate of flow of the mixed gas can be commanded by either discharging it from a gas-holder, or drawing it into a gas-receiver, in either case by a regulated pressure.

To observe the effect of a more or less rapid passage through the tube atmolyser, the impelling pressure was varied so as to allow a constant volume of half a litre of atmospheric air to pass through and be collected in different periods of time. The clay tube used in these particular experiments was not a tobacco-pipe, but a wide unglazed tube about 431 millims. (17 inches) long and 19 millims. (0.75 inch) in



internal diameter. It was required to place so wide a tube in a vertical position, and to admit the air by the upper and draw it off by the lower extremity of the tube. The proportion of oxygen in the half-litre of air collected was as follows:—

	Oxygen per cent.		
	Experiment 1.	Experiment 2.	Mean.
When collected in 1 minute ...	21.00	...	...
When collected in 13 minutes...	22.33	22.25	22.29
When collected in 75 minutes...	22.77	23.02	22.89
When collected in 120 minutes...	23.25	23.22	23.23
When collected in 304 minutes...	23.54	23.51	23.53

The proportion of oxygen in the air circulated appears thus to increase with the slowness of its passage through the tube atmolyser. The proportion of air drawn into the air-pump vacuum must be very large when the time is protracted; but the additional concentration of oxygen appears small.

The preceding observations being made by means of a porous tube which may be considered wide and of considerable capacity with reference to its internal surface, the experiment was varied by substituting a porous tube about eight times as long, very narrow, and therefore of small internal capacity. This second atmolyser was composed of twelve ordinary tobacco-pipe stems, each about 10 inches in length and of 1.9 millim. internal diameter, connected together by vulcanized caoutchouc adapters so as to form a single tube. Having flexible joints, the tube was folded up and placed within a glass cylinder that could be exhausted. Air was then circulated through this atmolyser by the pressure of several inches of water. The instrument appeared to work with most advantage when the air delivered at the exit-tube amounted to about one-fourth of a litre per hour. A volume of 268 cubic centimetres, which had circulated in one hour, was found to contain 24.37 per cent. of oxygen. The current was then made slower, so that only 108 cub. centims. of gas passed and were collected in one hour, but with little further concentration of the oxygen. The result, however, is interesting as being the highest concentration of oxygen yet obtained by an instrument of this kind. The air collected was composed of

Oxygen,	.	.	.	24.52
Nitrogen,	.	.	.	75.48
				100.00



The increase of oxygen is 3.5 per cent.; that is an increase of 16.7 upon 100 oxygen originally present in the air.

With the single pipe-stalk, 24 inches long, first described, the oxygen of atmospheric air was concentrated about 2 per cent. when one litre was transmitted in one hour. Of 450 cub. centims. of air collected in that time, the composition proved to be

Oxygen,	.	.	.	23.12
Nitrogen,	.	.	.	76.88
				<hr/> 100.00

About 9 litres were drawn into the vacuum at the same time.

The separation of the gases of atmospheric air is a severe trial of the powers of the atmolyser, owing to the small difference in the specific gravities of these gases. But where a great disparity in density exists, the extent of the separation may become very considerable.

Several experiments were made upon a mixture of equal volumes of oxygen and hydrogen carried through the single tube atmolyser, 24 inches in length.

1. Of the mixture described, 7.5 litres entered the tube and 0.45 litre was collected in one experiment. The mixture was composed as follows:

	Oxygen.		Hydrogen.
Before traversing the atmolyser,	50	+	50
After traversing the atmolyser,	92.78	+	7.22

2. In another similar experiment, 14 litres of the mixed gas entered the tube and 0.45 litre was delivered in a period of two hours. The result was—

	Oxygen.		Hydrogen.
Before traversing the atmolyser,	50	+	50
After traversing the atmolyser,	95	+	5

Here the proportion of hydrogen is reduced from 50 to 5 per cent.

3. Of the explosive mixture, consisting of 1 volume oxygen and 2 volumes hydrogen, 9 litres were transmitted and 0.45 litre collected in one hour. The change effected was found to be as follows:—

	Oxygen.		Hydrogen.
Before traversing the atmolyser,	33.33	+	66.66
After traversing the atmolyser,	90.7	+	9.3

The result in such experiments is striking, as the gas ceases to be explosive after traversing the porous tube, and a lighted taper burns in it as in pure oxygen. A mixture of oxygen and hydrogen is not explosive till the hydrogen rises to 11 per cent.

To illustrate the analogy of diffusion into a vacuum with diffusion



into air, the outer glass tube of the diffuser was now withdrawn, and the porous tube of the instrument was exposed directly to the air of the atmosphere. A mixture of equal volumes of oxygen and hydrogen was again transmitted at the same rate of velocity as in experiment 1.

The gas analysed and collected was found to consist of

Oxygen,	.	.	.	.	51.75
Hydrogen,	.	.	.	.	5.47
Nitrogen,	.	.	.	.	42.78
					<hr/>
					100.00

And may be represented as containing

Oxygen,	.	.	.	.	40.38
Hydrogen,	.	.	.	.	5.47
Air,	.	.	.	.	54.15
					<hr/>
					100.00

A nearly similar concentration of the oxygen of the mixed gas is here observed as appeared in experiment 1; but the gas collected is now diluted with air which has entered by diffusion. The external air manifestly discharges the same function in the latter experiment which the air-pump vacuum discharged in the former experiment.

#### *Interdiffusion of Gases—double diffusion.*

The diffusiometer was much improved in construction by Professor Bunsen, from the application of a lever arrangement to raise and depress the tube in the mercurial trough; but the mass of stucco forming the porous plate in his instrument appears too voluminous, and, from being dried by heat, is liable to detach itself from the walls of the glass tube. The result obtained of 3.4 for hydrogen, which diverges so far from the theoretical number, is, however, no longer insisted upon by that illustrious physicist. It is indeed curious that my old experiments generally rather exceeded than fell short of the theoretical number for hydrogen;  $\sqrt{0.06926} = 3.7994$ . With stucco as the material, the cavities existing in the porous plate form about one-fourth of its whole bulk, and affect sensibly the ratio in question according as they are or are not included in the capacity of the instrument. Beginning the diffusion always with these cavities, as well as the tube, filled with hydrogen, the numbers now obtained with a stucco plate of 12 millims. in thickness and dried without heat, were 3.783, 3.8, and 3.739 when the volume of the cavities of the stucco is added to both the air and hydrogen volumes diffused; and 3.931, 3.949, and 3.883 when such addition is not made to these volumes. The graphite plate, on the other hand,



being very thin, and the volume of its pores too minute to require to be taken into account, its action is not attended with the same uncertainty. With a graphite plate of 2 millims. in thickness, the number for hydrogen into air was 3.876, instead of 3.8; and for hydrogen into oxygen 4.124, instead of 4. With a graphite plate of 1 millim. in thickness, hydrogen gave 3.993 to air 1. With a plate of the same material 0.5 millim. in thickness, the proportional number for hydrogen to air rose to 3.984, 4.068, and 4.067. An equally considerable departure from the theoretical number was observed when hydrogen was diffused into oxygen or into carbonic acid, instead of air. All these experiments were made with dry gases and over mercury. It appears that the numbers are most in accordance with theory when the graphite plate is thick, and the diffusion slow in consequence. If the diffusion be very rapid, as it is with the thin plates, something like a current is possibly formed within the channels of the graphite, taking the direction of the hydrogen and carrying back in masses a little air, or the slower gas, whatever it may be. I cannot account otherwise for the slight predominance which the lighter and faster gas appears always to acquire in diffusing through the porous septum.

*Interdiffusion of Gases without an intervening septum.*

The relative velocity with which different gases diffuse is shown by the diffusimeter, but the absolute velocity of the molecular movement cannot be ascertained by the same instrument. For that purpose it appears requisite that a gas should be allowed to diffuse into air through a wide opening.

In certain recent experiments, a heavy gas, such as carbonic acid, was allowed to rise by diffusion into a cylindrical column of air, pretty much as the saline solution is allowed to rise into a column of water in my late experiments upon the diffusion of liquids. This method of gaseous diffusion appears to admit of considerable precision, and deserves to be pursued further. A glass cylinder of 0.57 metre (22.44 inches) in height had the lower tenth part of its volume occupied with carbonic acid, and the upper nine-tenths with air, in a succession of experiments: thermometer 16° Cent. After the lapse of a certain number of minutes, the upper tenth part of the volume was drawn off from the top of the jar and examined for carbonic acid. Before the carbonic acid appeared above, it had ascended, that is, it had diffused a distance of 0.513 metre, or rather more than half a metre. After the lapse of five minutes, the carbonic acid so found in two experiments amounted to 0.4 and 0.32 per cent. respectively. In seven minutes, the carbonic acid observed was 1.02 and 0.90 per cent.; mean 0.96 per cent. The effect of diffu-



sion is now quite sensible, and it may be said that about 1 per cent. of carbonic acid has diffused to a distance of half a metre in seven minutes.

A portion of carbonic acid has therefore travelled by diffusion at an average rate of 73 millims. per minute. It may be added that hydrogen was found to diffuse downwards, in air contained in the same cylindrical jar, at the rate of 350 millims. per minute, or about five times as rapidly as the carbonic acid ascended. In these experiments the glass cylinder was loosely packed with cotton wool, to impede the action of currents in the column of air; but this precaution was found to be unnecessary, as similar results were afterwards obtained in the absence of the cotton. To illustrate the regularity of the results, I may complete this statement by exhibiting the proportion of carbonic acid found in the upper stratum already referred to, after the lapse of different periods of time.

	Carbonic acid per cent.		
	Experiment 1.	Experiment 2.	Mean.
After 5 minutes .....	0·4	0·32	0·36
After 7 minutes .....	1·02	0·90	0·96
After 10 minutes .....	1·47	1·56	1·51
After 15 minutes .....	1·70	1·68	1·69
After 20 minutes .....	2·41	2·69	2·55
After 40 minutes .....	5·60	5·15	5·37
After 80 minutes .....	8·68	8·82	8·75

In eighty minutes the proportion of carbonic acid had risen to 8·75 per cent., 10 per cent. being the proportion which would indicate the completion of the process of diffusion.

The same intestine movement must always prevail in the air of the atmosphere, and with even greater velocity, in the proportion of 1 to 1·176, the relative diffusion-ratios of carbonic acid and air. It is certainly remarkable that in perfectly still air its molecules should spontaneously alter their position, and move to a distance of half a metre, in any direction, in the course of five or six minutes. The molecules of hydrogen gas disperse themselves to the distance of a third of a metre in a single minute. Such a molecular movement may become an agency of considerable power in distributing heat through a volume of gas. It appears to account for the high convective power observed in hydrogen, the most diffusive of gases.



## XVII.

ON THE ABSORPTION AND DIALYTIC SEPARATION OF  
GASES BY COLLOID SEPTA.<sup>1</sup>

From *Phil. Trans.* 1866, pp. 399-439.

PART I.—ACTION OF A SEPTUM OF CAOUTCHOUC.<sup>2</sup>

[MIXED gases must differ considerably in diffusibility and specific gravity, in order to separate from one another to any great extent in their molecular passage into a vacuum through a porous septum, such as the plate of graphite or the walls of an unglazed earthenware tube. The agency of atmolysis is therefore very limited in parting the oxygen and nitrogen of atmospheric air—gases which differ so little in density from each other.

Substances existing in the liquid condition often admit of being separated much more fully than gases, by the proper use of dialytic septa in addition to the agency of liquid diffusion.]

Evidently there cannot be anything like the dialysis of gases; for dialysis involves the passage of a substance through a septum composed of soft colloid matter, such as must be wholly destitute of open channels, and therefore be impermeable to gas as such. Still liquid dialysis may be imported into the treatment of gases, in consequence of the general assumption of liquidity by gases when absorbed by actual liquids or by soft colloids. Water when charged with air holds liquid oxygen and nitrogen in solution; and the latter substances then become amenable to liquid diffusion and dialysis, and so penetrate animal membrane in the act of respiration.

[A considerable time ago Dr. Mitchell of Philadelphia discovered a power in gases to penetrate india-rubber in a thin sheet, or in the form of the little transparent balloons which Dr. Mitchell was the first to prepare from that substance. He remarked in particular that such balloons collapse sooner when inflated with hydrogen than with atmospheric air, and still sooner when filled with carbonic acid; and he connected the latter fact with the observation that a solid piece of india-rubber is capable of absorbing its own volume of carbonic acid

<sup>1</sup> Received by the Royal Society June 20,—Read June 21, 1866.

<sup>2</sup> Several paragraphs have been crossed in pencil on the author's copy, but no sufficient authority was found for differing from the original version in the *Philos. Trans.*, a few words inserted, it is believed by the author, to explain the meaning being excepted. The paragraphs crossed are placed within brackets.



when left long enough in the pure gas. By means of a proper arrangement, Dr. Mitchell found that various gases passed spontaneously through the caoutchouc membrane, *when there was air on the other side*, with different degrees of velocity. "Ammonia transmitted in 1 minute as much as sulphuretted hydrogen in  $2\frac{1}{2}$  minutes, cyanogen in  $3\frac{1}{4}$  minutes, carbonic acid in  $5\frac{1}{2}$  minutes, nitrous oxide in  $6\frac{1}{2}$  minutes, arseniatted hydrogen in  $27\frac{1}{2}$  minutes, olefiant gas in 28 minutes, hydrogen in  $37\frac{1}{2}$  minutes, oxygen in 1 hour and 53 minutes, carbonic oxide in 2 hours and 40 minutes." The rate of penetration of nitrogen appeared to be even slower than that of carbonic oxide.<sup>1</sup>

It will be observed that those gases penetrate most readily which are easily liquefied by pressure, and which are also "generally highly soluble in water or other liquids." The memoir of Dr. Mitchell was ably commented upon, shortly after its publication, by Dr. Draper of New York, who also added many new observations on the passage of both gases and liquids through membranous septa. These early speculations, however, lose much of their fitness from not taking into account the two considerations already alluded to, which appear to be essential to the full comprehension of the phenomena—namely, that gases undergo liquefaction when absorbed by liquids and such colloid substances as india-rubber, and that their transmission through liquid and colloid septa is then effected by the agency of liquid and not gaseous diffusion. Indeed, the complete suspension of the gaseous function during the transit through colloid membrane cannot be kept too much in view.

Dr. Mitchell was led to infer, from a single casual observation, that rubber expands in volume when carbonic acid is absorbed—a result to be expected from the porosity of the solid mass, then assumed in explanation of the penetrativeness of gaseous fluids. But on placing 50 grms. of thin sheet rubber, 0.6 millim. in thickness, in carbonic acid over mercury, it was seen that the rubber gradually absorbed 0.78 volume of gas in twenty-four hours at  $15^{\circ}$ , of which 0.7 volume was taken up in the first hour. The mass of rubber was previously measured with care by the displacement of mercury in a specific-gravity bottle, and again when the rubber was charged with carbonic acid; it gave the same displacement of mercury within a hundredth of a gramme. No measurable change in the bulk of the rubber, therefore, had occurred. It may be added that the absorbent power of vulcanized rubber for

<sup>1</sup> "On the Penetrativeness of Fluids," by J. K. Mitchell, M.D., *Philadelphia Journal of Medical Sciences*, vol. xiii. p. 36; or *Journal of the Royal Institution*, vol. ii. pp. 101 and 307; London, 1831.

See also *Treatise on the Forces which produce the Organization of Plants*, with an Appendix containing several Memoirs on Capillary Attraction, Electricity, and the Chemical Action of Light, by John William Draper, M.D.



carbonic acid appears to be less than that of rubber in its natural state, being found only 0.57 volume in a comparative experiment.]

The penetration of rubber by gases may be illustrated by their passage into a *vacuum*, as well as into an atmosphere of another gas, in the old experiments of Dr. Mitchell. The diffusiometer, consisting of a plain glass tube of about 22 millims. in diameter and nearly a whole metre in length, closed at the upper end by a thin plate of stucco, and open below, is taken advantage of in such experiments. A thin film of rubber from a small balloon is stretched over the upper end of the tube, where it is supported by the stucco plate, bound with copper wire, and cemented at the edges in contact with the glass with gutta percha softened by heat. If the tube be now filled with mercury and inverted, a Torricellian vacuum is obtained above, into which the air of the atmosphere gradually penetrates, passing through the film of rubber and depressing the mercurial column in the tube. In order to compare the penetration of different gases, a hood of thick vulcanized rubber, provided with a small entrance and exit tube for gas (such as is often used in gas experiments), is placed over the upper end of the diffusiometer described, and cemented to it by means of fused gutta percha. The gas to be operated upon can thus be conveyed from the apparatus in which it is generated, or from a gasometer in which the gas is stored, into the hood or upper chamber of the diffusiometer, and the excess of gas supplied be allowed to escape into the atmosphere by the exit-tube of the hood. The stucco plate used as a support to the film of rubber is so highly porous as not to add sensibly to the resistance experienced by the gases in passing through the rubber, and, having no absorbent power of its own, may be left entirely out of consideration.

A comparison was made of the passage through the rubber film, on the same day, of carbonic acid, hydrogen, oxygen, and nitrogen; barom. 773 millims., therm.  $23^{\circ}$  to  $23^{\circ}5$  C. The time during which the mercurial column fell 25 millims in the diffusiometer, namely, from 748 to 723 millims., was noted in seconds, and also from 723 to 698 millims. The gases were all carefully dried.

TABLE I.—Passage of Carbonic Acid in seconds.

Height of mercurial column in diffusiometer.	Experiment 1.	Experiment 2.	Experiment 3.
millims.			
748			
723	107	102	102
698	143	138	138
	250	240	240



The passage of carbonic acid thus exhibited will be found to be considerably more rapid than those of hydrogen and the two other gases which follow :—

TABLE II.

Height of mercurial column in diffusiometer.	Passage in seconds,					
	of Hydrogen.		of Oxygen.		of Nitrogen.	
	Experiment 1.	Experiment 2.	Experiment 1.	Experiment 2.	Experiment 1.	Experiment 2.
millims.						
748						
723	277 <sup>"</sup>	270 <sup>"</sup>	545 <sup>"</sup>	554 <sup>"</sup>	1413 <sup>"</sup>	1428 <sup>"</sup>
698	316	323	727	722	1832	1850
	593	593	1272	1276	3245	3278

A single experiment, made at the same time on the passage of atmospheric air, gave times of 1318" and 1524" for the two stages, or 2842" for the whole fall. The time of penetration of air is therefore intermediate between that of oxygen and nitrogen entering singly.

Although such numbers do not possess the close uniformity which appears in diffusion and transpiration experiments, for reasons which will immediately appear, yet they give a comparative estimate of the penetrativeness of the different gases through rubber, which may be available for some practical purposes.

Upon another occasion carbonic oxide and marsh-gas ( $\text{CH}_4$ ) were introduced into the comparison, the same film of rubber remaining upon the diffusiometer; barom. 768 millims., therm.  $19^{\circ}5$  C.

TABLE III.

Height of mercurial column in diffusiometer.	Passage in seconds,								
	of Carb. oxide.		of Hydrogen.		of Carbonic acid.			of Marsh-gas ( $\text{CH}_4$ ).	
	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.	Expt. 1.	Expt. 2.	Expt. 3.	Expt. 1.	Expt. 2.
millims.									
748									
723	1620 <sup>"</sup>	1631 <sup>"</sup>	435 <sup>"</sup>	434 <sup>"</sup>	125 <sup>"</sup>	119 <sup>"</sup>	117 <sup>"</sup>	803 <sup>"</sup>	821 <sup>"</sup>
698	1920	1924	505	511	170	169	172	1009	1045
	3540	3555	940	945	295	288	289	1812	1866

The results may be summed up by deducing the times in which a constant volume of the various gases is transmitted by the rubber, the time of passage of carbonic acid, which is the shortest, being taken as unity for the sake of comparison.



## Penetration of rubber by equal volumes of Gas.

	Time.
Carbonic acid, . . . . .	1
Hydrogen, . . . . .	2.470
Oxygen, . . . . .	5.316
Marsh-gas ( $\text{CH}_4$ ), . . . . .	6.325
Atmospheric air, . . . . .	11.850
Carbonic oxide, . . . . .	12.203
Nitrogen, . . . . .	13.585

Or, with the times taken equal, the volume of each gas which passes then expresses the velocity of penetration.

## Penetration of rubber in equal times.

	Velocity.
Nitrogen, . . . . .	1
Carbonic oxide, . . . . .	1.113
Atmospheric air, . . . . .	1.149
Marsh-gas ( $\text{CH}_4$ ), . . . . .	2.148
Oxygen, . . . . .	2.556
Hydrogen, . . . . .	5.500
Carbonic acid, . . . . .	13.585

Considering the circumstances in which the gases pass through the sheet of rubber into a vacuum, it is not to be expected that any relation will be found among the preceding numbers, as between the coefficients of diffusion in gases. The first absorption of the gas by rubber must depend upon a kind of chemical affinity subsisting between the material of the gas and substance of rubber, analogous to that attraction which is admitted to exist between a soluble body and its solvent, conducing to solution. Carbonic acid being soluble in ether and volatile oils, it is not wonderful that it is also dissolved by the hydrocarbons of rubber. The rubber being *wetted through* by the liquefied gas, the latter comes to evaporate into the vacuum, and reappears as gas on the other side of the membrane. Now it is known that such evaporation is the same into a vacuum and into another gas, being equally gas-diffusion in both circumstances. It is not indispensable, therefore, to have a vacuum on one side of the rubber membrane as in the experiments detailed above. A foreign gas will answer for the vacuum, as in the experiments of Dr. Mitchell.

The numbers for the velocity of passage of the different gases in the last Table may be taken also as representing not remotely the relative absorption and liquefaction of the various gases by the substance of rubber.

The passage of gases through rubber is also illustrated by the rapid collapse of the little balloon when filled with carbonic acid gas, or even with hydrogen, or with marsh-gas, as compared with atmospheric air. The converse fact is observed when the inflating gas is pure nitrogen :



then the balloon is found to become further distended after a few hours, in consequence of more oxygen entering from the atmosphere without, than of nitrogen escaping from the balloon during the same time; while the composition is being equalized on both sides of the membrane, and the gas within the balloon is finally of the same composition as the external air. A rubber balloon filled with nitrogen was found, when roughly gauged, to increase in diameter from 132 to 136 millims. in the course of twenty-four hours. On the other hand, a balloon filled with pure oxygen fell in the same time from 150 to 113 millims. in diameter.

[In forty-eight hours a balloon filled with hydrogen 154 millims. in diameter contracted to 87 millims., and then contained 250 cub. centims. gas, of which 53 cub. centims. were absorbed by pyrogallie acid and potash, showing the presence of 21·2 per cent. of oxygen, or sensibly the same proportion as in the external atmosphere.

If the upper end of a diffusimeter be closed by a thin sheet of rubber, and the instrument standing over mercury be filled with hydrogen gas, a contraction is observed to take place slowly, but to a greater extent ultimately than could be due to the diffusion of hydrogen as a gas. Beginning with 249 volume divisions of gas in the tube, the rise of the mercurial column, or reduction of volume, was 1·5 division in the first hour, 1·5 division in the second hour, 2·0 in the third hour, 3 in the fourth hour, and 51 divisions in the first twenty-four hours taken together. Then the rise in the following successive days was 42, 59, 37, 29, 13, 5, 1, 0·5, 0·5 (in two days), and 0·0, the original volume of 249 volumes of hydrogen being finally replaced by 53 volumes of atmospheric air; barom. 747 millims., therm. 21°·1. The ultimate replacing volumes are here as 1 to 4·7. In gas diffusion they are as 1 to 3·8.]

A balloon filled with air subsided in forty-eight hours from 150 to 147 millims. in diameter, from the mechanical effect alone of the elasticity of the membrane in compressing the enclosed gas. These little balloons vary from 0·75 to 1 gm. in weight. Supposing the form to be truly spherical, a balloon of 150 millims. in diameter would have a surface of 0·0706 square metre (5·905 inches in diameter and 0·08454 square yard of surface). Supposing the balloon to be 1 gm. in weight, the thickness of the membrane will be  $\frac{1}{70\cdot686}$  of a millim., with a specific gravity = 1, or  $\frac{1}{76\cdot01}$  of a millim., with a specific gravity = 0·93, the admitted density of pure rubber. This last is a thickness of  $\frac{1}{1930\cdot6}$  of an inch, or it would require nearly 2000 such films, laid upon each other, to form the thickness of a single inch. Yet such a film of rubber appears to have no porosity, and to resemble a film of liquid in its relation to gases—differing entirely in this respect from a thin sheet of paper, graphite, earthenware, or even gutta percha, as will appear here-



after. These last enumerated bodies appear all to be pervaded by open channels or pores, sufficiently wide to allow gases to be projected through by their own proper molecular movement of diffusion. But liquids and colloids have an unbroken texture, and afford no opportunity for gaseous diffusion. They form even in the thinnest film an impervious barrier to gas.

The penetration of rubber is much affected by temperature, and apparently in two different ways at the same time. An increase of temperature no doubt renders all gases less easily liquefied by pressure, and consequently less considerably absorbed by any liquid or colloid. But such an influence of heat appears to be counteracted in rubber by the tendency of that colloid to become more soft when heated, and to acquire more of liquid and less of solid properties. Certainly the rubber film becomes more and more permeable to gases as the temperature is elevated, within a moderate range. This was distinctly observed in operating with silk cloth varnished on one side with rubber, such as is sold as a waterproof material. Without anticipating a detail of the experiments, it may be stated in general terms that the same specimen of silk varnished with rubber was penetrated by air from the atmosphere passing into a vacuum, at the following rates per square metre of surface:—

At 4° C.,	by 0.56 cub. centim. of air in 1 minute.	
At 14° C.,	by 2.25	„ „
At 60° C.,	by 6.63	„ „

The volumes of gas are all reduced to barom. 760 millims. and therm. 20° C.

Such numbers are probably not strictly constant; for it appears that the effect of temperature upon rubber is much influenced by the length of time that the temperature is continued, the change in degree of softness with change of temperature requiring hours, or even days, fully to complete it. The rigidity of rubber under cold and its softening under warmth are well known to take place in a slow and gradual manner.

With the softening of rubber by heat, the *retentive* power of that substance for gases appears to be modified. Soft rubber, first charged with carbonic acid at 20°, and then made rigid by cold, appeared to lose its carbonic acid, when afterwards freely exposed to air, less rapidly than the same rubber equally charged but exposed from the first in its soft condition. The quantity of carbonic acid retained in the former case was 10.76 per cent., and in the latter 7.08 per cent. of the volume of the rubber, after a similar exposure of forty-eight hours. This point, although not sufficiently examined, is alluded to here on account of the



analogy which appears to hold between rubber and the malleable metals in a power to absorb a gas when they are softened by heat, and to retain the same gas with great tenacity when they are afterwards made rigid by cold.

The condensation of oxygen gas by masses of solid rubber punched out of a block was made the subject of observation, by placing 50 grms. of that substance within a jar of oxygen standing over mercury during a period of several days. From the rubber afterwards there was extracted, by the action of a vacuum continued for twenty-one hours, 6.21 cub. centims. of gas; of which 3.67 cub. centims. were oxygen, 0.14 carbonic acid, and the remainder chiefly nitrogen. Taking the bulk of the rubber at 53.8 cub. centims., the oxygen absorbed amounts to 6.82 per. cent. of the volume of the rubber. Oxygen then may be regarded as fully twice as soluble in rubber as the same gas is in water at the ordinary temperature. No experiment was made at a higher temperature; but as the penetrativeness of rubber is much increased by heat, the presumption is that the solubility of gases in rubber is increased in the same degree.

More than one attempt was made to identify the presence of free hydrogen in the substance of rubber after being kept in that gas for some time before a positive result was obtained. The absorbed hydrogen appears to be rapidly dissipated, owing to its extreme diffusibility as a gas.

*Dialytic separation of Oxygen from Atmospheric Air, (1.) by means of other gases, (2.) by means of a vacuum.*

1. A balloon of rubber filled with *hydrogen* and exposed to the atmosphere, gradually loses the form of gas, which is finally replaced by a considerably smaller volume of air, presenting a deceptive resemblance to the diffusion of hydrogen gas into air. When the progress of the entrance of air was observed at different stages of the exchange, it appeared that after three hours, when the balloon had fallen from 150 to 128 millims. in diameter, the composition of its contents was —

Oxygen,	.	.	8.98	41.6
Nitrogen,	.	.	12.60	58.4
Hydrogen,	.	.	78.42	
			<hr/> 100.00	<hr/> 100.0

Setting aside therefore the hydrogen still remaining, the balloon now contained a portion of a mixture of oxygen and nitrogen in the proportion of 41.6 volumes of the former to 58.4 volumes of the latter. This was the largest proportion of oxygen to the nitrogen observed; for the former gas has a tendency to flow back again to the external atmosphere when the hydrogen becomes small in volume; and the proportion



of oxygen becomes eventually no higher than 21 per cent. of the whole gases remaining in the balloon, including the hydrogen. Thus after six hours the proportion of oxygen was 33.63 to nitrogen 66.37 volumes, and after twenty-four hours oxygen 26.48 to nitrogen 73.52 volumes, the hydrogen constantly diminishing at the same time.

The entrance by infiltration of atmospheric air into a balloon of rubber inflated with *carbonic acid* gas brings us still nearer to a practical dialytic separation, as the carbonic acid can be withdrawn entirely by means of caustic alkali, after a certain time has elapsed, and the infiltrated air enriched with oxygen be dealt with by itself. A balloon containing carbonic acid, when placed in the atmosphere, was reduced in four hours from 160 to 90 millims. in diameter, and it had now acquired 199 cub. centims. of gas not dissolved by alkali. This gas was capable of reviving the combustion of wood burning without flame, and was found to consist of

Oxygen, . . . . .	37.1 vols.
Nitrogen, . . . . .	62.9 „
	<hr/> 100.0

To produce this concentration of oxygen, it is quite necessary that the operation be interrupted at an early stage, as was done in the last experiment; otherwise the oxygen diminishes again in proportion to the nitrogen, falling at last to the normal proportion of 21 per cent. as in the external air. [Thus a balloon inflated by carbonic acid to 150 millims. in diameter was found to lose nearly all its carbonic acid in the course of twenty-four hours. It gave 150 cub. centims. of gas after treatment with caustic potash. This was air of the composition,

Oxygen, . . . . .	22.6
Nitrogen, . . . . .	77.4
	<hr/> 100.0

and exhibited therefore no material augmentation in the proportion of oxygen.]

It may be inferred, from the familiar fact that air dissolved in water contains so high a proportion as 30 per cent. of oxygen, that if carbonic acid gas were divided from atmospheric air by a film of *water*, the former gas would come to be charged through the film with air bearing the same high proportion of 30 per cent. of oxygen. But it is not easy to imitate this experiment unless the dividing film is supported by a membrane of some sort. The air from the atmosphere, which entered a fresh ox-bladder preserved humid and inflated with carbonic acid, was found to possess 24.65 per cent. of oxygen to 75.35 of nitrogen, which is but a small increase in the proportion of oxygen. But the thickness of the membrane here was too great, and other circumstances of the experiment were unfavourable.



A balloon of rubber inflated to 150 millims. in diameter with carbonic acid was submerged in water, at  $22^{\circ}\text{C}$ ., for forty-eight hours. Only a small portion of carbonic acid remained in the residual gas, which, after being washed with potash, consisted of

Oxygen,	.	.	.	.	25.77
Nitrogen,	.	.	.	.	74.23
					<hr/> 100.00

2. With the colloid septum properly supported over a vacuous space, as by a stucco plate in the diffusiometer covered by a film of rubber (p. 237), a considerable separation of mixed gases can be effected. The constituents of atmospheric air appear to be carried through a film of rubber into a vacuum, nearly in the same relative proportion as the same gases penetrate singly (p. 239). The velocities of nitrogen and oxygen passing separately were observed to be as 1 to 2.556, and hence by calculation,

Oxygen,	$21 \times 2.556 = 53.676$	.	.	40.46
Nitrogen,	$79 \times 1 = 79$	.	.	59.54
				<hr/> 100.00

Hence air dialysed by the rubber septum should consist of 40.46 oxygen and 59.54 nitrogen in 100 volumes. Now air from the atmosphere was found to enter the vacuum of the 48-inch diffusiometer-tube, through a disk of rubber 22 millims. in diameter, to the amount of 3.48 cub. centims. in twenty-one hours, under the pressure of the atmosphere; therm.  $23^{\circ}$  to  $24^{\circ}\text{C}$ . Of the 3.48 cub. centims. of gas so collected, 2 cub. centims. were absorbed by pyrogallie acid and potash, representing 42.53 *per cent. of oxygen* in the dialysed air. Here the gas was transferred from the diffusiometer for examination by depressing the diffusiometer in mercury, and using a very narrow tube of rubber as a gas-siphon communicating between the gas in the diffusiometer and a jar inverted in the mercurial trough. The elastic tube is first filled with mercury, and, being of considerable length, a portion of it is drawn repeatedly through the fingers so as to throw the mercury and aspirated gas into the collecting receiver. The transference of gases in such circumstances may also be effected with much advantage by means of the vacuum-tube invented by Dr. Hermann Sprengel, as will immediately be shown.

The process of dialytic separation by means of a rubber septum may be varied in three points,—(1.) in the condition of the rubber septum, which may be a film of rubber formed from caoutchouc varnish as well as from distended sheet rubber; (2.) in the nature of the support given to the septum, which may be a backing of cotton cloth or of silk (common waterproof cloth prepared by means of caoutchouc varnish, in short), as well as a plate of stucco, earthenware, or wood; and (3.) in

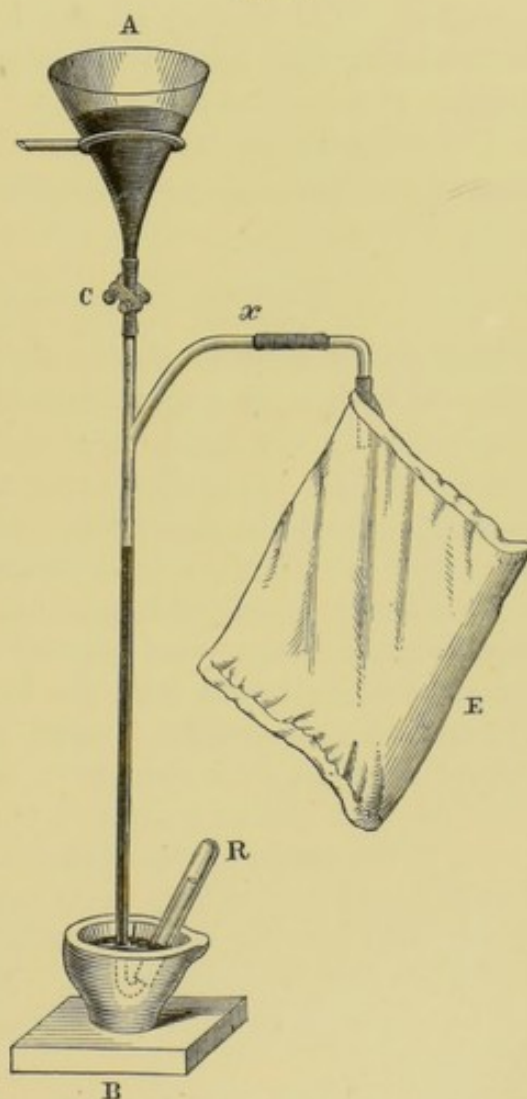


the means had recourse to for sustaining a vacuum, or at least a considerable degree of exhaustion, on one side of the dialytic septum, while atmospheric air, or any other gaseous mixture to be dialysed, has access to the other side of the same septum. Or the air to be dialysed may be compressed on one side of the septum, and left of the usual tension on the other side, inequality of tension on the two sides of the septum being all that is required to induce penetration.

The pneumatic instrument of Dr. Sprengel (fig. 1) is peculiarly applicable to researches of the present kind. Indeed, without the use of his invention some parts of this inquiry would have been practically impossible.<sup>1</sup> The instrument was originally offered by the inventor as the means of producing a vacuum, or as an air-pump. But by bending the lower end of the straight fall-tube, the instrument may be further made to deliver gas into a receiver, and be used with advantage as the means of transferring small volumes of gas from one vessel to another.

While the mercury in the funnel A is allowed to flow downward into the barometer-tube CB, of  $2\frac{1}{2}$  millims. in diameter, by relaxing the clamp upon the adapter tube of rubber at C, a connexion is also made with the close receiver to be exhausted, such as an air-tight bag E, by means of the branch tube  $\alpha$ . The air in E, gaining access to the Torricellian vacuum, is swept on by the falling mercury, and delivered below into the small gas-receiver R, previously filled with mercury and inverted over mercury in the mortar B below. The principal difficulty in obtaining a good vacuum in E by means of this apparatus arises from the necessity of joining the glass tubes in more than one place by means of adapter tubes of rubber.

FIG. 1.



<sup>1</sup> Researches on the Vacuum, by Hermann Sprengel, Ph. D., *Chemical Society's Journal*, ser. 2, vol. iii. p. 9 (January 1865).



The directions given by Dr. Sprengel on this point require to be closely followed:—"The connexions between the glass tubes are made of well-fitting black vulcanized caoutchouc tubing, sold under the name of French tubing. This is free from metallic oxides, which render the tubing porous. Besides this all these joints are bound with coils of copper wire, which is easily accomplished with a pair of pliers." The joints should also be coated with gutta percha liquefied by heat, or with fused rubber. An exhausting-syringe, or air-pump, may often be used with advantage to begin the exhaustion, and to withdraw the greater bulk of the air, if the receiver is large, the Sprengel tube being reserved to complete the exhaustion. The vacuum appears to be as perfect as can be formed in a barometer-tube filled with unboiled mercury, and to come within 1 millim. of the barometric gauge.

The following modifications of the experiment exhibit the dialytic action of caoutchouc in its various forms.

1. *India-rubber between double cotton cloth vulcanized.*

This was a common elastic carriage-bag 18 inches by 15. The surface of both sides amounted to 0.3482 square metre. The bag was pressed flat by the hands, and still further exhausted by means of Sprengel's tube. After all the contents of the bag were extracted and the collapse complete, the Sprengel tube began again to throw out air in a slow but exceedingly regular manner. A small portion of sawdust, or of sand, introduced beforehand into the bag, appeared to be useful in preventing the sides coming together too closely, but was not essential. The air thus extracted from the bag in one hour amounted to 15.65 cub. centims., or sensibly 1 cubic inch; therm.  $23^{\circ}$  to  $24^{\circ}$  C. Such dialysed air, from three successive experiments of one hour each, contained 38, 40.3, and 41.2 per cent. of oxygen, the inferior proportion of oxygen in the earlier experiments being no doubt due to a small residue of undialysed air remaining in the bag before exhaustion. This dialysed air rekindled glowing wood, so as to illustrate the direct separation of oxygen gas from atmospheric air. For the purposes of combustion, it may be viewed as air from which one-half of the inert nitrogen has been withdrawn.

It will be convenient to express the permeability of the colloid septum with uniform reference to a square metre of area, and to an hour, or to a single minute of time. Here, for a square metre of cloth, the passage of air amounted to 44.95 cub. centims. (3 cubic inches nearly) per hour, or to 0.749 cub. centim. per minute.

The view which the observation suggests of the nature of such an air-tight fabric is, that it may be truly impenetrable to air when the



composition and tension of the air are the same on both sides of the cloth; but it is penetrable when a vacuum or a reduced state of tension is maintained on one side of the cloth and not on the other. The compression of the air confined in a bag would no doubt have a similar effect, and then the flow would be in an outward direction. But there is no evidence of a porous structure in the varnished cloth. The gases of atmospheric air would pass through actual openings according to the law of gaseous diffusion, which favours the nitrogen or lighter gas, while it is the oxygen which is found to pass through the material most readily in these experiments. The imbibition of the liquefied gas by the substance of the rubber, with the subsequent evaporation of this liquid into the vacuum on the other side, is all the explanation required.

## 2. *Vulcanized india-rubber tubing.*

A stout caoutchouc tube with an external diameter of 13 millims. (half an inch), an internal diameter of 9 millims., thickness of 2 millims., and length of 3.658 metres (4 yards) was exhausted, one end being closed and the other end connected with the Sprengel pump. The gas collected in thirteen hours amounted to 11.25 cub. centims.; therm.  $20^{\circ}$  to  $23^{\circ}$  C. This gas contained 37.8 per cent. of oxygen. The gaseous penetration is not great in so thick a tube, and there is reason to fear the influence of gaseous diffusion to a small extent. The admission of air would be equally sensible if the tube were occupied by coal-gas, or any other foreign gas, instead of being vacuous. As the inner surface of the tube amounted to 0.1034 square metre and the passage of air to 0.8653 cub. centim. per hour, the passage for a square metre would be 8.37 cub. centims. per hour, or 0.14 cub. centim. per minute. The rate of penetration through the tube-walls appears to be one-fifth of what was found for the rubber cloth.

## 3. *Sheet rubber, 1 millim. in thickness.*

Although an increased thickness was no doubt attended by slowness of passage, it was of interest to observe whether the proportion of oxygen per cent. might not at the same time be varied. The sheet used was still, however, as thin as the manufacturer could succeed in cutting from a solid cylinder of wrought rubber by the usual method. The rubber was not vulcanized. The sheet of rubber was made into a bag having 0.149 square metre (231 square inches) of surface, a double thickness of felted carpet being placed within the folds of rubber. A glass quill tube, cemented to the bag, communicated with the interior of the cavity, and was connected at the other end with Sprengel's tube. After the first exhaustion of the gaseous contents of the bag, for which



the aid of an exhausting syringe or air-pump is useful, air continued to infiltrate through the sheet rubber, but very slowly. Of the dialysed air 11.45 cub. centims. were collected in four hours. This air contained 41.48 per cent. of oxygen, with a sensible trace of carbonic acid. The penetration for a square metre amounts to 19.2 cub. centims. of air per hour, or 0.32 cub. centim. per minute.

The same bag, left exhausted for eighteen hours, was found afterwards to yield at once 41.6 cub. centims. of air, containing 40.3 per cent. of oxygen, which had accumulated in the cavity of the bag; therm. about 20° C.

From a larger bag of similar thin sheet rubber, having a surface of 640 square inches, distended by ten or twelve ounces of sawdust, 21.35 cub. centims. of dialysed air were obtained in one hour; barom. 761 millims., therm. 19° 5 C. This dialysed air appeared to consist of

Oxygen,	.	.	.	.	41.80
Carbonic acid,	.	.	.	.	0.94
Nitrogen,	.	.	.	.	57.26
					<hr/> 100.00

It does not appear, then, that the increased thickness of the rubber septum tends to increase the proportion of oxygen in the dialysed air, while this thickness causes the passage to be proportionally slower. The oxygen appears to attain, but never to exceed, at 20° C., the proportion of 41.6 to 58.4 nitrogen.

The thick rubber brings notably into view the carbonic aid of the air. The small proportion of this gas in air is probably increased in all experiments with the rubber septum, however thin. It was observed to rise so high in a small crowded room, as to negative the inflaming action of the oxygen on smouldering wood. But rubber appears to have a power to charge itself gradually from atmospheric air with about half per cent. of its volume of carbonic acid. This carbonic acid, accumulated in thick sheet rubber, appears again to be carried on by the other gases imbibed in a dialytic experiment.

#### 4. *Thin Balloons of india-rubber.*

These little balloons were made available for the dialytic passage of air into a vacuum by filling them with sifted sawdust through a funnel, an operation which requires some address. The balloon collapsed upon the sawdust, which formed an interior ball, the sides of rubber still retaining a thickness of about one-fiftieth of a millimetre. The rubber is not vulcanized. Such a ball, of which the original rubber weighed 0.76 gm., still remained 95 millims. in diameter after the air was exhausted.



It was found, when exhausted, to admit 19.6 cub. centims. of dialysed air in forty-one minutes; barom. 579 millims., and therm.  $19^{\circ}$  C. The same air possessed 41.32 per cent. of oxygen. The ball had a surface of 0.0283 square metre, and it dialysed 0.48 cub. centim. of air in one minute. For a square metre of surface this is a passage of 16.9 cub. centims. per minute. The passage therefore is about fifty times faster than through a sheet of rubber of 1 millim. in thickness, while the high proportion of oxygen is sensibly the same. Such a ball was found to dialyse air in the same manner for more than a month, if protected from mechanical injury.

[Three such balls, each containing twenty-three ounces of sifted sawdust, were made to act together, by connecting them with three dependent branches from the same horizontal glass tube. The horizontal tube was connected at one end with an ordinary air-pump, which produced a good vacuum by thirty or forty strokes of the piston. The other end of the horizontal glass tube was attached to a good Sprengel apparatus of the largest admissible size, constructed by Messrs. Elliot of the Strand. It was found, however, that the dialysed air entered rather more rapidly than it could be extracted by a single Sprengel apparatus. This was at the rate of 5 cub. centims. in one minute; therm. about  $20^{\circ}$  C. The dialysed air contained 40.5 per cent. of oxygen.]

The greatest amount of aërial dialysis per square metre was obtained by means of a rubber bag, larger than usual, and weighing 1.55 gm. When filled with the sawdust and exhausted, this bag still remained of 143 millims. in diameter, and with a surface therefore of 0.0642 square metre. The air which passed through amounted to 17.05 cubic centims. in ten minutes; therm. about  $20^{\circ}$ . This air gave 40.7 per cent. of oxygen. For a square metre of surface, this is the passage of 26.5 cub. centims. per minute, the highest which has yet been observed.

[In the thin transparent envelope of the little balloon of rubber we have a colloid substance in the most favourable form yet applied to the dialysis of mixed gases. But there is still much room for improvement in the mode of using the thin septum in question. The balls are apt to contract considerably, owing to their elasticity, in the operation referred to, of filling them with sawdust; their walls become at the same time thicker and less quickly pervious. A mode of destroying the elasticity of the membrane when in its most attenuated condition, so that the balloon might be cut open and the membrane spread out without shrinking, would be very useful. Instead of depending upon the interior support of sawdust, the membrane could then be stretched over a more convenient frame to support it, of thin porous deal, of unglazed earthenware, and even of a felted fabric, or several thicknesses of unsized paper supported by a slight frame, so as to form a hollow



cavity that admitted of being exhausted of air. The attention of manufacturers of rubber might be advantageously directed to the preparation and proper support of the thinnest possible septa of that material.]

The varnish of rubber which appeared to offer the best septum on drying, was a thin solution of rubber in 200 times its weight of chloroform. Four or five coats of this varnish required to be applied to a surface of wood, or of unglazed earthenware, to form an air-tight envelope. The film appeared to exceed in thickness the rubber balloons, and it dialysed air less rapidly. But a better result may be expected at the hands of experienced manufacturers.

[The thin rubber membrane of the balloons was stretched over the ends of glass tubes already closed with a plate of porous stucco—and also over the mouths of small glass bulbs or osmometers, closed with a disk of porous wood or of unglazed earthenware, and which presented a surface of one-hundredth of a square metre. The membrane of the balloon could only be applied while double; but after the covering was securely bound to the glass and cemented with fused gutta percha at the edges, the outer coating was torn off, so as to leave only a single thickness of rubber as the dialytic septum. A bulb of the kind described, when exhausted by a Sprengel pump, gave afterwards 16·36 cub. centims. of dialysed air in two hours, containing by analysis 41·3 per cent. of oxygen, therm. 23° C.; in the following two hours, 17·35 cub. centims. of air, containing 42·6 per cent. of oxygen. This last is at the high rate, for a square metre of surface, of 14·46 cub. centims. per minute.]

5. *Silk cloth varnished with rubber on one side, slightly vulcanized.*

This is a thin but close silk fabric, much used for waterproof garments. It appears also to be employed, when dyed of a fancy colour, in the preparation of artificial flowers and for other purposes. The silk cloth is of a single thickness; and the coating of rubber, which is of a black colour, appears on one side only. It is a much superior material to the ordinary cotton fabrics, which are double, with the two varnished sides pressed together, and is much more to be depended upon for being sound and free from pores than the "waterproof" cotton cloth. The silk cloth, however, should always be tested by examining air dialysed by means of it. If the proportion of oxygen falls below 40 per cent. the silk is unsound at one or more spots. These spots may generally be discovered by wetting one side of the silk with a sponge and observing where the passage of water is indicated by a visible stain on the other side. The defective spot may be covered by a small disk of sheet rubber applied warm to the surface. Such varnished silk, although not the most rapid in its dialytic action, was more convenient in use than any other septum hitherto tried.



The varnished silk stretched over a disk of porous earthenware (for support) closing the mouth of the small glass bell-jar or osmometer, which has an opening of one hundredth part of a square metre, gave 10 cub. centims. of dialysed air in one hour, containing 42.2 per cent. of oxygen; barom. 767 millims., therm.  $23^{\circ}5$ . For a square metre of surface this is a passage of 2.77 cub. centims. of air per minute.

A small bag, useful for experimental purposes, was constructed of a portion of the same varnished silk, 0.53 metre in length by 0.27 metre in width, which had therefore a surface of 0.143 square metre. The varnished side was turned inwards. Between the folds of the silk was placed a double thickness of common felt carpet or a piece of wadding, so as to occupy the interior of the bag. A glass quill tube also entered the bag to the depth of a few inches, and projected as much outside, so as to admit of being connected, by means of a sound adapter tube of French rubber, with a Sprengel pump, as shown in fig. 1 (page 245). The edges of the silk cloth were cemented round by caoutchouc varnish, to a depth of 10 millims., so as to close the bag; and care was taken also to cement the glass tube well to the edges of the bag. When the silk bag is exhausted of air, it remains nearly flat, and feels hard like a piece of cardboard. Such an *air-dialyser* is further improved by interposing a strong glass flask or bottle, of one or two litres in capacity, between the bag and the pump, so that both are exhausted of air at the same time. The flask must be strong enough to bear the full pressure of the atmosphere without breaking. An auxiliary air-pump, to produce the first exhaustion, cannot well be dispensed with where the space to be made vacuous is so considerable; the Sprengel tube is brought into action afterwards. The advantage gained by the vacuous flask, and even by the thick wadding placed within the bag, is that they form a magazine in which the dialysed air can be allowed to accumulate for several hours or a whole day, and from which the air may afterwards be drawn quickly by the Sprengel tube for the purpose of experiment. A narrow glass receiver tube, which can be closed by the thumb, may be used to take 5 or 6 cub. centims. for an observation on the inflammation of a chip of wood in the highly oxygenated air. When the proportion of oxygen is under 33 per cent. the wood is not rekindled; but in the ordinary action of this dialyser the oxygen is seldom found under 40 per cent. The best result is obtained when the exhaustion is within half an inch of the barometric vacuum. When the pressure was allowed to fall to one-half or one-third of an atmosphere, the proportion of oxygen was lessened by 2 or 3 per cent.

The action of heat and cold on the penetrability of rubber is considerable, as has already been stated. Operating with the dialysing-bag described, without any intermediate flask, the volume of air collected



in twenty minutes was 6.35 and 6.57 cub. centims. in two consecutive experiments; barom. 760 millims., therm.  $20^{\circ}$ . For a square metre the rate is 2.22 and 2.29, average 2.25 cub. centims. per minute. The proportion of oxygen was, in the first experiment 42.5, and in the second 41.66 per cent.

When the same dialysing-bag was kept at a temperature of  $60^{\circ}$  C., the volume of air collected in seven minutes was 6.22 and 7.06 cub. centims. For the square metre this amounts to 6.21 and 7.05, mean 6.65 cub. centims. per minute. The passage of air through rubber is therefore almost exactly three times as quick at  $60^{\circ}$  as at  $20^{\circ}$  C.

Again, the dialysing-bag was kept at  $4^{\circ}$  C. by being surrounded by ice and salt. The air now collected in seventy-two minutes was 5.78 and 5.77 cub. centims. in volume—for a square metre 0.56 cub. centim. per minute. The passage of air through rubber thus appears to be four times as slow at  $4^{\circ}$  C. as it is at  $20^{\circ}$ . The proportion of oxygen in the dialysed air increased at the same time. In the two portions of air collected at  $4^{\circ}$  the oxygen was 46.75 and 47.43 per cent. The increase of oxygen at a low temperature was confirmed in other experiments; but it appeared at the same time that the rubber was liable to acquire a true porosity to a slight extent when retained for some hours about  $0^{\circ}$  C. The rubber then allowed air to pass through it containing no more than 28 or even 23 per cent. of oxygen, and in volume still very small. The rubber has become rigid by the cold, and is now acting feebly as a porous substance, allowing a little gas-diffusion to take place through its substance. Such a condition, which is accidental to caoutchouc at a low temperature, appears to be constant with gutta percha, a harder material, at  $20^{\circ}$  C., and even higher temperatures.

A large bag of varnished silk with a surface of 1.672 square metre (two square yards) was found still more convenient. It was, however, rather beyond the exhausting-power of the largest Sprengel pump. It yielded in eight minutes, without any collecting flask, 22, 21.55, and 21.5, mean 21.68 cub. centims. This was a supply of 2.71 cub. centims. per minute, and was at the rate, for a square metre, of 1.62 cub. centim. per minute. The supply would have been about a half more if the dialysed air had not gained upon the pump. The air of the first and last observations contained respectively 41.89 and 41.85 per cent. of oxygen.

The usual proportion of oxygen in air dialysed by rubber appears to be about 41.6 per cent.; and it may be described as atmospheric air deprived of one-half of its usual proportion of nitrogen. A single dialysis of air therefore carries the experimenter already half-way from air to pure oxygen as the final result. But the gain by a second dialysis could not be so great, as it would only withdraw one-half of the nitrogen that remained after the first operation, a third dialysis one-



half of the nitrogen remaining after the second operation, and so on—each step of the concentration of the oxygen being obtained at a greater cost than the last, and the best conceivable result being only a good approximation. The practical problem which is suggested by the air-dialyser is to attain the means on a large scale of reducing to one-half, or so, the proportion of nitrogen in atmospheric air, to be applied to certain useful purposes.

#### 6. *Percolation of air through gutta percha and other septa.*

Thin transparent sheets of a certain material represented as air and water tight are in common use. It is often spoken of as consisting of caoutchouc, but appears to have a body of gutta percha, softened probably by a drying-oil. From its softness and thinness, this sheet of gutta percha appeared at first highly promising. But it appears not to be free from small apertures for any considerable surface. When a small sound portion was operated upon, air was found to percolate through it very slowly. In a tube diffusiometer of 1.3 metre in length and 20 millims. in diameter, closed at the top with this septum supported by stucco, the mercurial column fell from 28.7 to 22.625 inches in  $18\frac{1}{2}$  hours. The gas which had entered above the mercury measured 13.54 cub. centims., and was found to contain 20.2 oxygen to 79.8 nitrogen—a proof that the air had entered by gas diffusion. The material is in fact of sufficient porosity to permit the molecular passage of gases in a slow manner.

Varnishes of gelatine and of drying-oil have been tried as dialytic septa, but hitherto without marked results.

### PART II.—ACTION OF METALLIC SEPTA AT A RED HEAT.

#### *Platinum.*

The surprising passage of gases through the homogeneous substance of a plate of fused platinum or of iron, at a red heat, discovered by MM. H. Ste.-Claire Deville and Troost, may possibly prove to be analogous in its mode of occurrence to the passage of gases through the rubber septum. At the same time it must be admitted that such an hypothesis as that of liquefaction can only be applied in a general and somewhat vague manner to bodies so elastic and volatile at an elevated temperature as the gases generally must be, and hydrogen in particular. Still some degree of absorbing and liquefying power can scarcely be denied to a soft or liquid substance, in whatever circumstances it may be found, with such a patent fact before us as the retention by fused silver of 18 or 20 volumes of oxygen at a red heat. It may safely be



assumed that the tendency of gases to liquefaction, however much abated by temperature, is too essential a property of matter to be ever entirely obliterated.

A little consideration also shows that the absorption of gas by a liquid or by a colloid substance is not a purely physical effect. The absorption appears to require some relation in composition—as where both the gas and the liquid are hydrocarbons, and the affinity or attraction of solution can come into play. May a similar analogy be looked for, of hydrogen to liquid or colloid bodies of the metallic class?

With reference to the mechanical pores of a solid mass, liquids are probably more penetrating than gases. The former show often a power of adhesion to solids, while gases appear to be essentially repulsive. A degree of minute porosity is conceivable, which will admit a liquid, but may be impassable to a gas, even under its molecular movement of diffusion.

Finally, there is presented to us a bold and original conjecture by M. Deville, in explanation of his own observations. It is clearly expressed in the following quotation taken from the last publication of M. Deville on this subject:—

“La perméabilité de la matière est d’une nature toute différente dans les corps homogènes, comme le fer et le platine, et dans des pâtes plus ou moins discontinues, resserrées par la cuisson ou la pression, comme la terre à creuset, la plombagine, dont M. Graham s’est servi dans ses mémorables expériences. Dans les métaux, la porosité résulte de la dilatation que la chaleur fait éprouver aux espaces intermoléculaires; elle est en relation avec la forme des molécules que l’on peut toujours supposer régulières, et avec leur alignement que détermine le clivage ou les plans de facile fracture des masses cristallisées. C’est cet intervalle intermoléculaire que le phénomène de la porosité des métaux purs et fondus accuse avec une évidence éclatante, c’est aussi par ce phénomène qu’on peut espérer de calculer la distance des molécules solides aux températures élevées où les gaz peuvent s’y introduire.”

A new kind of porosity in metals is imagined, of a greater degree of minuteness than the porosity of graphite and earthenware. This is an intermolecular porosity due entirely to dilatation. The intermolecular porosity of platinum and iron is not sufficient to admit any passage of gas at low temperatures, but is supposed by M. Deville to be developed by the expansive agency of heat upon the metals, and to become sensible at the temperature of ignition. Such a species of porosity, if it exists, may well be expected to throw light on the distances of solid molecules at elevated temperatures, when gases introduce themselves. The ready passage through platinum of some gases,



particularly of hydrogen, and the difficult passage of others, render such molecular views the more remarkable.

The passage of hydrogen through the substance of heated platinum appears in its most simple aspect when the gas is allowed to make its way through the metal into a vacuous space. The experiment of M. Deville, where a tube of platinum charged with nitrogen is placed within a large porcelain tube charged with hydrogen,<sup>1</sup> was modified by placing the platinum tube, closed at one end, in communication by the other (open) extremity with the Sprengel pump, so that a vacuum was substituted for the nitrogen. It was then easy to observe that a vacuum in the platinum tube was preserved for hours when the external gas admitted into the annular space between the porcelain and platinum tubes was either atmospheric air or hydrogen at the natural temperature. The tubes being placed across an empty furnace, the latter was now lighted; and it was seen that, with air circulating outside the platinum, the vacuum remained undisturbed, even when the temperature of the tubes rose to a bright red heat. But when dry hydrogen was driven through the same annular space, the platinum, while continuing impermeable at all temperatures below a dull red heat, began to admit hydrogen to the vacuum as soon as the external porcelain tube became visibly red-hot. In seven minutes the Sprengel pump now delivered 15.47 cub. centims. of gas, of which 15.27 cub. centims. appeared, by explosion with oxygen, to be hydrogen.

In a repetition of the last experiment, hydrogen dried by sulphuric acid was again allowed to circulate in excess outside the platinum. After a vacuum was once obtained within the platinum tube, the gas delivered by the Sprengel pump, in the cold, during a period of forty minutes, amounted to no more than a bubble of the size of a pin-head, showing the tightness of the apparatus. The Sprengel pump being constantly kept in action, the tubes were now heated to redness, and then gradually to a temperature approaching a white heat. The gas delivered each five minutes was found to be 13, 15.5, 17.4, 16.9, 18.6 cub. centims. as the temperature rose. These volumes are referred to a temperature of 20° and barometer of 760 millims. The last observation gives a passage of 3.72 cub. centims. of hydrogen per minute. The platinum tube employed here was joined without solder, having been drawn from a mass of platinum which had been aggregated by fusion. It was similar in this respect to the tube employed by M. Deville. The tube was 0.812 metre in length (32 inches) and 1.1 millim. in thickness, with an internal diameter of 12 millims. But only a portion of about 200 millims. (8 inches) of the tube were heated to redness in the furnace experiment. The inner surface of the heated portion has therefore

<sup>1</sup> *Comptes Rendus*, vol. lvii. p. 965.



an area of 0.0076 square metre. Hence one square metre of heated platinum delivers 489.2 cub. centims. of hydrogen per minute. This result admits of comparison with the passage of gases through a septum of rubber. In the most favourable circumstances, when the thin membrane of a rubber balloon was employed, the passage of air into a vacuum was at the rate of 26.5 cub. centims. per square metre in one minute. The passage of hydrogen may be taken as 4.8 times as rapid as that of atmospheric air, or at 127.2 cub. centims. per minute. But while the thickness of the platinum septum was 1.1 millim., that of the rubber film was only one-seventieth part of a millimetre. Hence we have the ultimate comparison :—

Passage of hydrogen gas in one minute through a septum of 1 square metre :—

Through rubber 0.014 millim. in thickness, 127.2 cub. centims. at 20° C. ;

Through platinum 1.1 millim. in thickness, 489.2 cub. centims. at bright red heat.

If the permeation of hydrogen is due to the same agency in both septa, can the vast superiority of the platinum septum be connected with its greatly higher temperature ?

It was interesting now to turn from hydrogen to the passage of other gases through heated platinum. The experiments were all made in the same way, and at a full red heat. The temperature, it will be observed, was short of that at which the elements of water and carbonic acid are partially dissociated.

*Oxygen and Nitrogen.*—Atmospheric air, which may be taken to represent both of these gases, was now allowed to flow through the annular space between the tubes, the interior platinum tube being kept vacuous as usual. In one hour the gas collected by the constant action of a Sprengel pump amounted only to 0.3 cub. centim. Hydrogen in the same time would have given 211 cub. centims. It is very doubtful, too, whether the trifling fraction of a centimetre of gas collected had all passed through the platinum ; a part (or the whole of it) may have entered by the joints of the apparatus. Platinum, then, cannot be said to be sensibly permeable to either oxygen or nitrogen, even at a full red heat.

*Carbonic acid.*—This gas was supplied from a bottle containing marble, by the action of pure hydrochloric acid, the gas being afterwards washed with water and dried by sulphuric acid in its way to the exterior porcelain tube. In one hour the interior platinum tube yielded only three-tenths of a cubic centimetre of gas, of which, again, only an indeterminate small portion was condensed by baryta water and appeared to be carbonic acid. The passage of carbonic acid is therefore incalculably small at a full red heat.



*Chlorine*.—This gas, evolved slowly from a glass flask containing peroxide of manganese and hydrochloric acid, was washed by water, dried by sulphuric acid, and thrown as usual into the porcelain tube so as to occupy the annular space between the two tubes. A small tube containing slaked lime was interposed between the end of the platinum tube and the Sprengel pump, so as to absorb the chlorine, if any came through the substance of the platinum. After the tube had been heated for an hour, the lime was examined for chlorine, but did not contain a trace of that substance. A minute quantity of gas, probably air, amounting to 0.15 cub. centim., was collected during the time. Platinum, then, is not sensibly penetrated by chlorine at a red heat.

*Hydrochloric acid*, dried over sulphuric acid, was passed for one hour through the porcelain tube. About 0.5 cub. centim. of gas was collected from the platinum tube, which contained no hydrochloric acid and no free hydrogen. The ignited platinum, then, is not penetrated by hydrochloric acid; nor does it appear to dissociate the elements of that gas at the temperature of the experiment.

*Vapour of water*.—A stream of steam was carried for one hour through the porcelain tube. During that time half a cub. centim. of gas appeared to be drawn from the platinum tube, which gas contained no hydrogen. There is no evidence of the passage through the platinum of the vapour of water, nor of its decomposition.

*Ammonia*.—This gas appeared to be decomposed to a considerable extent in passing through the heated annular space, hydrogen passing freely at the same time through the ignited platinum. No trace of undecomposed ammonia, although the gas was transmitted in considerable excess, was discovered accompanying the free hydrogen found in the platinum tube. When the ammonia was evolved slowly, the quantity of hydrogen entering the platinum tube amounted to 16.4 cub. centims. in five minutes, or was sensibly the same as when pure hydrogen was carried through the annular space. Ammonia, then, appears to be incapable of penetrating the ignited platinum.

*Coal-gas*.—When coal-gas was carried through the porcelain tube, the following quantities of hydrogen came through the platinum in successive periods of twenty minutes each, 13.3 cub. centims., 5.2, and 8.8. The first portion, when exploded with oxygen, did not disturb baryta-water after condensation; 13.3 cub. centims. contained 13.16 cub. centims. of hydrogen. It appears, then, that the permeating gas was free hydrogen only, and that no compound of carbon present in coal-gas was capable of passing through the platinum. This may be held as excluding the passage of *carbonic oxide*, *marsh-gas*, and *olefiant gas*, all represented in the coal-gas.



*Hydrosulphuric acid.*—This gas, prepared from sulphide of antimony and hydrochloric acid, washed, and dried over chloride of calcium, was then circulated through the outer porcelain tube. The hydrosulphuric acid was nearly all decomposed into sulphur and hydrogen, the latter coming through the platinum at the rate of 9 cub. centims. in five minutes. A trace of hydrosulphuric acid may also have passed through, as the mercury of Sprengel's tube was slightly soiled; but no indication of this gas could be perceived in the hydrogen collected. It appears, then, that hydrosulphuric acid is to be classed among the non-penetrating gases. The result appears to be :—

- I. Gas capable of passing through a septum of platinum 1·1 millim. in thickness at a full red heat.

Hydrogen (211 cub. centims. per hour).

- II. Gases incapable of passing through a septum of fused platinum 1·1 millim. in thickness at a full red heat.

Oxygen, . . . .	(not to the extent of 0·2 cub. centim. per hour.)	
Nitrogen, . . . .	"	"
Chlorine, . . . .	"	"
Hydrochloric acid, .	"	"
Vapour of water, .	"	"
Carbonic acid, . .	"	"
Carbonic oxide, . .	"	"
Marsh gas ( $\text{CH}_4$ ), .	"	"
Olefiant gas, . . .	"	"
Hydrosulphuric acid,	"	"
Ammonia, . . . .	"	"

It remains to be discovered whether a sensible passage of any of these gases could be effected through a platinum septum much reduced in thickness, or through the same septum under the influence of a considerably higher temperature. A fallacious appearance of permeation is sometimes occasioned by the escape from the platinum itself of a small quantity of gas, particularly of carbonic oxide and hydrogen, as will immediately appear. The permeation is in consequence never unequivocal for the first hour or two that the platinum septum is heated.

[One of the curious experiments of M. Deville was repeated, in which hydrogen appears to escape from the platinum tube pretty much as the same gas would escape from a graphite diffusiometer—the platinum tube being full of hydrogen, while the annular space between the platinum and outer porcelain tube was occupied by atmospheric air. At the maximum temperature the supply of hydrogen to the platinum



tube was shut off, as that gas entered at one end of the tube, while the other end of the platinum tube was left in connexion with a barometer-tube dipping into a cistern of mercury. Immediately the mercury began to rise in the gauge tube from the passage of hydrogen outwards through the walls of the platinum tube; and the latter in the end became nearly vacuous from the complete escape of the hydrogen.

Heated platinum tube containing hydrogen; air outside.

Time.	Rise of mercury in gauge barometer.
0 minute.	0 millim.
10 minutes.	115 millims.
20     "	245     "
30     "	400     "
40     "	535     "
50     "	645     "
60     "	710     "

the actual height of the atmospheric barometer being 750 millims. at the same time. The tension of the residual gas was therefore no more than 40 millims. of mercury. The ratio between the volume of gas at the beginning and end of the hour is here as 18.75 to 1; whereas in a diffusion experiment of hydrogen into air, the ratio would be as 3.8 to 1. Further, the residual gas in the platinum tube still retained a small portion of hydrogen. Withdrawn by means of the Sprengel pump and examined, the residual gas in the platinum tube amounted to 3.56 cub. centims., and consisted of

Nitrogen,	3.22 cub. centims.
Hydrogen,	0.34     "
	<hr/> 3.56     "

The available capacity of the platinum tube was 113.1 cub. centims.; and when the tube was heated, the gas driven out by dilatation measured in the cold 39.5 cub. centims., leaving in the hot platinum tube 73.6 cub. centims. of gas estimated at 20° C. and barom. 760 millims.] It was found necessary in these experiments to stuff that portion of the platinum tube that was placed across the furnace and strongly heated, with asbestos, to give support to the tube when softened by the heat of ignition, and to prevent the tube from collapsing.

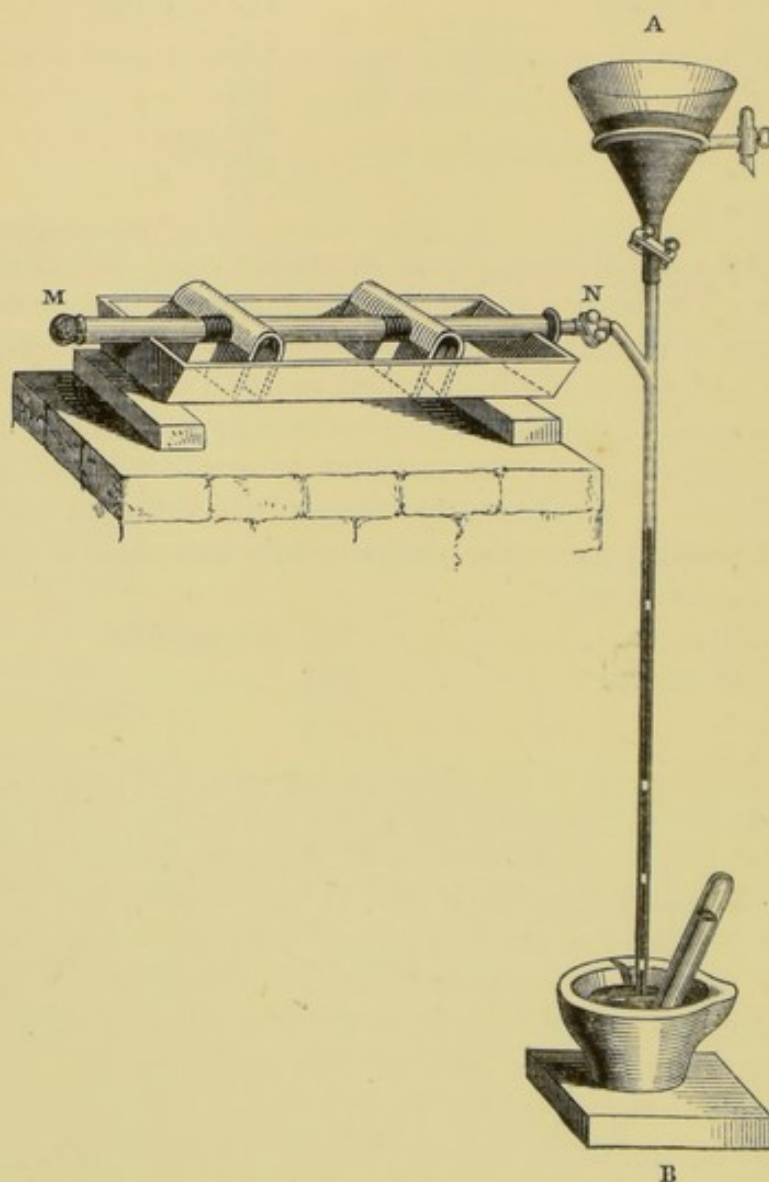
[It is difficult to say where the small volume of nitrogen found in the platinum tube, amounting to 3.22 cub. centims., actually came from. It appears too great in amount to have formed an impurity in the original hydrogen gas, or to have gained access to the vacuum through defective joinings in the apparatus. Its presence suggests the inquiry, admitting that nitrogen cannot pass alone through platinum into a vacuum, whether the same gas may not be enabled to pass, in some



small proportion, while hydrogen is simultaneously travelling through the platinum in the opposite direction. The liquid or the gaseous hydrogen occupying the platinum septum would thus form a vehicle or channel, by the help of which another analogous body like nitrogen might be conceived capable of passing through the platinum in small quantity, by a process of liquid or gaseous diffusion.]

*Absorption and detention of Hydrogen by Platinum.*—The passage of a gas through a colloid septum is preceded by the condensation of the

FIG. 2.



gas in the substance of the septum, according to the views taken in this paper. Is a plate of ignited platinum capable, then, of condensing and liquefying hydrogen gas? The subject could scarcely admit of experimental investigation without the application of the same useful



air-exhauster that was employed with the non-metallic colloids. The metal was always treated in the same manner; so that a description of the details of one experiment will apply to all.<sup>1</sup>

Platinum wire or plate being provided, the surface of the metal was first divested of all adhering oily matter, by boiling in caustic alkali and afterwards in distilled water.

The platinum, generally in the form of wire, was then introduced into a porcelain tube M, N (fig. 2), glazed both outside and inside, 0.55 metre in length and 23 millims. in internal diameter. This tube could be heated either by means of the combustion-furnace used for organic analysis, or by placing the tube across the chamber of a small cylindrical furnace. The porcelain tube was fitted at both ends with perforated corks, well cemented with fused gutta percha, and provided each with a small quill tube. Such may be described as the distillatory apparatus employed. It was connected at the end N with the Sprengel pump A B, to be used as an exhauster and transferrer of gas, by means of good caoutchouc adapters (not vulcanized), and at the other end M, with the apparatus for supplying dry hydrogen, atmospheric air, or any other gas. By a screw clamp upon the adapter at M, the tube could be closed, and the gas-producing apparatus then detached, leaving the porcelain tube shut at one end. A tube of the hard glass used in combustion analysis may be substituted for the porcelain tube in many such experiments. A less degree of heat suffices than was at first supposed.

The porcelain tube is exhausted by continuing the action of the Sprengel for ten or fifteen minutes, till small bubbles of gas cease to be delivered by the tube A B in the mercurial trough below. The sufficiency of the joints is thus first ascertained. Heat being then applied to the porcelain tube, its impermeability at a red heat will also be tested.

The platinum, when introduced, was confined to about two-thirds of the central portion of the porcelain tube, which could be conveniently heated. The apparatus obviously affords the means both of heating the platinum in a vacuum and also in an atmosphere of hydrogen or any other gas admitted into the interior of the porcelain tube at M.

*Fused platinum.*—Articles of manufactured platinum appear now to be prepared exclusively from the fused metal.

1. A quantity of clean platinum wire from fused metal, measuring 0.695 metre in length, 4.1 millims. in diameter, and 201 grms. in weight, was bent and introduced into the porcelain tube, which was then ex-

<sup>1</sup> Platinum in the peculiar condition of platinum-black absorbs 745 times its volume of hydrogen gas.—*Traité de Chimie Générale*, par MM. Pelouze et Frémy, t. iii. p. 398.



hausted. The platinum was first heated alone for an hour to drive off any natural gaseous product, and then dry hydrogen gas was admitted to the porcelain tube, the gas being evolved from pure sulphuric acid and pure zinc. The hydrogen was conveyed in excess into the porcelain tube, at a cherry-red heat, and the temperature was then allowed to fall in a gradual manner—a procedure which was found to promote the absorption of the gas. The platinum was thus retained for about twenty minutes in an atmosphere of hydrogen, at a temperature partly above and partly below dull redness, terminating with the lower temperature. After the fire was withdrawn and the tube allowed to cool, air or nitrogen was driven through it, and all free hydrogen thus expelled from the apparatus.

The closed tube was now exhausted in the cold, but no hydrogen came off. The platinum being still retained in a good vacuum, heat was again very gradually applied, and the action of the Sprengel pump maintained. Simultaneously with the first appearance of visible ignition, gas began to be evolved. In one hour, the porcelain tube being heated to redness, 2.12 cub. centims. of gas were collected, of which about one-third was collected in the first ten minutes. It was found, by explosion with oxygen, to consist of—

Hydrogen,	.	.	1.93 cub. centim.
Nitrogen,	.	.	0.19 „

Now, taking the specific gravity of the platinum wire at 21.5, the volume of 201 grms. of metal will be 9.34 cub. centims. Hence one volume of platinum held, the gas being measured cold,

0.207 vol. hydrogen.

The platinum did not appear sensibly altered in lustre, or in any other way, by its relation to the hydrogen.

2. The same piece of platinum wire was drawn out into four times its first length, and the experiment of charging with hydrogen was repeated. The platinum gave up at a red heat, maintained for one hour, 1.8 cub. centim. of gas, of which 1.6 cub. centim. was hydrogen. Here one volume of platinum appears to have held

0.171 vol. hydrogen.

The absorption of hydrogen has not been increased by increasing the surface of the metal.

In two further experiments upon the same platinum wire, the volume of hydrogen retained by one volume of platinum was—

3.	0.173 cub. centim. hydrogen.
4.	0.128 „ „



There is an evident tendency of the hydrogen taken up to diminish in quantity. These experiments have the advantage for comparison with the earlier observations on the penetration of a platinum septum by hydrogen gas, that both wire and tube had been drawn out from the same mass of fused metal. No iridium had been added to this platinum, as is sometimes done to increase the elasticity of the metal. The absorption of hydrogen is small, amounting, according to the mean of the four observations, to 17 per cent. of the volume of the platinum. At the temperature of a low red heat, when the absorption took place, the gas would be considerably dilated, to the extent of at least three times its volume stated above, or to about 51 per cent., half the volume of the platinum. It is to be considered whether an absorption of half a volume of gas would be sufficient to account for the observed penetration of a septum of metal 1.1 millim. in thickness. The data appear to favour an affirmative conclusion; but their value cannot be very decidedly estimated.

It appears necessary to recognise in platinum a new property, a power to absorb hydrogen at a red heat, and to retain that gas at a temperature under redness for an indefinite time. It may be allowable to speak of this as a power to occlude (to shut up) hydrogen, and the result as the *occlusion* of hydrogen by platinum.

The observation was extended to platinum in other conditions of form, but where, it is to be observed, the metal had not been fused, but only welded, and was not of recent manufacture.

5. Of the grey pulverulent spongy platinum, prepared from the ammonio-chloride, 22.2 grms. were heated by the combustion-furnace, and for half an hour allowed to cool gradually in dry hydrogen gas as in the preceding experiments. The volume of the platinum is 1.032 cub. centim. by calculation. In the first experiment it yielded to heat and the action of the Sprengel pump 2.2 cub. centims. of a gas which burned like hydrogen. In a second experiment the platinum yielded in one hour (when it appeared to be exhausted) 1.7 cub. centim. of gas, found by explosion to consist of hydrogen 1.52 cub. centim., and nitrogen 0.18 cub. centim. Here one volume of spongy platinum appears capable of occluding

1.48 vol. hydrogen.

6. Wrought platinum, in the form of plate from an old crucible cut up, after washing and ignition, was charged with hydrogen three times in succession. The weight of the platinum was 24.1 grms., and its volume 1.12 cub. centim. It yielded in seventy-five minutes 4.19 cub. centims. of gas, and in thirty minutes further 1.5 cub. centim. more, making together 5.69 cub. centims., of which 4.94 cub. centims. proved



to be hydrogen; therm.  $14^{\circ}2$ , barom. 760 millims. Not a trace of carbonic acid was found in the gas before or after explosion. Again, after a second charge, 5.12 cub. centims. of gas were given up in an hour, of which 4.4 were hydrogen; and lastly, 3.76 cub. centims. in an hour, of which 3.42 were hydrogen. Hence, occluded by 1 vol. wrought platinum—

5.53 vols. hydrogen.

4.93   "       "

3.83   "       "

The volume of occluded hydrogen is much larger than in the fused platinum, or even in the spongy platinum. It exhibits a tendency to fall off on repeating the experiment. But the declension in absorbing power may possibly be connected with the reduced duration of the exposure to hydrogen of the metal while cooling.

7. Wrought platinum, which had been formed many years ago into a small tube, weighing 64.8 grms., 0.322 metre in length and 5 millims. in diameter, was cut into three equal lengths for convenience in placing the metal within the porcelain tube, to be heated and charged with dry hydrogen. By an hour's exhaustion afterwards the platinum yielded 9.2 cub. centims. gas, of which 8.9 were hydrogen. The volume of the platinum itself was 3.9 cub. centims.; and one volume of metal had therefore occluded 2.28 vols. hydrogen, measured at about  $20^{\circ}$  C. In all such experiments, besides blowing out the free hydrogen by air, the apparatus was also thoroughly exhausted by the Sprengel pump in the cold, before the occluded hydrogen was extracted.

The lustre and appearance of the metallic platinum was not altered by the ingress of the hydrogen; but after the escape of the gas the platinum appeared whiter in colour.

Repeating the experiment, the gas collected by an hour's exhaustion was 8.7 cub. centims., of which 8.46 cub. centims. were hydrogen. Here the metal occluded 2.8 vols. of hydrogen.

The same platinum was a third time charged with hydrogen; but on this occasion the platinum was placed in a tube of hard glass, and the tube connected with the air-exhauster. The glass tube was heated by an oil-bath, and the platinum kept *in vacuo* at a temperature of  $220^{\circ}$  C. for an hour. Not a bubble of gas was evolved. The glass tube was afterwards heated by a small Bunsen burner, which was calculated to give a degree of heat little short of visible redness, still no hydrogen came off. The tube was now heated sufficiently to soften glass ( $500^{\circ}$ ). Gas began to come off, of which 1.8 cub. centim., containing 1.72 hydrogen, were collected in ten minutes. The glass tube having cracked, the whole apparatus was allowed to cool, and the platinum transferred to a



porcelain tube. Further heated by a combustion-furnace for one hour, the platinum gave off 8.6 cub. centims. gas, of which 8.2 were hydrogen. The platinum therefore appears to have occluded altogether 3.79 vols. of hydrogen.

The preceding experiment appeared to show a complete sealing up of the occluded hydrogen at low temperatures, seeing that, although nearly four volumes of gas were present, none escaped below a red heat. But to test the effect of time at the temperature of the atmosphere, the platinum, again charged with hydrogen, was sealed up hermetically in a glass tube, which it nearly filled, and not opened for two months. The air in the tube was then transferred and examined. It did not exhibit any reduction of volume under the electric spark or a pellet of spongy platinum. The air therefore appeared to contain no hydrogen; the latter had not diffused out, but, it is to be presumed, was retained by the platinum without loss. These experiments, although related last, were the first performed in this inquiry. The included hydrogen was never entirely extracted in an hour, and is probably understated. The gas always came off gradually, more than one-half of the whole in the first twenty or thirty minutes. The last results may be stated as follows:—

1 vol. hammered platinum occluded	2.28 vols. hydrogen.
” ” ”	2.80 ”
” ” ”	3.79 ”

The high absorbing power of the hammered platinum, or rather the low absorbing power of the fused metal, was ascribed to a mechanical difference between the two—to a more open texture in the former, permitting more free access of hydrogen, liquefied as it may be, to the interior of the metal.

8. The extrication of occluded hydrogen from platinum had always required a degree of temperature verging upon a red heat, even when aided by a vacuum; and this remains true of hydrogen originally absorbed at or near a red heat. But the fact appears to be compatible with the absorption of the gas, under the pressure of the atmosphere, at a considerably lower temperature. Thin platinum-foil was first deprived of a little natural gas by ignition *in vacuo* in the porcelain tube. The foil was afterwards placed in a glass tube and heated again in a stream of hydrogen, to a temperature not exceeding 230° C., for three hours, by means of an oil-bath, and further allowed to cool slowly in an atmosphere of the same gas for several hours. A second glass tube receiver, to which the platinum-foil was transferred, was exhausted, as usual, at 20° C. without any sensible evolution of gas. With a red heat superadded, gas came off in twenty minutes (but nearly all in the first seven minutes)



to the extent of 0.75 cub. centim., of which 0.56 cub. centim. proved to be hydrogen. The volume of 8.3 grms. of platinum is 0.385 cub. centim. Hence one volume of platinum-foil appears to take up, in three hours,

1.45 vol. hydrogen at 230° C.

9. The same portion of platinum-foil was again charged with hydrogen at a still lower temperature, namely between 97° and 100°, for three hours. Submitted to exhaustion at red heat, the platinum now gave off 0.5 cub. centim. of gas in thirty-five minutes, of which about 0.3 cub. centim. were hydrogen. One volume of platinum-foil has taken up

0.76 vol. hydrogen at 100°.

By this property platinum is connected with palladium, which of all metals appears to possess the power of absorbing hydrogen in the highest degree.

#### *Palladium.*

Of late years palladium has become comparatively uncommon; and some difficulty was experienced at first in procuring more than a gramme or two of the metal, in the form of thin foil. The palladium-foil first employed weighed 1.58 gm., and measured 0.133 cub. centim., taking the specific gravity of the metal at 11.86, and had a surface of 0.00902 square metre. It gave off, when heated *in vacuo* for one hour, 1.50 cub. centim. of natural gas, containing no compound of carbon, but consisting of hydrogen and air.

1. As it appeared from preliminary experiments that the occlusion of hydrogen by palladium was likely to be a phenomenon exhibited at a comparatively low range of temperature, the metal was heated in hydrogen no higher than 245° C., by an oil-bath, and allowed to cool very slowly, so as to pass through still lower ranges of temperature which might be favourable to the absorption of hydrogen. The metal, when afterwards transferred to the distillatory glass tube, appeared to give out nothing to a vacuum at 17° 8 C. and barom. 759 millims. But the moment the combustion-furnace was lighted under the tube, gas came off most freely. Of the first portion collected, 11.77 cub. centims. contained 11.74 cub. centims. hydrogen. The gas ceased to be evolved in fifteen minutes, when 69.92 cub. centims. were collected, of which the greater part came over in the first ten minutes. Hence palladium has taken up a large volume of gas when the temperature of the metal never exceeded 245° C.

1 vol. palladium held 526 vols. hydrogen.

2. In a similar experiment the temperature of absorption was still



further lowered with good effect. The palladium was exposed to hydrogen between  $90^{\circ}$  and  $97^{\circ}$  C. for three hours, and then allowed to cool in the gas for one hour and a half. Now placed in a glass tube, exhausted, and heated by a gas-flame, the palladium gave off gas in a continuous stream for twelve minutes, when it ceased. The gas amounted to 85.56 cub. centims., of which 96.8 per cent. was hydrogen; therm.  $17^{\circ}.5$ , barom. 764 millims.

1 vol. palladium held 643.3 vols. hydrogen.

By the care of my zealous assistant, Mr. W. C. Roberts, the hydrogen employed in these experiments was purified to the highest degree by passing it in succession through alcohol, water, caustic potash, and tubes of 0.7 metre each, filled with broken glass impregnated with nitrate of lead, sulphate of silver, and oil of vitriol. The gas was inodorous, and burned with a barely visible flame.

No alteration was sensible in the metallic appearance of the palladium-foil when charged with hydrogen, or when discharged. The foil was much crumpled and rather friable after repeated use; but this may have arisen from frequent handling.

3. Palladium appears to absorb hydrogen largely, even at natural temperatures, provided that the metal has been recently ignited *in vacuo*. The foil, without such preparation, was placed in a bottle of pure hydrogen for several hours, but yielded nothing when afterwards ignited in the Sprengel vacuum. The foil, however, being immediately returned after cooling to a stoppered bottle containing hydrogen, and left in the gas for a night, absorption now took place—air rushing in, on opening the stopper, as into a partial vacuum; therm.  $19^{\circ}$ . When the palladium-foil was afterwards transferred to a glass tube and connected with the Sprengel pump, it was found difficult to obtain a vacuum for some time, owing to hydrogen coming off at the temperature of the atmosphere. But after a fair vacuum was produced 6.96 cub. centims. were collected, of which 6.78 proved to be hydrogen. Heat was then applied, and 42 cub. centims. came over in five minutes, making altogether more than 50 cub. centims., or 376 volumes of gas. The absorption of hydrogen appears, then, to be suspended at a low temperature, unless the condition of the metal be favourable. The action of a plate of clean platinum in determining the combustion of explosive gas is equally critical at a low temperature.

4. A different specimen of palladium-foil, weighing 5.76 grms., and having a volume of 0.485 cub. centim., was charged with hydrogen, and discharged, more than once. In the second experiment, the foil was heated in hydrogen at  $100^{\circ}$  for three hours. Distilled afterwards in a



porcelain tube at a low red heat in the usual way, the palladium was found to have absorbed, at  $100^{\circ}$ ,

347.7 vols. of hydrogen measured at  $18^{\circ}2$  C. and barom. 756 millims.

5. So large an absorption of hydrogen should increase the weight of the palladium sensibly, notwithstanding the lightness of the gas. One litre, or 1000 cub. centims., of hydrogen at  $0^{\circ}$  C. and 760 millims. weighs 0.0896 gm. Of new palladium-foil, believed to be from *fused* metal, 5.9516 grms. increased to 5.9542, or by 0.0026 gm., when the metal was charged with hydrogen at  $100^{\circ}$  for four hours. This amounts to only 29.01 cub. centims. of hydrogen at  $0^{\circ}$  C. and 760 millims. barom. The gas actually extracted afterwards from the palladium did not exceed 34.2 cub. centims. at  $19^{\circ}$  C., and barom. 758 millims., equivalent to 31.84 cub. centims. at  $0^{\circ}$  C. and 760 millims. barom. The whole gas extricated (68 vols.) seems unusually small, but it corresponds closely enough with the volume calculated from the increase of the palladium in weight. An inferior absorbing power for hydrogen appears to be connected in both platinum and palladium with the fusion of the metal.

6. A portion of similar palladium-foil, charged with hydrogen, was found to have its gas reduced from 20.7 to 16.2 cub. centims. after exposure to the air for forty-two hours. The liquid hydrogen, whether held by the substance or in the pores of the metal, appears therefore to evaporate slowly at the temperature of the atmosphere, therm.  $19^{\circ}$ , barom. 752 millims.

7. Spongy palladium, from the ignition of the cyanide, being heated in hydrogen at  $200^{\circ}$ , and allowed to cool slowly in the same gas for four hours, the metal was found to have taken up 686 vols. of hydrogen.

Treated in a similar manner with air, spongy palladium exhibited no absorbing power for oxygen or nitrogen.

Hydrogen, condensed either in the palladium sponge or foil, was observed to have its chemical affinities enhanced. The palladium being placed in dilute solutions of the following substances for twenty-four hours in the dark at the ordinary temperature, the action of the hydrogen became manifest.

Persalt of iron became protosalt.

Ferri cyanide of potassium became ferrocyanide.

Chlorine-water became hydrochloric acid.

Iodine-water became hydriodic acid.<sup>1</sup>

<sup>1</sup> The power of platinum-black charged with hydrogen to communicate the latter element to organic compounds has lately been observed by M. P. de Wilde, following Dr. Debus.—*Bulletin de la Société Chimique*, Mars 1866.



Apart from hydrogen, the palladium sponge exhibits a power of selection and absorption of alcohol in preference to water. 30 grms. of the sponge were left in contact with 9.5 cub. centims. of dilute alcohol of specific gravity 0.893, for fifty-one hours, sealed in a tube. The supernatant liquid now drawn off to the extent of 3.9 cub. centims. was of specific gravity 0.901, while the portion retained by the palladium was found when distilled to be of specific gravity 0.885, or it was sensibly concentrated. This chemical action of palladium sponge was more than once verified. Platinum sponge, on the other hand, exhibited no indication of a similar separating power; nor did the sponge of iron reduced by hydrogen from the oxide.

8. Connected, it may be, with this chemico-molecular action of palladium is the variable absorptive power for different liquids exhibited by palladium-foil. Immersed in various liquids for an hour, and afterwards dried by pressure for a few seconds between folds of blotting-paper, a quantity of palladium-foil represented by 1000 was found to retain in its pores—

Of Water, . . . . .	1.18 part.
Of Alcohol (0.802), . . . . .	5.5 parts.
Of Ether, . . . . .	1.7 part.
Of Acetone (0.794), . . . . .	0.54 „
Of Glycerine, . . . . .	4.5 parts.
Of Benzol, . . . . .	3.5 „
Of Oil of sweet almonds, . . . . .	18.1 „
Of Castor-oil, . . . . .	10.2 „

The superior penetrativeness of alcohol over water is well marked; capillary action appears to merge into a chemical affinity. Liquid hydrogen would also appear as highly absorbable by palladium-foil. It would appear also to be separable from other gases (or liquids), as alcohol is from water, by the palladium-pores.

*Alloy of 5 palladium and 4 silver.*—The power to absorb hydrogen appears to extend to this alloy of palladium. A plate of the alloy, about 180 millims. in length, 31 millims. in width, and weighing 74.3 grms., was bent, so as to be able to enter a wide porcelain tube that could be exhausted of air when required. The volume of the palladium alloy was 6.21 cub. centims. The plate of metal being placed in the porcelain tube, had hydrogen gas passed over it at a low red heat for one hour, and was then allowed to cool slowly in the same gas. Taken out and examined, the metal was not visibly altered. For the extrication of gas the metal was distilled in the porcelain tube heated by jets of gas, and connected with the Sprengel pump, as usual. In seven minutes after the gas furnace was lit, 24 cub. centims. of gas came off;



in ten minutes more, 80.71 cub. centims.; and in seventy-five minutes more, 36.75 cub. centims., making altogether 141.46 cub. centims. Of this gas 127.74 cub. centims. proved to be hydrogen, the remainder being nitrogen, derived, no doubt, from the large imperfectly exhausted porcelain tube. The palladium alloy, in the form of a thick plate, appears therefore to have held

20.5 vols. hydrogen, measured at  $18^{\circ}2$  and barom. 756 millims.

This alloy of palladium becomes crystalline by heating, and appears to lose much of its absorbent power at the same time.

The conclusion, then, is that welded palladium, in the condition of thin foil, readily absorbs hydrogen, to the extent of upwards of 600 times the volume of the metal at a temperature under the boiling-point of water, upwards of 500 volumes at  $245^{\circ}$ , and less at higher temperatures, the metal being always surrounded by hydrogen under atmospheric pressure. Hydrogen is also largely absorbed, although less constantly, at ordinary temperatures. On the other hand, palladium already fully charged with hydrogen at or under  $100^{\circ}$ , and under the pressure of the atmosphere, begins to give out gas when exposed either to atmospheric air or to a vacuum at the original temperature of absorption; and the gas is freely discharged at  $200^{\circ}$  C.

It is probable that hydrogen enters palladium in the physical condition of liquid, whether the phenomenon proves to be analogous to the imbibition of ether, chloroform, and such solvents by the colloid india-rubber, or whether a certain porosity of structure in the palladium is required. The porosity of the metal is supposed to be of that high degree which will admit liquid but not gaseous molecules. Now the numerous liquid compounds of carbon and hydrogen have all a nearly similar density, generally a little under that of water. There is no reason to suppose that the density of liquid hydrogen would differ greatly from the hydrocarbon class; but then the surprising lightness of hydrogen gas must cause liquid hydrogen to yield a volume of vapour disproportionately large when compared with the former class of substances, or, indeed, with any other substance whatever. The absorption of hydrogen by palladium will appear, then, less extravagantly great when viewed as the absorption of a highly volatile liquid capable of yielding an exceedingly light vapour, rather than that of a gas.

An excellent opportunity of observing the penetration by hydrogen of a compact plate of palladium, 1 millim. in thickness, was afforded by a tube of that metal constructed by Mr. Matthey. This tube was said to have been welded from palladium near the point of fusion of the metal. The length of the tube was 115 millims., its internal diameter 12 millims., thickness 1 millim., and external surface 0.0053 of a square



metre. It was closed by thick plates of platinum soldered at both ends, one of the plates being perforated by a long small tube of platinum, by which the cavity of the palladium tube could be exhausted of air.

Now the closed palladium tube remained air-tight, when exhausted by the Sprengel tube, at the ordinary temperature, at  $260^{\circ}$ , and at a temperature verging on low redness, the gas without being atmospheric air. Hydrogen being then substituted as the external gas, the walls of the palladium tube still remained impermeable at a low temperature. No hydrogen gained the interior in three hours at  $100^{\circ}$ . But the temperature being gradually raised by means of an oil-bath to  $240^{\circ}$ , hydrogen then began to come through, and at a gradually increasing rate to  $265^{\circ}$ . The hydrogen then entered steadily at the rate of 8.67 cub. centims. in five minutes. This gives a rate of 327 cub. centims. for a square metre of surface per minute. Heated to a temperature just short of redness, the passage of hydrogen was increased to 11.2 cub. centims. in five minutes, or 423 cub. centims. for a square metre per minute.

With coal-gas as the external atmosphere the penetration of the palladium began about the same temperature, and was continued at  $270^{\circ}$  at the rate of 57 cub. centims. for a square metre of surface per minute. The penetrating gas had no odour of coal-gas, contained no trace of carbon, and appeared to be absolutely pure hydrogen. The exact isolation of the latter gas by septa of both platinum and palladium appears most extraordinary.

A quantitative determination of the hydrogen in a gaseous mixture could probably be effected by means of the hollow cylinder of palladium.

Is the power to penetrate the metals in question confined to hydrogen? It has been lately concluded by Dr. C. Wetherill that the turgescence of the ammonium amalgam depends entirely upon the retention of hydrogen gas-bubbles;<sup>1</sup> hydrogen, then, appears to exhibit an attraction of a peculiar kind for mercury. The ready liquefaction of the same gas by the platinum metals evinces also a powerful mutual attraction. The only other volatile body which has been observed to pass, like hydrogen, through a plate of palladium is common ether—and that at the atmospheric temperature, while a passage was denied to hydrogen at the same time. The palladium was in the form of foil. Although thin foil of this metal is generably visibly porous and allows air to pass through like a sieve, a tube diffusimeter, covered with a disk of the selected palladium foil, and standing over mercury, retained a volume of 40.5 millims. of air over a vertical column of 155 millims. of mercury for twenty-four hours without depression of the mercury. The air was dried by sticks of potash, but still it did not penetrate the palladium.

<sup>1</sup> *American Journal of Science*, vol. xlii. No. 124.



Dry hydrogen was then conducted to the upper surface of the palladium disk, but still without any penetration by that gas after several hours. Cotton-wool moistened with ether was now placed upon the disk, when, after eight minutes, the confined air within the tube began to expand; and in the course of an hour longer, the 40.5 volumes of confined air increased to 90.4 (thermometer  $18^{\circ}.5$ , barometer 758), when the expansion ceased. The increase of volume appeared to be due entirely to ether-vapour, absorbable by a pellet charged with sulphuric acid. Why hydrogen proved to be incapable of penetrating the palladium in such circumstances it is difficult to say. It can only be imagined that the palladium foil may have previously condensed on its surface a minute film of foreign matter, which rendered the palladium inactive to hydrogen, but not to ether-vapour.

On the other hand, the penetrating power of hydrogen, here referred to the liquefaction of that gas, appears not to be solely confined to metallic septa. There is reason to suspect that in diffusing through a plate of graphite hydrogen passes in a small proportion as a liquid, without any counterdiffusion of air. Hence the constant excess observed of the diffusive coefficient of hydrogen, which came out 3.876, 3.993, and 4.067,<sup>1</sup> instead of the theoretical number 3.8, corresponding to the density of the gas referred to air. Such phenomena of gaseous penetration suggest a progression in the degree of porosity. There appear to be (1.) pores through which gases pass under pressure or by capillary transpiration, as in dry wood and many minerals, (2.) pores through which gases do not pass under pressure, but pass by their proper molecular movement of diffusion, as in artificial graphite, and (3) pores through which gases pass neither by capillary transpiration nor by their proper diffusive movement, but only after liquefaction, such as the pores of wrought metals and the finest pores of graphite.

#### *Osmium-iridium.*

A portion of small grains of osmium-iridium, amounting to 2.528 grms., was exposed to hydrogen through all descending temperatures from a red heat, as the preceding metals had been treated. The osmium-iridium was then heated again to redness in the Sprengel vacuum, to extricate any hydrogen that might have been absorbed. But only a bubble or two of gas, too minute to be measured, passed over in fifteen minutes, at a red heat. Osmium-iridium, then, exhibits no absorbent power for hydrogen—a result which is consistent with the crystalline character of the substance.

<sup>1</sup> *Philosophical Transactions*, 1863, p. 404.



*Copper.*

The power to occlude gases appears not to be confined to palladium and platinum among the metals. The exact experiments of M. Dumas, by which the atomic weights of the leading elements were definitely settled, afford an indication of the absorption of hydrogen gas by spongy metallic copper reduced from the oxide, sufficient to affect the weight of the metal to the extent of about 3 parts in 100,000.<sup>1</sup>

1. With the view of applying the method of extracting gas followed in the treatment of the preceding metals, so much oxide of copper was reduced by hydrogen as was calculated to yield 50 grms. of metallic copper. The reduced metal was again heated to redness and slowly cooled in a stream of dry hydrogen. After free exposure to the air for a few minutes, the metal was now submitted, at a red heat, to the action of the Sprengel pump. It then gave off in one hour 3.35 cub. centims. of gas, measured cold, which appeared to be pure hydrogen (the explosion with oxygen indicated 3.4 hydrogen). Taking the specific gravity of copper at 8.85, 50 grms. of that metal would be 5.65 cub. centims. in volume, and the result is that

1 vol. reduced copper sponge occludes 0.6 vol. hydrogen.

Hydrogen being about 12,000 times as light as copper (at 15°), 1 part of gas by weight has been taken up by 20,000 parts of metal.

2. The same weight and volume of fine copper, in the form of wire, thoroughly cleaned, was exposed to hydrogen at a red heat, and then submitted to exhaustion for one hour. It gave 2.6 cub. centims. gas, of which 2 cub. centims. were hydrogen, and the remaining 0.6 principally carbonic oxide. It may be represented that

1 vol. wrought copper occludes 0.306 vol. hydrogen.

Where a metal, such as wrought copper, may contain small quantities of carbon and oxygen, an obvious cause will exist for the production and evolution of carbonic oxide under the influence of heat. Gas so generated appears to be added to the occluded hydrogen when extricated, in the last experiment.

*Gold.*

1. A quantity of gold was precipitated from the assay cornettes used below by means of oxalic acid. The gold weighed 93.3 grms., with a

<sup>1</sup> *Annales de Chimie et de Physique*, 3 sér. t. viii. p. 205. The observations of M. Melsens show that 240 grms. of copper may fix about 0.007 gm. of hydrogen, most being fixed when the oxide of copper is reduced by hydrogen at a low temperature. In the subsequent oxidation of the copper the gas does not come out suddenly, but in a gradual manner.



volume of 4.83 cub. centims., taking the specific gravity of the metal as 19.31. Exhausted at a red heat without any further treatment, the reduced gold yielded 3.4 cub. centims. of gas, which may therefore be supposed to be gas usually present in gold reduced in the manner described. This is 0.704 vol. of the gold. The occluded gas in precipitated gold gave to analysis

0.05	cub. centim.	Oxygen.
1.50	„	„ Carbonic acid.
1.85	„	„ Carbonic oxide, etc.
<hr/>		
3.40		

2. Of the original cornettes of fine gold, from gold assays conducted several months before, 93.3 grms., having a volume of 4.83 cub. centims., were submitted without any further treatment to aspiration at a red heat. The gold gave up in the first half hour 9.45 cub. centims of gas, and in the second half hour 0.8 cub. centim., making together 10.25 cub. centims. Hence 1 volume of the gold cornettes appears to hold 2.12 volumes of gas. This gas consisted of

6.70	cub. centims.	Carbonic oxide.
1.50	„	„ Carbonic acid.
1.58	„	„ Hydrogen.
0.44	„	„ Nitrogen.
0.03	„	„ loss.
<hr/>		
10.25		

The cornettes do not appear ever to assume again so much gas as they first acquired in the assay muffle. It follows that the weight of a gold cornette is increased about 2 parts in 10,000 by the weight of occluded gas. As the gold also retains 7 or 8 parts of silver in 10,000, it follows that the absolute quantity of gold in a cornette is less than the weight of the cornette as indicated by the balance, by 1 part in 1000. This does not disprove the accuracy of the usual gold assay, which is always made in comparison with gold of known composition as a check, and is therefore *relatively* true.

3. The same volume of gold cornettes, amounting to 4.83 cub. centims., heated again in carbonic oxide gas, gave up afterwards 1.6 cub. centim. of occluded gas, composed of

1.4	cub. centim.	Carbonic oxide.
0.2	„	„ Carbonic acid.
<hr/>		
1.6		

4. The same mass of gold cornettes heated in hydrogen gas, gave



up afterwards in one hour 2.7 cub. centims. of gas, which appeared to consist of

2.34	cub. centims.	Hydrogen.
0.36	„	„ Nitrogen, etc.
<hr/>		
2.70		

The power of this metal to occlude hydrogen gas is very sensible. The metal here appears to hold 0.48 volume of hydrogen gas. The same gold, when dissolved and precipitated, was also found capable of holding 0.44 volume of hydrogen.

5. The same mass of cornettes, heated in carbonic acid gas, gave up afterwards in one hour 1.05 cub. centim. gas, in which baryta-water showed the presence of

0.78 cub. centim. Carbonic acid.

The charged cornettes were always freely exposed to air for some time before occluded gas was extracted from them and measured, so as to allow the escape of any loosely attached gas.

6. The same cornettes were heated and cooled in a stream of dry air, in like manner as they had been treated with other gases. The occluded air given out in one hour amounted in two different experiments to 1.15 and 0.95 cub. centim. respectively. The gas of the second experiment gave

0.82	cub. centim.	Nitrogen	= 86.3
0.08	„	„ Carbonic acid	= 8.4
0.05	„	„ Oxygen	= 5.3
<hr/>			
0.95			100.0

The whole occluded air amounts to 0.2 volume of the gold, and is principally *nitrogen*. The indifference of gold to oxygen is remarkable, and contrasts with the power of silver to occlude the same gas.

### *Silver.*

1. Fine silver, in the form of wire, 2 millims. in diameter, with its surface duly purified, was first heated alone in the porcelain tube, and then exhausted of gas by the Sprengel tube in the usual way. The natural gas derived from this metal was small in quantity, and it appeared to come off almost entirely in one hour. The silver wire weighed 108.8 grms., and had a volume of 10.37 cub. centims., taking the specific gravity of pure silver as 10.49. The gas extracted amounted to



2.2 cub. centims. in thirty minutes.

0.8 " " "

3.0 " " in one hour.

The gas consisted of

2.4 cub. centims. Carbonic acid.

0.6 " " Carbonic oxide.

3.0

Silver wire therefore appeared to hold occluded 0.289 volume of gas, principally carbonic acid. There is reason, however, to suppose that the occluded gas may really be oxygen, and that the latter was converted into carbonic acid at the temperature of extrication, by a trace of carbon existing in the fine silver.

2. The same quantity of silver wire was now charged with hydrogen, by being heated to redness and afterwards cooled slowly in that gas. The gas extricated amounted to

2.3 cub. centims. in forty-five minutes.

0.2 " " in fifteen minutes.

2.5 " " in one hour.

The gas consisted of

2.2 cub. centims. Hydrogen.

0.3 " " Nitrogen, etc.

2.5

The fine silver had therefore occluded 0.211 volume of hydrogen. The metal acquired a beautiful frosted appearance on the surface; and by repeated heating it became highly crystalline and brittle.

3. The same portion of silver was now charged with oxygen. The occluded gas given off amounted to

7.5 cub. centims. in thirty minutes.

0.3 " " "

7.8 " " in one hour.

The gas consisted of

7.6 cub. centims. Oxygen.

0.2 " " Nitrogen, etc.

7.8

The silver therefore held occluded 0.745 volume of oxygen. This gas, like the hydrogen in platinum, was permanently fixed in the metal



at all temperatures below an incipient red heat. It did not tarnish the bright metallic surface of the silver, or produce any appearance suggestive of the oxidation of a metal.

4. The same portion of silver, after being dissolved in acid, precipitated as chloride, and reduced again, was exposed to atmospheric air at a red heat, and afterwards exhausted. The gas given off amounted to

5.56 cub. centims. in fifteen minutes.

0.30	„	„	„
5.86			

Of this gas 5.56 cub. centims., or nearly the whole, proved to be oxygen gas; or the silver held occluded 0.545 volume of oxygen. This silver had been purified from the chloride, and it contained no trace of copper.

When silver, of British Standard (that is, containing 7.5 per cent. of copper), is exposed to air or oxygen at a low red heat, the silver becomes almost black on the surface from oxidation of the copper. Silver wire in this blackened state gave off several volumes of oxygen under the action of heat and a vacuum. Much of the superficial oxide disappeared at the same time. It appeared as if the operation tended to the reduction of the superficial oxide of copper, oxygen being liberated, and the copper absorbed by the mass of silver.

5. A specimen of silver reduced from the oxide, in the form of sponge, which was considered pure, but was not analysed, occluded 6.15, 8.05, and 7.47 volumes of oxygen, in successive experiments, without any visible tarnish of the surface. Can the attraction or affinity of silver for oxygen, which enables the pure metal to occlude that gas, be enhanced by the presence of a mere trace of some positive metal like copper?

6. The same specimen of fritted silver was found to occlude, in successive experiments,

0.907 vol. Hydrogen.

0.938 „ „

0.486 „ Carbonic acid.

0.545 „ „

0.156 „ Carbonic oxide.

Hydrogen and carbonic acid, as well as oxygen, appear to be taken up in larger proportion by this silver than by the former specimen of the same metal.

7. Of pure silver highly laminated, 500 leaves, weighing 12.5 grms., were exposed to air at a red heat, and thereafter exhausted at the same temperature. The silver (1 vol.) gave up 1.37 volume of oxygen, 0.20 volume of nitrogen, and 0.04 volume of carbonic acid.



It appears that silver has a relation to oxygen similar to that exhibited by platinum, palladium, and iron to hydrogen. The power of silver and of litharge in a state of fusion to absorb oxygen, and to allow that gas to escape on solidification, may be connected with the observed capacity of the colloid metal, softened by heat, to absorb the same gas, although to a less extent.

### *Iron.*

The penetration of iron by hydrogen is demonstrated as clearly by MM. Deville and Troost as that of platinum. A thin tube of cast steel, 3 or 4 millims. in thickness, already enclosing hydrogen gas in its cavity, was surrounded by air or by nitrogen gas circulating in an annular space between the steel tube mentioned and a wider external porcelain tube. In the absence of any visible pores in the steel, hydrogen made its way through the substance of the metal, and escaped into the annular space as soon as the system of tubes was exposed to a red heat. A nearly if not entirely complete vacuum was formed within the iron tube.<sup>1</sup> In another modification of the experiment, carbonic oxide from an uncertain source appeared within the iron tube, particularly when the temperature was most elevated.<sup>2</sup>

Wrought iron, in the form of thin wire (No. 23), about 0.4 millim. in diameter, first carefully cleaned with caustic alkali and water, was heated alone in the porcelain tube exhausted of air, for the purpose of eliminating any natural gases.

1. Of the iron wire referred to, 46 grms., with a volume of 5.9 cub. centims., the specific gravity of the metal being taken at 7.8, were heated by the open combustion-furnace. Gas came off freely at a red heat,—

(1) In fifteen minutes, 15.6 cub. centims., containing 3.5 cub. centims. carbonic acid, or 22.4 per cent.

(2) In fifteen minutes, 7.17 cub. centims., containing 0.52 cub. centim. or 7.2 per cent. of carbonic acid. The gas of this and the following stages of observation now burnt with a blue flame, and was principally carbonic oxide.

(3) In thirty minutes, 10.4 cub. centims., of which 6.86 cub. centims. were carbonic oxide.

(4) In thirty minutes, 8.16 cub. centims., of which 0.12, or 1.4 per cent. was carbonic acid.

(5) In thirty minutes, 5.52 cub. centims., of which 0.03 was carbonic acid—that is, 0.5 per cent.

Hence 46 grms. of wrought iron have in two hours given off 46.85

<sup>1</sup> *Comptes Rendus*, t. lvii. p. 965 (1863).

<sup>2</sup> *Ibid.* t. lix. p. 102 (1864).



cub. centims. of gas, measured at about  $15^{\circ}$  C.; or 1 volume of iron has discharged 7.94 volumes of gas, of which about two-thirds was carbonic oxide; and the metal does not appear to be yet quite exhausted. Iron is a metal not unlikely to contain small quantities of carbon and oxygen, both in chemical union with iron; and the gas extricated may partly be due to a reaction of these elements upon each other at a red heat.

2. In another similar experiment upon 32 grms. of clean iron wire (No. 21), measuring 4.1 cub. centims., the iron was heated in a small glass tube, to exclude the idea of the conceivable permeability of the porcelain tube. The iron gave off gas at a pretty uniform rate, which amounted in an hour to 29.8 cub. centims., of which 4.44 cub. centims. were carbonic acid, and the remainder principally carbonic oxide, with hydrogen and a trace of a hydro-carburet. Here the iron wire gave off 7.27 volumes of gas.

3. In a third experiment on thin iron wire (No. 23), the extrication of the natural gases at a red heat was pushed to a greater degree of exhaustion. The weight of the iron was 39 grms., and its volume 5 cub. centims. In the first and second hour the gas collected was 45 cub. centims.; in the third hour 10.85 cub. centims.; in the fourth and fifth hours 5.65 cub. centims.; in the sixth hour 0.9 cub. centim., and in the seventh hour 0.7 cub. centim. The iron appears to be now nearly exhausted, after the extrication of 63.1 cub. centims., or 12.55 volumes of gas.

It is evident that iron cannot be safely dealt with in experiments upon the permeation or upon the absorption of gases, till these gases, whether self-produced or pre-existing, are first extricated from the metal. The carbonic oxide observed in the tube experiments of M. Deville may have been derived from the same source.<sup>1</sup>

4. To observe the absorption of hydrogen, the mass of exhausted iron wire remaining after the last experiment was heated to redness, and cooled gradually in the same gas. The metal was afterwards freely exposed to air (as usual) to get rid of any loosely attached hydrogen. Now exhausted again by the Sprengel pump at a low red heat, the iron gave 2.5 cub. centims. of gas in one hour, but the greater portion in the first ten minutes, consisting of

2.3	cub. centims.	Hydrogen.
0.2	„	„ Carbonic oxide, etc.
2.5		

The iron appears therefore to be capable of holding 0.46 volume of

<sup>1</sup> The gases which escape from cast iron in a state of fusion have been examined by M. L. Caillietet. They appear to contain from 49 to 58 per cent. of carbonic oxide, 34 to 39 of hydrogen, and 8 to 12 of nitrogen.—*Comptes Rendus*, t. lxi. p. 850 (1865).



hydrogen. The wire became white, like galvanized iron. This was confirmed in a second observation, a thicker wire holding 0.42 vol. hydrogen.

5. The same specimen of iron was now charged with carbonic oxide gas, in the manner it had previously been charged with hydrogen. It was also freely exposed to air. The iron wire remained soft, was not capable of becoming hard when heated red-hot and suddenly cooled, and was not altered in aspect or in solubility in acids. The gas extricated by the air-exhauster amounted to

9.45 cub. centims. in 13 minutes.			
2.43	„	5	„
8.05	„	42	„
3.15	„	60	„
23.08	„	in two hours.	

Of this gas 20.76 cub. centims. proved to be carbonic oxide. *Pure iron, then, is capable of taking up at a low red heat, and holding when cold, 4.15 volumes of carbonic oxide gas.* This fact was confirmed in various other experiments. It explains partly, if not entirely, the abundance of carbonic oxide observed among the natural gases of iron in experiments 1, 2, and 3. In the course of its preparation wrought iron may be supposed to occlude six or eight times its volume of carbonic oxide gas, which is carried about ever after. How the qualities of iron are affected by the presence of such a substance, no way metallic in its characters, locked up in so strange a way, but capable of reappearing, under the influence of heat, at any time, with the elastic tension of a gas, is a subject which metallurgists may find worthy of investigation.

The relations of the metal iron to carbonic oxide gas appear to be altogether peculiar. They cannot fail to have a bearing upon the important process of *acieration*. The intervention of carbonic oxide in the usual process of the cementation of iron with charcoal, long recognised by accurate observers, may be said now to be placed beyond all doubt by the recent beautiful research of M. Margueritte.<sup>1</sup> Hitherto the decomposing action of the iron upon carbonic oxide has been supposed to be exercised only at the external surface of the metal. A surface-particle of the iron has been supposed to assume one half of the carbon belonging to an equivalent of carbonic oxide ( $C_2O_2$ ), while the remaining elements diffused away into the air as carbonic acid ( $CO_2$ ), to reacquire carbon from the charcoal placed near, and to become capable of repeating the original action. It is now seen that such a process need not be confined to the surface of the iron bar, but may occur throughout the substance of the metal, in consequence of the prior

<sup>1</sup> *Annales de Chimie*, etc., 4 sér. t. vi., 1865.



penetration of the metal by carbonic oxide. The direct contact and action of carbon (in the form either of diamond or charcoal) upon iron is allowed to produce cast iron and not steel. It appears that the diffused action of carbonic oxide is the proper means of distributing the carbon throughout the mass of iron. The blistering of the bar appears to testify to the necessary production and evolution of carbonic acid, owing to the decomposition of the carbonic oxide in the interior of the bar.

The inquiry suggests itself whether acieration would not be promoted by alternation of temperature frequently repeated. The lowest red heat, or a temperature even lower, appears to be most favourable to the absorption of carbonic oxide by iron, or for impregnating the metal with that gas; while a much higher temperature appears to be required to enable the metal to decompose carbonic oxide, to appropriate the carbon, and become steel. The action of a high temperature is made very clear by M. Margueritte. The process of acieration, it seems then, should be divided into two distinct stages, conducted at very different temperatures,—the first to introduce carbonic oxide into the iron, and the second to decompose the carbonic oxide so introduced. The carbonic oxide once safely occluded by the iron, the metal might even be cooled and preserved in the air, the second heating being postponed for any length of time. Such alternations of temperature are not unlikely to occur by accident during the usual long process of cementation; but they might be properly regulated with advantage, and the process may admit of being abridged in point of time.

Antimony, as a highly crystallizable metal, was exposed to hydrogen gas both above and below the point of fusion of the metal, and afterwards submitted to exhaustion in the usual manner. No hydrogen was extricated.

## XVIII.

### ON THE OCCLUSION OF HYDROGEN GAS BY METEORIC IRON.

From *Proceedings of the Royal Society*, vol. xv. p. 502, May 16, 1867. [*Comptes Rendus*, May 27, 1867, vol. lxiv. p. 1067; Poggendorff's *Annal.* vol. cxxxi. (1867), p. 151].

SOME light may possibly be thrown upon the history of such metals found in nature as are of a soft colloid description, particularly native iron, platinum, and gold, by an investigation of the gases which they



hold occluded, such gases being borrowed from the atmosphere in which the metallic mass last found itself in a state of ignition. The meteoric iron of Lenarto appeared to be well adapted for a trial. This well-known iron is free from any stony admixture, and is remarkably pure and malleable. It was found by Wehrle to be of specific gravity 7.79, and to consist of—

Iron, . . . . .	90.883
Nickel, . . . . .	8.450
Cobalt, . . . . .	0.665
Copper, . . . . .	0.002

From a larger mass a strip of the Lenarto iron 50 millimetres by 13 and 10 millimetres, was cut by a clean chisel. It weighed 45.2 grammes, and had the bulk of 5.78 cubic centimetres. The strip was well washed by hot solution of potassa, and then repeatedly by hot distilled water, and dried. Such treatment of iron, it had been previously found, conduces in no way to the evolution of hydrogen gas when the metal is subsequently heated. The Lenarto iron was enclosed in a new porcelain tube, and the latter being attached to a Sprengel aspirator, a good vacuum was obtained in the cold. The tube being placed in a trough combustion furnace, was heated to redness by ignited charcoal. Gas came off rather freely, namely—

In 35 minutes, . . . . .	5.38 cub. centims.
In 100 minutes, . . . . .	9.52 „
In 20 minutes, . . . . .	1.63 „
In 2 hours 35 minutes, . . . . .	16.53 „

The first portion of gas collected had a slight odour, but much less than that of the natural gases occluded by ordinary malleable iron. The gas burned like hydrogen. It did not contain a trace of carbonic acid, nor any hydrocarbon vapour absorbable by fuming sulphuric acid. The second portion of gas collected, consisting of 9.52 cub. centims., gave by analysis—

Hydrogen, . . . . .	8.26 cub. centims.	. . . . .	85.68
Carbonic oxide, . . . . .	0.43 „	. . . . .	4.46
Nitrogen, . . . . .	0.95 „	. . . . .	98.6
	9.64 „	. . . . .	100.00

The Lenarto iron appears, therefore, to yield 2.85 times its volume of gas, of which 86 per cent. nearly is hydrogen. The proportion of carbonic oxide is so low as  $4\frac{1}{2}$  per cent.

The gas occluded by iron, from a carbonaceous fire, is very different, the prevailing gas then being carbonic oxide. For comparison a quan-



tity of clean horse-shoe nails was submitted to a similar distillation. The gas collected from 23·5 grammes of metal (3·01 cub. centims.) was—

In 150 minutes,	.	.	5·40 cub. centims.
In 120 minutes,	.	.	2·58 „
In 4 hours 30 minutes,	.	.	7·98 „

The metal has given 2·66 times its volume of gas. The first portion collected appeared to contain, of hydrogen 35 per cent., of carbonic oxide 50·3, of carbonic acid 7·7, and of nitrogen 7 per cent. The latter portion collected gave more carbonic oxide (58 per cent.) with less hydrogen (21 per cent.), no carbonic acid, the remainder nitrogen. The predominance of carbonic oxide in its occluded gases appears to attest the telluric origin of iron.

Hydrogen has been recognised in the spectrum-analysis of the light of the fixed stars, by Messrs. Huggins and Miller. The same gas constitutes, according to the wide researches of Father Secchi, the principal element of a numerous class of stars, of which  $\alpha$  Lyrae is the type. The iron of Lenarto has no doubt come from such an atmosphere, in which hydrogen greatly prevailed. This meteorite may be looked upon as holding imprisoned within it, and bearing to us, hydrogen of the stars.

It has been found difficult, on trial, to impregnate malleable iron with more than an equal volume of hydrogen, under the pressure of our atmosphere. Now the meteoric iron gave up about three times that amount, without being fully exhausted. The inference is that the meteorite has been extruded from a dense atmosphere of hydrogen gas, for which we must look beyond the light cometary matter floating about within the limits of the solar system.

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## XIX.

### ON THE OCCLUSION OF HYDROGEN GAS BY METALS.

From *Proceedings of the Royal Society*, June 11, 1868, vol. xvi. p. 422. [*Comptes Rendus*, May 25, 1868, vol. lxvi. p. 1014; *Archives des Sciences*, June 1868, vol. xxxii. p. 148; *Annales de Chimie et de Physique* [4] vol. xiv. p. 315; Poggendorff's *Annal.* vol. cxxxiv. 1868, p. 321; *Philosophical Magazine* [4], vol. xxxvi. p. 63.]

In my experiments, already published, on the occlusion of hydrogen by the metals palladium, platinum, and iron, the absorption of the gas was observed to be of uncertain occurrence at low temperatures, but was insured by heating the metal, whether in the form of sponge or



aggregated by hammering, and allowing it to cool slowly and completely in a hydrogen atmosphere. This fact was referred to the condition of absolute purity of the metallic surface being essential to the first absorbing action, as it is to the action of platinum-foil or wire in determining the combustion of the gaseous mixture of oxygen and hydrogen, as observed by Faraday. A new method of charging the metals with hydrogen at low temperatures has lately presented itself, which is not without interest.

When a plate of zinc is placed in dilute sulphuric acid, hydrogen is freely evolved from the surface of the metal, but no hydrogen is occluded and retained at the same time. A negative result was indeed to be expected from the crystalline structure of zinc. But a thin plate of palladium immersed in the same acid, and brought into metallic contact with the zinc, soon becomes largely charged with the hydrogen, which is then transferred to its surface. The charge taken up in an hour by a palladium plate, rather thick, at  $12^{\circ}$  amounted to 173 times its volume.

The absorption of hydrogen was still more obvious when the palladium plate was constituted the negative electrode in acidulated water to a Bunsen battery of six cells. The evolution of oxygen gas at the positive electrode continuing copious, the effervescence at the negative electrode was entirely suspended for the first twenty seconds, in consequence of the hydrogen being occluded by the palladium. The final absorption amounted to 200.4 volumes, and was greater in amount than the volume of hydrogen occluded by the same plate heated and cooled in an atmosphere of the gas, which did not exceed 90 volumes.

It is worthy of remark that, although the hydrogen enters the palladium, and no doubt pervades the whole mass of the metal in such circumstances, the gas exhibits no disposition to leave the metal and escape into a vacuum, at the temperature of its absorption. Thus a thin plate of palladium, charged with hydrogen in the manner described, was washed, dried by a cloth, and then sealed up in an exhausted glass tube. On breaking the tube under mercury after two months, the vacuum was found perfect. No hydrogen had vaporized in the cold (about  $12^{\circ}$ ); but on the application afterwards of a heat of  $100^{\circ}$  and upwards, 333 volumes of gas were evolved from the metal.

A similar result was obtained on making a hollow palladium cylinder, of which the length was 115 millimetres, diameter 12 millimetres, and thickness 1 millimetre, the negative electrode in an acid fluid, while the closed cavity of the cylinder was kept exhausted by means of a Sprengel aspirator. No hydrogen whatever passed through into the vacuous cavity in several hours, although the gas was no doubt abundantly absorbed by the outer surface of the cylinder, and pervaded the metal throughout.



It appears, then, that when hydrogen is absorbed by palladium, the volatility of the gas may be entirely suppressed; and hydrogen may be largely present in metals without exhibiting any sensible tension at low temperatures. Occluded hydrogen is certainly no longer a gas, whatever may be thought of its physical condition. The same conclusion was indicated by another series of experiments, in which it was found that, to be occluded by palladium, and even by iron, hydrogen does not require to be applied under much pressure, but, on the contrary, when highly rarefied is still freely absorbed by these metals.

The occluded hydrogen is readily extracted from palladium by reversing the position of the latter in the decomposing cell of the battery, so as to cause oxygen to be evolved on the surface of the metal. The hydrogen is then drawn out as rapidly as it had previously entered the palladium, and the metal is exhausted in a complete manner by such treatment. When palladium charged with hydrogen is left exposed to the atmosphere, the metal is apt to become suddenly hot, and to lose its gas entirely by spontaneous oxidation.

Platinum may be charged with hydrogen by voltaic action, as well as palladium, but with the usual inferior proportion of gas. The charge of hydrogen taken up in a decomposing voltaic cell by old platinum in the form of a tube, of the thickness of a small crucible, was 2.19 volumes. This absorbed gas was also readily withdrawn from the platinum, and oxidized on reversing the place of the metal in the decomposing cell. The platinum acquired its well-known polarizing power in virtue of the occluded hydrogen. This power was retained by the metal after being washed with pure water and wiped with a cloth, and was brought into action on placing the metal in dilute acid. The temperature required to expel the hydrogen so absorbed by platinum was found to be little short of a red heat, although the gas had entered the metal at a low temperature.

Soft iron, left some time in a dilute acid, occluded 0.57 volume of hydrogen. This charge of gas was also retained at low temperatures, and did not escape into a vacuum till the temperature was raised nearly to redness. This proves that, like platinum, iron is not penetrated through in the cold by hydrogen, the temperature of emission being elevated considerably.<sup>1</sup>

While hydrogen was absorbed freely by palladium and platinum as negative plates, no oxygen whatever was absorbed by plates of the same metals in the position of positive electrodes. Oxygen gas was dis-

<sup>1</sup> In M. Cailletet's experiment of exposing a thin sheet of iron to an acid, the metal is no doubt penetrated through by hydrogen in the cold, but apparently from the penetrating agency of the acid which is insinuating itself into the metal at the same time.—*Comptes Rendus*, 4 Mai 1868.



engaged freely on the surface of the latter without being condensed. A platinum plate which had acted for several hours as a positive electrode gave afterwards, when submitted to heat with exhaustion, a small trace of carbonic acid, but no oxygen.

The familiar igniting power of platinum sponge (or clean plate) upon a jet of hydrogen in the air seems to depend solely upon the influence of the metal upon its occluded hydrogen. The hydrogen appears to be polarized, and to have its attraction for oxygen greatly heightened. I beg to offer the following representation of this phenomenon, with an apology for the purely speculative character of the explanation. The gaseous molecule of hydrogen being assumed to be an association of two atoms, a hydride of hydrogen, it would follow that it is the attraction of platinum for the negative or "chlorylous" atom of the hydrogen molecule which attaches the latter to the metal. The tendency, imperfectly satisfied, is to the formation of a hydride of platinum. The hydrogen molecule is accordingly polarized, *orienté*, with its positive or "basylous" side turned outwards, and having its affinity for oxygen greatly enlivened. It is true that the two atoms of a molecule of hydrogen are considered to be inseparable; but this may not be inconsistent with the replacement of such hydrogen atoms as are withdrawn, on combining with oxygen, by other hydrogen atoms from the adjoining molecules. It is only necessary to suppose that a pair of contiguous hydrogen molecules act together upon a single molecule of the external oxygen. They would form water, and still leave a pair of atoms, or a single molecule of hydrogen, attached to the platinum.

The oxidation of alcohol, ether, and similar hydrocarbons, through the agency of platinum, likewise appears to be always an immediate consequence of a similar polarization of the hydrogen of those substances, or of some other oxidable constituent.

As has already been remarked, it does not follow that, because a gas is occluded by a metal, under the pressure of the atmosphere, at a low temperature, the gas will also escape from the metal into a vacuum at the same temperature, a much higher temperature being often required for the expulsion of the gas than for its first absorption. This is particularly true of carbonic oxide occluded by iron. Cast iron is much too porous for such experiments, and allows carbonic oxide, equally with other gases, to pass through abundantly by the agency of gaseous diffusion. Even with malleable iron there is a difficulty in observing, owing to the long time during which that metal continues to discharge carbonic oxide from its own store of that gas. But a malleable iron tube, first thoroughly deprived of its natural gas, was found to allow carbonic oxide to pass through it into a vacuum very slowly compared with hydrogen, although the volume of carbonic oxide which the metal



is capable of absorbing is very sensible, amounting to 4 volumes, and more considerable than the volume of hydrogen which the same metal can occlude. Carbonic oxide did not sensibly pass through iron of 1·7 millimetre in thickness till the temperature was greatly elevated; and then the passage of gas was, in a minute—

Of carbonic oxide, at a full red heat, 0·284 cub. centims. per square metre of surface.

Of hydrogen oxide, at a full red heat, 76·5 cub. centims. per square metre of surface.

The condition of hydrogen as occluded by a colloidal metal may be studied with most advantage in its union with palladium, where the proportion of gas held is considerable. In the pulverulent spongy state, palladium took up 655 volumes of hydrogen; and so charged it gave off no gas *in vacuo* at the ordinary temperature, nor till its temperature was raised to nearly 100°. Hammered palladium foil has been observed to take up quite as much gas. But the condition in which palladium appears to be most absorptive is when precipitated from a solution of about 1·6 per cent. of the chloride, by the action of a voltaic battery, in the form of a compact metal. Palladium is not one of the metals readily thus precipitated; but it may be thrown down upon a thin platinum wire, in brilliant laminae, by the action of a large single cell. The palladium after a time detaches itself from the wire, exhibiting a bright white metallic surface where it had been in contact with the platinum, and a dull surface, suggesting metallic arsenic, on the side exposed to the acid. As so prepared, it does not contain any occluded hydrogen. But the metallic films, when heated to 100° in hydrogen, and allowed to cool slowly for an hour in the same gas, were found to occlude 982·14 volumes of gas, measured with thermometer at 11°, and barometer at 756 millimetres. This is the largest absorption of hydrogen observed. From the palladium so charged there was a slight indication of the escape of hydrogen into a vacuum, with extreme slowness in the cold. This charged palladium is represented by weight as

Palladium 1·0020 grm.,	.	.	.	99·277
Hydrogen 0·0073 grm.,	.	.	.	·723
				<hr/> 100·000

It is in the proportion of one equivalent of palladium to 0·772 equivalent of hydrogen,<sup>1</sup> or there is an approximation to single equivalents Pd H. But the idea of definite chemical combination is opposed by various considerations. No visible change is occasioned to the metallic palladium by its association with the hydrogen. Hydrides of certain

<sup>1</sup> H=1, Pd=106·5.



metals are known, as the hydride of copper (Wurtz) and the hydride of iron (Wanklyn); but they are brown pulverulent substances with no metallic characters. Indeed, a hydride of palladium itself can be formed, but not preserved, on account of its great instability. Following the process of M. Wurtz for the hydride of copper, nitrate of palladium was boiled with sulphuric acid, and the sulphate of palladium (a red crystalline salt) prepared. A solution of this salt, with an excess of sulphuric acid, was precipitated by the hypophosphite of soda; a black powder fell, which speedily underwent decomposition at  $0^{\circ}$ , evolving copious volumes of hydrogen gas. The final residue appeared to be pure palladium, of its usual black amorphous appearance, and with no trace of crystallization. It is singular that this palladium precipitate contained no occluded hydrogen; and even when heated, and afterwards exposed to an atmosphere of hydrogen in the usual manner, the palladium black so prepared condensed no sensible quantity of that gas.

I am inclined to conclude that the passage of hydrogen through a plate of metal is always preceded by the condensation or occlusion of the gas. But it must be admitted that the rapidity of penetration is not in proportion to the volume of gas occluded; otherwise palladium would be much more permeable at a low than at a high temperature. A plate of that metal was sensibly exhausted of hydrogen gas at  $267^{\circ}$ , but continued permeable, and in fact increased greatly in permeability, at still higher temperatures, and without becoming permeable to other gases at the same time. In a striking experiment, a mixture of equal volumes of hydrogen and carbonic acid was carried through a small palladium tube, of which the internal diameter was 3 millimetres, and the thickness of the wall 0.3 millimetre. From the outer surface of this tube gas escaped into a vacuum, at a red heat, with the enormous velocity of 1017.54 cub. centims. per minute for a square metre of surface. This gas did not disturb baryta-water. It was pure hydrogen.

A still more rapid passage of hydrogen was observed through the substance of a hollow cylinder of palladium 1 millimetre in thickness, at a higher temperature, approaching the melting-point of gold. The palladium cylinder being enclosed in a porcelain tube charged with pure hydrogen, was exhausted as usual, and gave 105.8 cub. centims. of gas in five minutes, measured with bar. 753 millims., therm.  $10^{\circ}$ . As the external surface of the palladium tube amounted to 0.0053 square metre, the passage of gas was

3992.22 cub. centims. from a square metre of surface per minute.

The rate of penetration of hydrogen through the same palladium tube, at the lower temperature of  $265^{\circ}$  C., was previously observed to be

327 cub. centims. from a square metre of surface per minute.



The velocity of penetration thus appears to increase in a rapid ratio with the temperature.

When carbonic acid was substituted for hydrogen, at the same high temperature, a very minute penetration was perceived, amounting to

1.86 cub. centim. from a square metre of surface per minute.

This gives for carbonic acid one twenty-thousandth part of the rate of hydrogen. Whether it is a penetration of the same sort, although greatly less in degree, or rather the consequence of a sensible porosity in the palladium (of which it would become the measure), remains uncertain.

The quantity of hydrogen held by the metal at these high temperatures may become too small to be appreciated; but I presume it is still present, and travels through the metal by a kind of rapid cementation. This extreme mobility is a singular property of hydrogen, which was involved in the fundamental discovery, by MM. H. Sainte-Claire Deville and Troost, of the passage of that gas through plates of iron and platinum at high temperatures.

The marked rapidity of the passage of the same gas through a thin sheet of caoutchouc appears to be more capable of explanation on known principles. Caoutchouc of less than 0.1 millimetre in thickness, if impregnated with hydrogen, loses its gas entirely by the most momentary exposure to the air. A tube of 2 millimetres in thickness, through which hydrogen and carbonic acid were singly passed, each for an hour, was found to retain—

Of hydrogen,	.	.	.	0.0113 volume.
Of carbonic acid,	.	.	.	0.2200 „

The absorption, then, is in the proportion of 1 hydrogen to 20 carbonic acid; but the comparative rate of penetration of the two gases through a sheet of caoutchouc is as 1 hydrogen to  $2\frac{1}{2}$  carbonic acid; or the hydrogen moves eight times as rapidly as the density of its solution would indicate. But these gases differ in diffusibility as carbonic acid 1 to hydrogen 4.7. The rapid passage of hydrogen through caoutchouc is thus partly explained by the rapid manner in which that gas is brought to one surface of the sheet and conveyed away from the other by gaseous diffusion. Again, both substances travel through the substance of the caoutchouc by their diffusibility *as liquids*. Suppose hydrogen in that form to be nearly as much more diffusive than the other substance as it is when both are gaseous, then the observed rapid passage of hydrogen through caoutchouc would appear to be fully accounted for.

Liquid diffusion has also a bearing upon the rapid dissemination of



hydrogen through a soft colloid metal, like palladium or platinum, at a high temperature. The liquid diffusion of salts in water is known to be six times as rapid at  $100^{\circ}$  as at  $0^{\circ}$ . If the diffusion of liquid hydrogen increases with temperature in an equal ratio, it must become a very rapid movement at a red heat. Although the quantity absorbed may be reduced (or the channel narrowed), the flow of liquid may thus be increased in velocity. The whole phenomena appear to be consistent with the solution of liquid hydrogen in the colloid metal. The "solution affinity" of metals appears to be nearly confined to hydrogen and carbonic oxide, so that metals are not sensibly penetrated by other gases than these.

## XX.

ON THE RELATION OF HYDROGEN TO PALLADIUM, AND  
ON HYDROGENIUM.

From *Proceedings of the Royal Society*, vol. xvii. pp. 212, 500, Jan. 14, 1869. [*Comptes Rendus*, Jan. 18, and June 28, 1869, vol. lxviii. pp. 101, 1511; *Annals de Chimie et de Physique* [4], vol. xvi. p. 188; *Chemical News*, vol. xix. p. 478; *Reichete der deutschen chemischen Gesellschaft*, No. 2, 1869; *Annalen der Chemie*, vol. clii. p. 168; *Philosophical Magazine*, December 1869; Poggendorff's *Annalen der Physik*, vol. cxxxviii. (1869), p. 49.]

It has often been maintained on chemical grounds that hydrogen gas is the vapour of a highly volatile metal. The idea forces itself upon the mind that palladium with its occluded hydrogen is simply an alloy of this volatile metal, in which the volatility of the one element is restrained by its union with the other, and which owes its metallic aspect equally to both constituents. How far such a view is borne out by the properties of the compound substance in question will appear by the following examination of the properties of what, assuming its metallic character, would have to be named *Hydrogenium*.

1. *Density*.—The density of palladium when charged with eight or nine hundred times its volume of hydrogen gas is perceptibly lowered; but the change cannot be measured accurately by the ordinary method of immersion in water, owing to a continuous evolution of minute hydrogen bubbles which appears to be determined by contact with the liquid. However, the linear dimensions of the charged palladium are altered



so considerably that the difference admits of easy measurement, and furnishes the required density by calculation. Palladium in the form of wire is readily charged with hydrogen by evolving that gas upon the surface of the metal in a galvanometer containing dilute sulphuric acid as usual.<sup>1</sup> The length of the wire before and after a charge is found by stretching it on both occasions by the same moderate weight, such as will not produce permanent distension, over the surface of a flat graduated measure. The measure was graduated to hundredths of an inch, and by means of a vernier, the divisions could be read to thousandths. The distance between two fine cross lines marked upon the surface of the wire near each of its extremities was observed.

Expt. 1.—The wire had been drawn from welded palladium, and was hard and elastic. The diameter of the wire was 0.462 millimetre; its specific gravity was 12.38, as determined with care. The wire was twisted into a loop at each end and the mark made near each loop. The loops were varnished so as to limit absorption of gas by the wire to the measured length between the two marks. To straighten the wire, one loop was fixed, and the other connected with a string passing over a pulley and loaded with 1.5 kilogramme, a weight sufficient to straighten the wire without occasioning any undue strain. The wire was charged with hydrogen by making it the negative electrode of a small Bunsen's battery consisting of two cells, each of half a litre in capacity. The positive electrode was a thick platinum wire placed side by side with the palladium wire, and extending the whole length of the latter within a tall jar filled with dilute sulphuric acid. The palladium wire had, in consequence, hydrogen carried to its surface, for a period of 1½ hour. A longer exposure was found not to add sensibly to the charge of hydrogen acquired by the wire. The wire was again measured and the increase in length noted. Finally the wire, being dried with a cloth, was divided at the marks, and the charged portion heated in a long narrow glass tube kept vacuous by a Sprengel aspirator. The whole occluded hydrogen was thus collected and measured; its volume is reduced by calculation to bar. 760 millims., and therm. 0° C.

The original length of the palladium wire exposed was 609.144 millims. (23.982 inches), and its weight 1.6832 grm. The wire received a charge of hydrogen amounting to 936 times its volume, measuring 128 cubic centims., and therefore weighing 0.01147 grm. When the gas was ultimately expelled, the loss as ascertained by direct weighing was 0.01164 grm. The charged wire measured 618.923 millims., showing an increase in length of 9.779 millims. (0.385 inch). The increase in linear dimensions is from 100 to 101.605, and in cubic capacity, assuming the expansion to be equal in all directions, from 100 to 104.908. Supposing

<sup>1</sup> *Proceedings of the Royal Society*, p. 422, 1868.



the two metals united without any change of volume, the alloy may therefore be said to be composed of

	By volume.	
Palladium, . . .	100	or 95.32
Hydrogenium, . . .	4.908	or 4.68
	104.908	100

The expansion which the palladium undergoes appears enormous if viewed as a change of bulk in the metal only, due to any conceivable physical force, amounting as it does to sixteen times the dilatation of palladium when heated from  $0^{\circ}$  to  $100^{\circ}$  C. The density of the charged wire is reduced, by calculation, from 12.3 to 11.79. Again, as 100 is to 4.91, so the volume of the palladium, 0.1358 cubic centim., is to the volume of the hydrogenium, 0.006714 cubic centim. Finally, dividing the weight of the hydrogenium, 0.01147 gm., by its volume in the alloy, 0.006714 cubic centim., we find

Density of hydrogenium, . . . . . 1.708

The density of hydrogenium, then, appears to approach that of magnesium, 1.743, by this first experiment.

Further, the expulsion of hydrogen from the wire, however caused, is attended with an extraordinary contraction of the latter. On expelling the hydrogen by a moderate heat, the wire not only receded to its original length, but fell as much below that zero as it had previously risen above it. The palladium wire first measuring 609.144 millims., and which increased 9.77 millims., was ultimately reduced to 599.444 millims., and contracted 9.7 millims. The wire is permanently shortened. The density of the palladium did not increase, but fell slightly at the same time, namely, from 12.38 to 12.12, proving that this contraction of the wire is in length only. The result is the converse of extension by wire-drawing. The retraction of the wire is possibly due to an effect of wire-drawing in leaving the particles of metal in a state of unequal tension, a tension which is excessive in the direction of the length of the wire. The metallic particles would seem to become mobile, and to right themselves in proportion as the hydrogen escapes; and the wire contracts in length, expanding, as appears by its final density, in other directions at the same time.

A wire so charged with hydrogen, if rubbed with the powder of magnesia (to make the flame luminous), burns like a waxed thread when ignited in the flame of a lamp.

Expt. 2.—Another portion of the same palladium wire was charged with hydrogen in a similar manner. The results observed were as follows:—



Length of palladium wire, . . . . .	488.976	millims.
The same with 867.15 volumes of occluded gas, . . . . .	495.656	„
Linear elongation, . . . . .	6.68	„
Linear elongation on 100, . . . . .	1.3663	„
Cubic expansion on 100, . . . . .	4.154	„
Weight of palladium wire, . . . . .	1.0667	gram.
Volume of palladium wire, . . . . .	0.08072	cub. cent.
Volume of occluded hydrogen gas, . . . . .	75.2	„
Weight of same, . . . . .	0.00684	gram.
Volume of hydrogenium, . . . . .	0.003601	cub. cent.
From these results is calculated		
Density of hydrogenium, . . . . .	1.898.	

Expt. 3.—The palladium wire was new, and on this occasion was well annealed before being charged with hydrogen. The wire was exposed at the negative pole for two hours, when it had ceased to elongate.

Length of palladium wire, . . . . .	556.185	millims.
Same with 888.303 volumes hydrogen, . . . . .	563.652	„
Linear elongation, . . . . .	7.467	„
Linear elongation on 100, . . . . .	1.324	„
Cubic expansion on 100, . . . . .	4.025	„
Weight of palladium wire, . . . . .	1.1675	gram.
Volume of palladium wire, . . . . .	0.0949	cub. centim.
Volume of occluded hydrogen gas, . . . . .	84.3	cub. centims.
Weight of same, . . . . .	0.007553	gram.
Volume of hydrogenium, . . . . .	0.003820	cub. centim.
These results give by calculation		
Density of hydrogenium, . . . . .	1.977.	

It was necessary to assume in this discussion that the two metals do not contract nor expand, but remain of their proper volume on uniting. Dr. Matthiessen has shown that in the formation of alloys generally the metals retain approximately their original densities.<sup>1</sup>

In the first experiment already described, probably the maximum absorption of gas by wire, amounting to 935.67 volumes, is attained. The palladium may be charged with any smaller proportion of hydrogen by shortening the time of exposure to the gas (329 volumes of hydrogen were taken up in twenty minutes), and an opportunity be gained of observing if the density of the hydrogenium remains constant, or if it varies with the proportion in which hydrogen enters the alloy. In the following statement, which includes the three experiments already reported, the essential points only are produced.

<sup>1</sup> *Philosophical Transactions*, 1860, p. 177.



TABLE.

Volumes of Hydrogen occluded.	Linear expansion in millimetres.		Density of Hydrogenium.
	From	To	
329	496·189	498·552	2·055
462	493·040	496·520	1·930
487	370·358	373·126	1·927
745	305·538	511·303	1·917
867	488·976	495·656	1·898
888	556·185	563·652	1·977
936	609·144	618·923	1·708

If the first and last experiments only are compared, it would appear that the hydrogenium becomes sensibly denser when the proportion of it is small, ranging from 1·708 to 2·055. But the last experiment of the Table is perhaps exceptional; and all the others indicate considerable uniformity of density. The mean density of hydrogenium, according to the whole experiments, excluding that last referred to, is 1·951, or nearly 2. This uniformity is in favour of the method followed for estimating the density of hydrogenium.

On charging and discharging portions of the same palladium wire repeatedly, the curious retraction was found to continue, and seemed to be interminable. The following expansions, caused by variable charges of hydrogen, were followed on expelling the hydrogen by the retractions mentioned.

	Elongation.			Retraction.	
1st Experiment	9·77	millims.,	.	9·70	millims.
2d	5·765	"	.	6·20	"
3d	2·36	"	.	3·14	"
4th	3·482	"	.	4·95	"
				23·99	

The palladium wire, which originally measured 609·144 millims., has suffered, by four successive discharges of hydrogen from it, a permanent contraction of 23·99 millims.; that is, a reduction of 3·9 per cent. on its original length. The contractions will be observed to exceed in amount the preceding elongations produced by the hydrogen, particularly when the charge of the latter is less considerable. With another portion of wire the contraction was carried to 15 per cent. of its length by the effect of repeated discharges. The specific gravity of the contracted wire was 12·12, no general condensation of the metal having taken place. The wire shrinks in length only.

In the preceding experiments the hydrogen was expelled by exposing



the palladium placed within a glass tube to a moderate heat short of redness, and exhausting by means of a Sprengel tube; but the gas was also withdrawn in another way, namely, by making the wire the positive electrode, and thereby evolving oxygen upon its surface. In such circumstances a slight film of oxide of palladium is formed on the wire, but it appears not to interfere with the extraction and oxidation of the hydrogen. The wire measured,

		Difference.
Before charge, . . .	443.25 millims.	
With hydrogen, . . .	449.90 „	+ 6.65 millims.
After discharge, . . .	437.31 „	— 5.94 „

The retraction of the wire therefore does not require the concurrence of a high temperature. This experiment further proved that a large charge of hydrogen may be removed in a complete manner by exposure to the positive pole (for four hours in this case); for the wire in its ultimate state gave no hydrogen on being heated *in vacuo*.

That particular wire, which had been repeatedly charged with hydrogen, was once more exposed to a maximum charge, for the purpose of ascertaining whether or not its elongation under hydrogen might now be facilitated and become greater in consequence of the previous large retraction. No such extra elongation, however, was observed on charging the retracted wire more than once; and the expansion continued to be in the usual proportion to the hydrogen absorbed. The final density of the wire was 12.18.

The wire retracted by heat is found to be altered in another way, which appears to indicate a molecular change. When the gas has been expelled by heat, the metal gradually loses much of its power to take up hydrogen. The last wire, after it had already been operated upon six times, was again charged with hydrogen for two hours, and was found to occlude only 320 volumes of gas, and in a repetition of the experiment, 330.5 volumes. The absorbent power of the palladium had therefore been reduced to about one-third of its maximum.

The condition of the retracted wire appeared, however, to be improved by raising its temperature to full redness by sending through it an electrical current from a battery. The absorption rose thereafter to 425 volumes of hydrogen, and in a second experiment to 422.5 volumes.

The wire becomes fissured longitudinally, acquires a thready structure, and is much disintegrated on repeatedly losing hydrogen, particularly when the hydrogen has been extracted by electrolysis in an acid fluid. The palladium in the last case is dissolved by the acid to some extent. The metal appeared, however, to recover its full power to absorb hydrogen, now condensing upwards of 900 volumes of gas.



The effect upon its length of simply annealing the palladium wire by exposure in a porcelain tube to a full red heat, was observed. The wire measured 556·075 millims. before, and 555·875 millims. after heating; or a minute retraction of 0·2 millim. was indicated. In a second annealing experiment, with an equal length of new wire, no sensible change whatever of length could be discovered. There is no reason, then, to ascribe the retraction after hydrogen, in any degree, to the heat applied when the gas is expelled. Palladium wire is very slightly affected in physical properties by such annealing, retaining much of its first hardness and elasticity.

2. *Tenacity*.—A new palladium wire, similar to the last, of which 100 millims. weighed 0·1987 grm., was broken, in experiments made on two different portions of it, by a load of 10 and of 10·17 kilogrammes. Two other portions of the same wire, fully charged with hydrogen, were broken by 8·18 and by 8·27 kilogrammes. Hence we have—

Tenacity of palladium wire, . . . . .	100
Tenacity of palladium and hydrogen, . . . . .	81·29

The tenacity of the palladium is reduced by the addition of hydrogen, but not to any great extent. It is a question whether the degree of tenacity that still remains is reconcileable with any other view than that the second element present possesses of itself a degree of tenacity such as is only found in metals.

3. *Electrical conductivity*.—Mr. Becker, who is familiar with the practice of testing the capacity of wires for conducting electricity, submitted a palladium wire, before and after being charged with hydrogen, to trial, in comparison with a wire of German silver of equal diameter and length, at 10°·5. The conducting power of the several wires was found as follows, being referred to pure copper as 100 :—

Pure copper, . . . . .	100
Palladium, . . . . .	8·10
Alloy of 80 copper + 20 nickel, . . . . .	6·63
Palladium + hydrogen, . . . . .	5·99

A reduced conducting-power is generally observed in alloys, and the charged palladium wire falls 25 per cent. But the conducting-power remains still considerable, and the result may be construed to favour the metallic character of the second constituent of the wire. Dr. Matthiessen confirms these results.

4. *Magnetism*.—It is given by Faraday as the result of all his experiments, that palladium is “feebly but truly magnetic;” and this element he placed at the head of what are now called the paramagnetic metals. But the feeble magnetism of palladium did not extend to its



salts. In repeating such experiments, a horse-shoe electro-magnet of soft iron, about 15 centims. (6 inches) in height, was made use of. It was capable of supporting 60 kilogs., when excited by four large Bunsen cells. This is an induced magnet of very moderate power. The instrument was placed with its poles directed upwards; and each of these was provided with a small square block of soft iron terminating laterally in a point, like a small anvil. The palladium under examination was suspended between these points in a stirrup of paper attached to three fibres of cocoon silk, 3 decimetres in length, and the whole was covered by a bell glass. A filament of glass was attached to the paper, and moved as an index on a circle of paper on the glass shade divided into degrees. The metal, which was an oblong fragment of electro-deposited palladium, about 8 millims. in length and 3 millims. in width, being at rest in an equatorial position (that is, with its ends averted from the poles of the electro-magnet), the magnet was then charged by connecting it with the electrical battery. The palladium was deflected slightly from the equatorial line by  $10^\circ$  only, the magnetism acting against the torsion of the silk suspending thread. The same palladium charged with 604.6 volumes of hydrogen was deflected by the electro-magnet through  $48^\circ$ , when it set itself at rest. The gas being afterwards extracted, and the palladium again placed equatorially between the poles, it was not deflected in the least perceptible degree. The addition of hydrogen adds manifestly, therefore, to the small natural magnetism of the palladium. To have some terms of comparison, the same little mass of electro-deposited palladium was steeped in a solution of nickel, of sp. gr. 1.082, which is known to be magnetic. The deflection under the magnet was now  $35^\circ$ , or less than with hydrogen. The same palladium being afterwards washed and impregnated with a solution of protosulphate of iron of sp. gr. 1.048, of which the metallic mass held 2.3 per cent. of its weight, the palladium gave a deflection of  $50^\circ$ , or nearly the same as with hydrogen. With a stronger solution of the same salt, of sp. gr. 1.17, the deflection was  $90^\circ$ , and the palladium pointed axially.

Palladium in the form of wire or foil gave no deflection when placed in the same apparatus, of which the moderate sensitiveness was rather an advantage in present circumstances; but when afterwards charged with hydrogen, the palladium uniformly gave a sensible deflection of about  $20^\circ$ . A previous washing of the wire or foil with hydrochloric acid, to remove any possible traces of iron, did not modify this result. Palladium reduced from the cyanide and also precipitated by hypophosphorous acid, when placed in a small glass tube, was found to be not sensibly magnetic by our test; but it always acquired a sensible magnetism when charged with hydrogen.

It appears to follow that hydrogenium is magnetic, a property which



is confined to metals and their compounds. This magnetism is not perceptible in hydrogen gas, which was placed both by Faraday and by M. E. Becquerel at the bottom of the list of diamagnetic substances. This gas is allowed to be upon the turning-point between the paramagnetic and diamagnetic classes. But magnetism is so liable to extinction under the influence of heat, that the magnetism of a metal may very possibly disappear entirely when it is fused or vaporised, as appears to be the case with hydrogen in the form of gas. As palladium stands high in the series of the paramagnetic metals, hydrogenium must be allowed to rise out of that class, and to take place in the strictly magnetic group, with iron, nickel, cobalt, chromium, and manganese.

5. *Palladium with Hydrogen at a high Temperature.*—The ready permeability of heated palladium by hydrogen gas would imply the retention of the latter element by the metal even at a bright red heat. The hydrogenium must in fact travel through the palladium by cementation, a molecular process which requires time. The first attempts to arrest hydrogen in its passage through the red-hot metal were made by transmitting hydrogen gas through a metal tube of palladium with a vacuum outside, rapidly followed by a stream of carbonic acid, in which the metal was allowed to cool. When the metal was afterwards examined in the usual way, no hydrogen could be found in it. The short period of exposure to the carbonic acid seems to have been sufficient to dissipate the gas. But on heating palladium foil red-hot in a flame of hydrogen gas, and suddenly cooling the metal in water, a small portion of hydrogen was found locked up in the metal. A volume of metal amounting to 0.062 cubic centim. gave 0.080 cubic centim. of hydrogen; or, the gas, measured cold, was 1.306 times the bulk of the metal. This measure of gas would amount to three or four times the volume of the metal at a red heat. Platinum treated in the same way appeared also to yield hydrogen, although the quantity was too small to be much relied upon, amounting only to 0.06 volume of the metal. The permeation of these metals by hydrogen appears therefore to depend on absorption, and not to require the assumption of anything like porosity in their structure.

The highest velocity of permeation observed was in the experiment where four litres of hydrogen (3992 cub. centims.) per minute passed through a plate of palladium 1 millim. in thickness, and calculated for a square metre in surface, at a bright red heat a little short of the melting-point of gold. This is a travelling movement of hydrogen through the substance of the metal with the velocity of 4 millimetres per minute.

6. *Chemical Properties.*—The chemical properties of hydrogenium also distinguish it from ordinary hydrogen. The palladium alloy pre-



precipitates mercury and calomel from a solution of the chloride of mercury without any disengagement of hydrogen; that is, hydrogenium decomposes chloride of mercury, while hydrogen does not. This explains why M. Stanislas Meunier failed in discovering the occluded hydrogen of meteoric iron, by dissolving the latter in a solution of chloride of mercury; for the hydrogen would be consumed, like the iron itself, in precipitating mercury. Hydrogen (associated with palladium) unites with chlorine and iodine in the dark, reduces a persalt of iron to the state of protosalt, converts red prussiate of potash into yellow prussiate, and has considerable deoxidizing powers. It appears to be the active form of hydrogen, as ozone is of oxygen.

The general conclusions which appear to flow from this inquiry are, that in palladium fully charged with hydrogen, as in the portion of palladium wire now submitted to the Royal Society, there exists a compound of palladium and hydrogen in a proportion which may approach to equal equivalents.<sup>1</sup> That both substances are solid, metallic, and of a white aspect. That the alloy contains about 20 volumes of palladium united with a volume of hydrogenium; and that the density of the latter is about 2, a little higher than magnesium, to which hydrogenium may be supposed to bear some analogy. That hydrogenium has a certain amount of tenacity, and possesses the electrical conductivity of a metal. And finally, that hydrogenium takes its place among magnetic metals. The latter fact may have its bearing upon the appearance of hydrogenium in meteoric iron, in association with certain other magnetic elements.

I cannot close this paper without taking the opportunity to return my best thanks to Mr. W. C. Roberts for his valuable co-operation throughout the investigation.

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## XXI.

### SPECULATIVE IDEAS RESPECTING THE CONSTITUTION OF MATTER.<sup>2</sup>

From the *Philosophical Magazine* for February 1864.

It is conceivable that the various kinds of matter, now recognised as different elementary substances, may possess one and the same ultimate or atomic molecule existing in different conditions of movement. The essential unity of matter is an hypothesis in harmony with the

<sup>1</sup> *Proceedings of the Royal Society*, 1868, p. 425.

<sup>2</sup> *Ibid.* 1863, p. 620.



equal action of gravity upon all bodies. We know the anxiety with which this point was investigated by Newton, and the care he took to ascertain that every kind of substance, "metals, stones, woods, grain, salts, animal substances, etc.," are similarly accelerated in falling, and are therefore equally heavy.

In the condition of gas, matter is deprived of numerous and varying properties with which it appears invested when in the form of a liquid or solid. The gas exhibits only a few grand and simple features. These again may all be dependent upon atomic and molecular mobility. Let us imagine one kind of substance only to exist, ponderable matter; and further, that matter is divisible into ultimate atoms, uniform in size and weight. We shall have one substance and a common atom. With the atom at rest the uniformity of matter would be perfect. But the atom possesses always more or less motion, due, it must be assumed, to a primordial impulse. This motion gives rise to volume. The more rapid the movement the greater the space occupied by the atom, somewhat as the orbit of a planet widens with the degree of projectile velocity. Matter is thus made to differ only in being lighter or denser matter. The specific motion of an atom being inalienable, light matter is no longer convertible into heavy matter. In short, matter of different density forms different substances—different inconvertible elements as they have been considered.

What has already been said is not meant to apply to the gaseous volumes which we have occasion to measure and practically deal with, but to a lower order of molecules or atoms. The combining atoms hitherto spoken of are not therefore the molecules of which the movement is sensibly affected by heat with gaseous expansion as the result. The gaseous molecule must itself be viewed as composed of a group or system of the preceding inferior atoms, following as a unit laws similar to those which regulate its constituent atoms. We have indeed carried one step backward, and applied to the lower order of atoms, ideas suggested by the gaseous molecule, as views derived from the solar system are extended to the subordinate system of a planet and its satellites. The advance of science may further require an indefinite repetition of such steps of molecular division. The gaseous molecule is then a reproduction of the inferior atom on a higher scale. The molecule or system is reached which is affected by heat, the diffusive molecule, of which the movement is the subject of observation and measurement. The diffusive molecules are also to be supposed uniform in weight, but to vary in velocity of movement, in correspondence with their constituent atoms. Accordingly the molecular volumes of different elementary substances have the same relation to each other as the subordinate atomic volumes of the same substances.



But further, these more and less mobile or light and heavy forms of matter have a singular relation connected with equality of volume. Equal volumes of two of them can coalesce together, unite their movement, and form a new atomic group, retaining the whole, the half, or some simple proportion of the original movement and consequent volume. This is chemical combination. It is directly an affair of volume, and only indirectly connected with weight. Combining weights are different, because the densities, atomic and molecular, are different. The volume of combination is uniform, but the fluids measured vary in density. This fixed combining measure—the *metron* of simple substances—weighs 1 for hydrogen, 16 for oxygen, and so on with the other “elements.”

To the preceding statements respecting atomic and molecular mobility, it remains to be added that the hypothesis admits of another expression. As in the theory of light we have the alternative hypotheses of emission and undulation, so in molecular mobility the motion may be assumed to reside either in separate atoms and molecules, or in a fluid medium caused to undulate. A special rate of vibration or pulsation originally imparted to a portion of the fluid medium enlivens that portion of matter with an individual existence, and constitutes it a distinct substance or element.

With respect to the different states of gas, liquid and solid, it may be observed that there is no real incompatibility with each other in these physical conditions. They are often found together in the same substance. The liquid and the solid conditions supervene upon the gaseous condition rather than supersede it. Gay-Lussac made the remarkable observation that the vapours emitted by ice and water, both at  $0^{\circ}$  C., are of exactly equal tension. The passage from the liquid to the solid state is not made apparent in the volatility of water. The liquid and solid conditions do not appear as the extinction or suppression of the gaseous condition, but something *superadded* to that condition. The three conditions (or constitutions) probably always coexist in every liquid or solid substance, but one predominates over the others. In the general properties of matter we have, indeed, to include still further (1) the remarkable loss of elasticity in vapours under great pressure, which is distinguished by Mr. Faraday as the Cagnard Latour-state, after the name of its discoverer, and is now undergoing an investigation by Dr. Andrews, which may be expected to throw much light upon its nature; (2) the colloidal condition or constitution, which intervenes between the liquid and crystalline states, extending into both and affecting probably all kinds of solid and liquid matter in a greater or less degree. The predominance of a certain physical state in a substance appears to be a distinction of a kind with those distinctions recognised in natural history



as being produced by unequal development. Liquefaction or solidification may not therefore involve the suppression of either the atomic or the molecular movement, but only the restriction of its range. The hypothesis of atomic movement has been elsewhere assumed, irrespective of the gaseous condition, and is applied by Dr. Williamson to the elucidation of a remarkable class of chemical reactions which have their seat in a mixed liquid.

Lastly, molecular or diffusive mobility has an obvious bearing upon the communication of heat to gases by contact with liquid or solid surfaces. The impact of the gaseous molecule, upon a surface possessing a different temperature, appears to be the condition for the transference of heat, or the heat movement, from one to the other. The more rapid the molecular movement of the gas the more frequent the contact with consequent communication of heat. Hence, probably, the great cooling power of hydrogen gas as compared with air or oxygen. The gases named have the same specific heat for equal volumes, but a hot object placed in hydrogen is really *touched* 3·8 times more frequently than it would be if placed in air, and 4 times more frequently than it would be if placed in an atmosphere of oxygen gas. Dalton had already ascribed this peculiarity of hydrogen to the high "mobility" of that gas. The same molecular property of hydrogen recommends the application of that gas in the air-engine, where the object is to alternately heat and cool a confined volume of gas with rapidity.



# S A L T S.

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## I.

### ON EXCEPTIONS TO THE LAW THAT SALTS ARE MORE SOLUBLE IN HOT THAN IN COLD WATER; WITH A NEW INSTANCE.

From *Philosophical Magazine and Annals of Philosophy*, ii. 1827, pp. 20-26.

THE bodies which have been observed to possess this anomalous solubility are the hydrate of lime and the sulphate of soda: its detection in the first case we owe to Mr. Dalton, and in the latter to M. Gay-Lussac. The phosphate of magnesia, a body like the hydrate of lime of sparing solubility, appears from our experiments to belong to the same class.

To form phosphate of magnesia, phosphate of soda and sulphate of magnesia in crystals were separately dissolved in water, in the proportion of 21 parts of the former to 15·375 parts of the latter, or of an integrant particle of each. These solutions were mixed and set aside. Within twenty-four hours the phosphate of magnesia had precipitated, generally in tufts of short acicular crystals, while sulphate of soda remained in solution. According to Dr. Thomson this salt is composed of

One atom phosphoric acid,	.	3·5
One atom magnesia,	.	2·5
Seven atoms water,	.	7·875
		<hr/>
		13·875

It is *efflorescent*, rapidly losing its water of crystallization when exposed to the air, and falling down in a white powder.

The crystals were drained, purified with great care by repeated agitation with water, and finally thrown upon a filter with more water, and allowed to dry. Solutions were obtained by occasionally agitating the salt with pure water during three or four days, in the proportion of 2 ounces phosphate of magnesia to 1 pint of water. The solutions were then decanted off and filtered. Although the water drained from the



crystals upon the filter was nearly tasteless, yet the solutions thus obtained were of a sweetish taste, which was sufficiently perceptible.

A quantity of the solution, in the preparation of which distilled water only had been employed, was gradually heated by immersion in the water-bath. Before the bath had arrived at  $120^{\circ}$ , the solution became turbid, and it assumed more and more of a milky appearance as the heat increased, till the temperature settled at  $212^{\circ}$ , when a cloudy precipitate slowly subsided, and the supernatant liquid became nearly transparent. The precipitate was found not to differ in its sensible properties from phosphate of magnesia deprived of its water of crystallization.

To determine the solubility of this salt at different temperatures, a solution was prepared by repeated agitation with water, for more than a week, of a quantity of the salt from which already three solutions had been derived. The temperature was about  $45^{\circ}$ .

8000 grains of this solution, carefully filtered, were evaporated to dryness on the sand-bath. The residue was found to be 10.75 grains anhydrous phosphate of magnesia. Hence 744 grains water dissolve 1 grain of the anhydrous salt.

8000 grains of the same solution, in a glass-stoppered phial, were heated to  $212^{\circ}$  in the water-bath and retained for some time at that temperature. When the precipitate had subsided, a large portion of the transparent liquid was decanted off, and the remainder with the precipitate thrown upon a filter while still hot. It weighed when accurately dried 3.8 grains. Hence 8000 grains water at  $212^{\circ}$  retain in solution  $10.75 - 3.8 = 6.95$  grains; or 1151 grains water retain in solution 1 grain of anhydrous phosphate of magnesia. Hence 1 part water dissolves of anhydrous phosphate of magnesia,

at $45^{\circ}$	.	.	.	$\frac{1}{744}$ ;
at $212^{\circ}$	.	.	.	$\frac{1}{1151}$ .

Of the hydrate, or phosphate of magnesia in the state of crystals, 1 part water will therefore dissolve

at $45^{\circ}$	.	.	.	$\frac{1}{322}$ ;
at $212^{\circ}$	.	.	.	$\frac{1}{498}$ .

The precipitate by heat was exceedingly bulky and not crystallized. It did not amount in general to so much as 3.8 grains from 8000 grains of the solution. Indeed, the mean of seven experiments made upon different solutions was 2.5 grains of precipitate. But it was found that the amount of the precipitate depended much upon the time and agitation employed in effecting the solution, as it is difficult to saturate water with this salt. It is evident, therefore, that not the mean but the greatest result will approach nearest to the truth.



Phosphate of magnesia boiled in water for several hours, afterwards yielded solutions possessing this property. By the heat, the crystals assumed the appearance in the water of having effloresced.

Phosphate of soda and sulphate of magnesia were added separately to solutions of phosphate of magnesia, in the proportion of 10 grains to 1000 grains solution, without influencing in the slightest degree the amount or appearance of the precipitate.

Phosphate of magnesia appears to be much more soluble in the acids than in water; at least it was observed to dissolve with facility in the following acids, even when in a very dilute state—acetic, oxalic, phosphoric, muriatic, nitric, and sulphuric. The addition of the smallest quantity of any of these acids to the aqueous solution prevents the appearance of the usual precipitate by heat, by increasing the solvent power of the menstruum.<sup>1</sup>

In prosecuting this subject I had occasion to make several observations.

Mere continuance of the heat had no effect in increasing the amount of the precipitate, in the solutions of hydrate of lime or of phosphate of magnesia, provided no part of the solution was at any time converted into vapour. When filtered solutions of lime and phosphate of magnesia, which had formerly been heated, were again subjected to a temperature of  $212^{\circ}$  by complete immersion in the water-bath in close vessels, and retained at that temperature for several hours, no additional precipitate appeared. But when heat of greater intensity was applied to elevate the temperature of the solution to  $212^{\circ}$ , this was seldom the case. When such a solution was heated by the flame of a spirit-lamp, even in a close vessel, a slight precipitate generally appeared. When the vessel, although close, was only occupied in part by the solution, the precipitate was greater; and when the space occupied by the solution bore so small a proportion to the whole capacity of the vessel, that the solution might be made to boil, and be condensed in the upper part of the vessel and returned without loss,—the precipitate might be increased *ad libitum*, particularly in the case of lime-water. The cause of the precipitate appears to be the same in all these cases. The moment a drop of the solution is converted into vapour, it deposits the quantity of lime or salt that it held in solution; and in the case of bodies which dissolve so sparingly and with so much difficulty, as the hydrate of lime and phosphate of magnesia, although the water be returned again to the solution, it is incapable of re-dissolving what it has deposited. We know that it would be a hopeless task to form a saturated solution of

<sup>1</sup> The experiment of the partial precipitation of phosphate of magnesia in solution, by heat, has been repeated successfully by my friend Mr. A. Steel, in the laboratory of Dr. Thomson, with great care and very pure materials.



lime, by agitating with the water no more than the few grains which it is capable of dissolving; and in the case before us, when the lime is once deposited the same difficulty should be experienced in taking it up.

These observations show the advantage of employing the water-bath in heating the solutions,—a procedure which was always followed by the author, and by which he regularly obtained precipitates of hydrate of lime as well as of phosphate of magnesia. They also account for a phenomenon in the solubility of lime observed by Mr. Richard Phillips, which otherwise appears anomalous.<sup>1</sup>

Mr. Phillips heated a quantity of lime-water in a flask, the neck of which was elongated by a tube, to prevent the access of carbonic acid gas from the atmosphere, and made to boil till 1-13th part was dissipated in vapour. From the deposition which mere elevation of temperature would occasion without any evaporation, the quantity of lime in solution would be reduced to  $\frac{1}{1270}$ th part, but it was found to amount to no more than  $\frac{1}{1505}$ . But much more of the solution would be converted into vapour during the boiling, than what actually escaped, the cool sides of the long tube being singularly adapted to condense the rising vapour and return it to the solution, supposing that the tube had any elevation; while the hydrate of lime, which had been deposited in hard crystals, would not admit of being re-dissolved in an appreciable degree.

It is evident that this effect of *cohobation* will take place not only in lime-water and the solution of phosphate of magnesia, but to a certain extent in all bodies of difficult solubility. I have observed it to a considerable extent in the solution of sulphate of lime, even when greatly diluted, and believe that the deposit from slight boiling observed in many mineral waters, and generally attributed to the dissipation of carbonic acid gas, depends in some instances upon this cause. However weak the solution may be, it is evident that a portion of the salt may be deposited in this way.

It had occurred to us as a method of determining the relative solubility at different temperatures of bodies of this class, to form a saturated solution at the lowest temperature, and dilute it with water till it ceased to deposit at the high temperature. But this method was found inconvenient from the difficulty of incorporating the solution with the water added.

4000 grains lime-water were diluted with 2000 grains water, agitated and set aside for two hours. Upon being then heated in the water-bath to  $212^{\circ}$ , a precipitate appeared, which being received upon a filter and dried was found to amount to nearly 2 grains hydrate of lime. Phosphate of magnesia similarly treated gave 12 grains of precipitate.

4000 grains lime-water diluted with an equal quantity of pure water, and occasionally agitated for three days in a stoppered phial, became

<sup>1</sup> *Annals of Philosophy*, N. S., vol. i. p. 109.



slightly turbid upon being carefully heated in the water-bath, and deposited a small quantity of hydrate of lime, of which 0.15 grain was recovered. The solution of phosphate of magnesia in the same circumstances yielded a precipitate, which although it rendered the solution much more turbid, did not amount to so much.

It was found, as might be expected from the previous experiments, that the deposit by heat from lime-water was not diminished sensibly by being allowed to remain in the solution till it became cool, or was not re-dissolved upon cooling. Hence it is unnecessary to filter the solution while hot. The phosphate of magnesia, however, appeared to be re-dissolved in a more sensible degree, probably from the state of extreme division in which it is deposited. At least 2.3 grains of precipitated phosphate of magnesia were obtained by filtering at  $212^{\circ}$ , while an equal quantity of the same solution, allowed to cool with occasional agitation before filtration, gave a precipitate which did not exceed 2 grains. In appearance, the precipitate had suffered a very great reduction.

The rapidity with which phosphate of magnesia *effloresces* when exposed to the atmosphere led us, from theoretical considerations, to look for this anomaly in its solubility. Efflorescence in the hydrates of the salts certainly indicates a weak affinity for water at the atmospheric temperature—an attraction or affinity, too, which is much diminished by slight elevation in temperature. If the attraction subsisting between the salt and water, when in solution, be of the same nature as that between the base and water when in the state of a solid hydrate, we might expect the striking power of heat in weakening the affinity or attraction, to affect the solubility of the salt at different temperatures. Even supposing that the solvent power of water increased to a certain extent with rise in temperature, yet this rapid diminution of the attraction of the salt for water as the temperature rose, might counteract and eventually overcome the increasing power of the solvent, in salts so efflorescent as phosphate of magnesia or sulphate of soda. Hence the solubility of such salts might begin to lessen, when the temperature was raised beyond a certain point.

As the hydrates of all the salts, whether they may be efflorescent at the temperature of the atmosphere or not, are decomposed by heat, the cause assigned, as counteracting the increase of the solvent power of water with temperature, if it exists, must be general, and influence to a greater or less extent the solubility at different temperatures of all salts whatever. In fact, the consequence necessarily follows from it, that for every salt there is a point in the scale of temperature above which it ceases to become more soluble in water, and diminishes in solubility. In the case of the efflorescent salts, whose affinity for water, when in the state of hydrate, is much impaired by slight elevation of temperature,



this point of temperature appears to be low—in some cases under  $212^{\circ}$ ; in the case of hydrates which retain their water with more force it will be higher, and in hydrates which require a considerable heat to decompose them, the maximum point of solubility will be proportionally high, and such as would require the retention of the solvent in the liquid state by vast pressure, in order to be exhibited.

In that extensive class of salts which do not form solid combinations with water, we do not possess such a clew to their solubility at different temperatures. They may, therefore, be subject in some cases to this anomaly in solubility as well as the efflorescent salts. Indeed the theory is not applicable even to all the hydrates without distinction. There is a class of hydrates, in which the combination between the base and water appears to differ essentially from that of the ordinary hydrates of the salts. This class comprehends the hydrates of the alkalies, the earths and metallic oxides, and these appear not to be subject to the law.

Many salts, oxides and earths of this class are known to be deprived of solubility by exposure to a considerable heat. This arises from the loss of the water with which they were previously combined, and not, as it is often supposed, from the action of heat in hardening and increasing the cohesion of the particles of such bodies. For if we examine the solubility of these bodies, we shall find it necessary to suppose, that at no time is the simple substance itself dissolved, but always an original and intimate compound of the substance with water. These compounds are of a higher order than the common hydrates, and frequently require peculiar circumstances for their formation. Silica is a good instance. Dried and destitute of water it is altogether insoluble, and cannot be made again to form a solid combination with water, but in a state of previous and intimate combination with water it is soluble. It is evident then that the solution should be viewed not as a solution of silica, but as a solution of hydrate of silica. The alkalies are in the same situation; and the fact strikingly illustrates our position, that when the alkalies dissolve in alcohol they are still in the state of hydrates. The combination between water and lime in slaked lime is of this superior kind, so that lime-water may be considered not as a solution of lime, but as a solution of hydrate of lime. The water appears to be in more close union with the lime, than the water of crystallization of salts to which efflorescence is confined. It is therefore no objection to the theory that hydrate of lime is more soluble in cold than in hot water, and yet does not effloresce. Were the hydrate of lime to form a loose compound with an additional quantity of water, like the water of crystallization of ordinary salts, then if that hydrate did not effloresce, the circumstance would be inimical to the theory.

The coincidence of efflorescence with diminished solubility at high



temperatures, in the case of sulphate of soda, is favourable to the view taken of the connection between these properties. If the solubility of the efflorescent salts were examined particularly, more of them probably would give indications of the same property.

Carbonate of magnesia in crystals is very efflorescent, and according to Butini<sup>1</sup> it is more soluble in cold than in hot water impregnated with carbonic acid.

## II.

### AN ACCOUNT OF THE FORMATION OF ALCOATES, DEFINITE COMPOUNDS OF SALTS AND ALCOHOL ANALOGOUS TO THE HYDRATES.<sup>2</sup>

From *Edinb. Roy. Soc. Trans.* xi. 1831, pp. 175-193. [*Phil. Mag.* iv. 1828, pp. 265-272, 331-336; *Journ. de Pharm.* xv. 1829, pp. 105-124; *Poggend. Annal.* xv. 1829, pp. 150-153; *Quart. Journ. of Science*, ii. 1828, pp. 442, 443; Schweigger, *Journ.* lvi. (= *Jahrb.* xxvi.) 1829, pp. 180-203.]

In determining the solubility of salts and other bodies in alcohol, it is desirable to operate with a spirit wholly free from water. But anhydrous or absolute alcohol is formed with difficulty, even by the most improved process—that of Richter. In rectifying alcohol from chloride of calcium, as recommended by Richter, I have never obtained it under the specific gravity 0.798 at the temperature of 60°, by a single distillation; but upon rectifying this product again from new chloride of calcium, I generally succeeded in reducing it to 0.796, which is the specific gravity of the standard alcohol of that chemist. The following experiment illustrates this process.

Four measures of alcohol of the specific gravity 0.826 were poured into a retort, and a quantity of well-dried chloride of calcium, amounting to three-fourths of the weight of the alcohol, gradually added with occasional agitation. Much of the salt was dissolved with the evolution of heat; and the combination was promoted by boiling the whole for a few minutes, the vapour being condensed in the neck of the retort, and returned to the solution. A receiver was then adjusted to the mouth of the retort, and the distillation conducted so slowly that the alcohol was condensed entirely in the neck of the retort, and fell drop by drop into the receiver,—nearly two seconds elapsing between the fall of each drop. The first measure of alcohol which came over was of the specific gravity

<sup>1</sup> "Sur le Magnésie." *Vide* Thomson's System, under Salts of Magnesia.

<sup>2</sup> Read 17th December 1827.



0·800, at  $60^{\circ}$ ; the second measure, 0·798; and the third measure, 0·801: the distillation was then discontinued. These three measures were mixed together, and subjected to a second distillation, which was conducted in the same manner; and two measures of alcohol obtained of the specific gravity 0·796. It was found that further rectification did not reduce the specific weight of the alcohol below 0·796. From the analysis of alcohol by Saussure, and the determination of the specific weight of its vapour by Gay Lussac, there can be little doubt that the alcohol thus obtained is perfectly anhydrous. It is true that such alcohol still contains oxygen and hydrogen to the amount of an atomic proportion of water; but this proportion of oxygen and hydrogen is essential to the constitution of alcohol,—the partial abstraction of it converting alcohol into ether, and its total abstraction converting alcohol into olefiant gas; while the supposition that the oxygen and hydrogen exist in the state of water is altogether gratuitous.

The process of Richter is exceedingly tedious, from the necessity of conducting it so slowly, and the waste of alcohol is considerable. I tried newly burnt quicklime instead of chloride of calcium, and distilled by the heat of a saline water-bath. If it is merely our object to obtain alcohol perfectly free from water, no process could be more effectual. The product was of the specific gravity 0·794; but it contained a trace of ether, to which the extraordinary lowness of its specific gravity is attributable; and had an empyreumatic odour, notwithstanding the moderate temperature at which the distillation was conducted. This likewise is a very slow process.

The process which I preferred is founded on the principle of Mr. Leslie's frigorific apparatus. The alcohol is concentrated by being placed under the receiver of an air-pump, with quicklime. A large shallow basin is covered to a small depth with recently burnt lime in coarse powder, and a smaller basin containing three or four ounces of commercial alcohol is made to rest upon the lime: the whole is placed upon the plate of an air-pump, and covered over by a low receiver. Exhaustion is continued till the alcohol evinces signs of ebullition, but no further. Of the mingled vapours of alcohol and water which now fill the receiver, the quicklime is capable of combining with the aqueous vapour only, which is therefore quickly withdrawn, while the alcohol vapour is unaffected. But as water, unless it has an atmosphere of its own vapour above it, cannot remain in the alcohol, more aqueous vapour rises. This vapour is likewise absorbed, and the process goes on till the whole water in the alcohol is withdrawn. Several days are always required for this purpose, and in winter a longer time than in summer. The following cases exhibit the rate, according to which the water is withdrawn. The first experiment was made in summer. Four ounces



of alcohol of the specific gravity 0·827 were concentrated. The specific gravity was taken every twenty-four hours, and the following series of results obtained :—

0·827

0·817

0·808

0·802

0·798

0·796

In this case the whole water was withdrawn in five days, but occasionally a period somewhat longer is required, although it rarely exceeds a week. In winter the alcohol generally requires to be exposed to the lime for a day or two longer than in summer. The following rate of concentration was observed in one case in winter, the quantity of alcohol and other circumstances being the same as in the former experiment :—

0·825

0·817

0·809

0·804

0·799

0·797

0·796

Quicklime, as a porous substance, appears to be capable of condensing a small portion of alcohol vapour. It is therefore improper to use it in great excess. In one case, in which three pounds of quicklime were employed with four ounces of alcohol, about one-sixth of the alcohol was lost from this absorption. The quicklime should never exceed three times the weight of the alcohol, otherwise the quantity of alcohol absorbed becomes sensible. It should be spread over as great a surface within the receiver as possible.

In Richter's process it is improper to operate upon more than a few ounces of alcohol at a time; as when a large quantity of materials is introduced into the retort, the heat necessary to disengage the alcohol in the centre of the mass inevitably expels the water left in the chloride of lime, at the points where it is more exposed to the heat. In the air-pump also, only a few ounces can in general be concentrated at a time. But in a tall receiver, two or three shallow basins of quicklime can be supported at a little height above each other, each of them containing a small basin of alcohol resting in it. Or the process might be conducted with facility on the large scale, by means of a tight box of any size, furnished with numerous shelves, which might be covered with quicklime in powder, and support a large number of basins of alcohol. The



box might be sufficiently exhausted of air by means of a syringe, for it is not necessary that the exhaustion be nearly complete; and indeed more inconvenience is to be apprehended from a complete than from an imperfect exhaustion. After producing the exhaustion, no further attention would be necessary; and upon opening the box at the expiration of a week or ten days, the alcohol would be found anhydrous. It is evident that absolute alcohol, procured by this process, could be sold at a price but little exceeding its original cost. It would moreover be of much greater value for the purposes for which it is employed in the arts and medicine. I believe, however, that, by the excise laws as they at present exist, no rectifier of spirits is permitted to concentrate alcohol beyond a certain strength. Licensed apothecaries alone are allowed to prepare and sell absolute alcohol.<sup>1</sup>

Alcohol may be concentrated in a close vessel with quicklime, without exhausting; but the process goes on much more slowly, at least at the temperature of the air. The experiment was tried at a high temperature, by heating in a water-bath a large bottle with a very wide mouth, containing a quantity of alcohol at the bottom, and quicklime suspended over it in a linen bag. When the water-bath attained the temperature of  $150^{\circ}$ , the bottle was corked, and the bath prevented from becoming hotter. Much of the lime was very quickly converted into hydrate, and the alcohol considerably concentrated. But the process is troublesome, and much inferior to that in which the air-pump is employed.

In the place of quicklime, sulphuric acid cannot be substituted in the foregoing process as an absorbing liquid, from a remarkable property which it possesses. It is capable of absorbing the vapour of absolute alcohol, in the same manner as it absorbs the vapour of water. I was led to make this observation from a consideration of the phenomena which attend the mixing of alcohol and sulphuric acid. Nearly as much heat is evolved as if water had been added to the acid, even although absolute alcohol be employed. Alcohol is also retained by the acid when heated to  $500^{\circ}$  or  $600^{\circ}$ , or at a temperature when the alcohol would be decidedly in the state of vapour,—which indicates the possibility of the same relation between sulphuric acid and alcohol vapour that subsists between water and those gases which it detains in the liquid state, such as ammoniacal gas, when they would naturally

<sup>1</sup> Care should be taken that the temperature be nearly equable during the experiment; otherwise, when the atmosphere becomes cold, a condensation of alcohol vapour takes place upon the cooled bell-glass, which runs down upon the plate of the pump. The experiment, therefore, should not be performed in a room with a fire, or near a window, but in a dark closet or press. From the manner in which I performed the experiment, this condensation had never been experienced by myself; but Dr. Duncan, junior, observed it, on repeating the process.



assume the elastic form. But besides merely *detaining* such gases, water can condense and absorb them. Sulphuric acid, besides merely detaining alcohol vapour, might therefore condense and absorb it.

As alcohol, like water, occasions cold by its evaporation, it may be substituted for water in Mr. Leslie's frigorific apparatus, sulphuric acid being retained as the absorbing liquid. In circumstances precisely similar, it was found that the thermometer, the bulb of which was covered with cotton, fell to  $7^{\circ}$  when moistened with water, but when moistened with absolute alcohol its temperature fell to  $-24^{\circ}$ . Continuance of the pumping during the experiment, as is done in the case of ether, had a prejudicial effect. But alcohol diluted with a third of water was found to have as great a cooling power as absolute alcohol. The advantage to be derived from the great volatility of alcohol appears to be counterbalanced in part by the small latent heat of its vapour. Probably a mixture of alcohol and water, in certain proportions, would produce the greatest degree of cold attainable by this process. Sulphuric acid loses its power to absorb alcohol vapour by being diluted with water. When impregnated with alcohol vapour, the acid becomes of a pink colour; but no appreciable quantity of gas is emitted at the temperature of the atmosphere, even in the vacuum of an air-pump.

From one experiment, water appears to have the power to induce the evaporation of alcohol by absorbing its vapour, as sulphuric acid does, but much more feebly. Two cups, one containing alcohol and the other pure water, were enclosed together in a tin canister which was nearly air-tight, and set aside in a quiet place for six weeks. The cups were not in contact, but a little apart from each other. At the expiration of that period it was found, on opening the canister, that the cup which originally contained pure water, now contained a mixture of water and alcohol, while the alcohol remaining in the other cup was of diminished strength. Professor Leslie informs me, that he performed a similar experiment a considerable time ago, although no account of it was published. But the absorption of alcohol vapour by water is so feeble as not to occasion a sensible reduction of temperature in the alcohol.

Chloride of calcium is disqualified as an absorbent of aqueous vapour in the purification of alcohol, for the same reason as sulphuric acid. I find that chloride of calcium absorbs the vapour of absolute alcohol, and runs into a liquid, or it *deliquesces* in alcohol vapour. A small quantity of this substance was suspended in a little capsule, at the height of two inches above a quantity of absolute alcohol, in a close vessel. In the course of twenty-four hours it was entirely resolved into a liquid, just as if it had been suspended over water. The liquid proved to be a solution of chloride of calcium in absolute alcohol. The experiment was frequently repeated. As salts which deliquesce from the absorption



of aqueous vapour are always capable of forming hydrates, I was led from the observation of this fact to attempt the formation of analogous compounds of alcohol and salts,—to which I now proceed.

These solid compounds of salts and alcohol, which are definite and imperfectly crystallizable, may be denominated *Alco-ates*,—a designation which is not unexceptionable, but appeared to me preferable to the name *Vinate*, as there is a sulpho-vinous acid, or to any other name that might have been imposed upon them.

The alcoates which I succeeded in forming are not numerous. They were formed simply by dissolving the salts previously rendered anhydrous, in absolute alcohol, with the assistance of heat. On cooling, the alcoates were deposited in the solid state. The crystallization was generally confused, but in some cases crystalline forms appeared of a singular description. The crystals are transparent, decidedly soft, and easily fusible by heat in their alcohol of crystallization, which is generally considerable, amounting in one instance to nearly three-fourths of the weight of the crystals.

#### 1. *Alcoate of Chloride of Calcium.*

Pure muriate of lime was dried as much as possible on a sand-bath of the temperature of  $600^{\circ}$  or  $700^{\circ}$ , and then slowly heated to redness, and retained for some time at that temperature. The dry chloride of calcium thus obtained dissolves in absolute alcohol at  $60^{\circ}$  with great facility, and with the production of much heat, sometimes occasioning the boiling of the solution. The quantity of chloride taken up increases with the temperature; and at  $173^{\circ}$ , the boiling point of alcohol, 10 parts alcohol dissolve 7 parts chloride of calcium. This solution is thick and viscid, but perfectly transparent, provided the chloride be pure. It boils at  $195^{\circ}$ , alcoholic as well as aqueous solutions boiling at higher temperatures than the pure liquids. The viscosity of the solution of chloride of calcium increases greatly as it cools. Bright crystalline stars soon appear on the surface and on the sides of the vessel, which have been moistened by the solution. The solution, however strong, never crystallizes instantaneously, but gradually, in thin transparent and colourless plates, the forms of which cannot be made out, except on the surface of the solution and sides of the vessel.—To obtain the alcoate in a state of absolute purity, it is necessary to form a solution so weak, that, while hot, it will pass through thin filtering paper; and afterwards to concentrate the filtered solution by heat. A solution of one part chloride of calcium in five parts alcohol passes through the filter. It is remarkable that the most distinct crystalline forms are not obtained from the slow crystallization of comparatively weak solutions;



but in solutions which have been fully saturated, or nearly so, at the boiling temperature. In the former case, the crystalline plates are large, but confused, and nothing but angles can be made out; while in the latter, the forms, under which the plates appear on the surface of the solution, and to the greater advantage, on the sides of the vessel, are generally distinct. These plates are always small, often beautiful, and delicately striated; and they always present the form of isosceles triangles. In general, four of these triangular figures are grouped with their apices together; and if similar, they form a square. But, as more frequently happens, the opposite pairs of triangles only are similar; and the figure presented is a rectangular parallelogram, divided by two diagonal lines into four triangles. The resolution of the rectangle into triangular figures is rendered perceptible by the discontinuance of the striæ, and the formation of clear diagonal lines, which have a beautiful effect. These crystals cannot be removed from the phial in which they are formed without injury, from their softness. Exposed to the air, they speedily deliquesce from the absorption of hygrometric moisture. The heat of the hand is sufficient to melt them. The whole of the alcohol is expelled by a heat amounting to  $250^{\circ}$ , and pure chloride of calcium remains, which emits nothing else upon being heated to redness.

A quantity of this alcoate was dried, first by strong pressure between many folds of linen, and then by pressure between folds of blotting paper. The alcoate, carefully dried in this way, had a white appearance much resembling bleached wax, and was soft, but without tenacity.

Ten grains were heated in a glass capsule, till the whole alcohol was driven off. There remained 4.1 grains chloride of calcium. The atomic weight of chloride of calcium is 7, and that of alcohol 2.875. In the alcoate, 4.1 grains chloride of calcium were combined with 5.9 grains alcohol.

$$4.1 : 5.9 :: 7 : 10.0731.$$

In a second analysis, in which 20 grains of alcoate were employed, the result was precisely similar, as 8.2 grains chloride of calcium remained, which is just double what was obtained in the previous case from half the quantity of alcoate. If this alcoate should be considered a compound of one equivalent proportion of chloride of calcium, and three and a half proportions alcohol, the alcohol would amount to 10.0625, which approaches very nearly to the experimental results. But it would be better to express the composition of the alcoate thus:—

Two atoms chloride of calcium,	14.
Seven atoms alcohol, . . .	20.125
	<hr/>
	34.125



In the solution of chloride of calcium, no crystallization takes place at the temperature of  $50^{\circ}$ , when the alcohol exceeds the proportion of 10 parts to 4 parts of the dry salt. But the solution crystallizes readily when further concentrated. A solution saturated at  $170^{\circ}$ , and which consisted of 10 parts alcohol and 7 parts chloride of calcium, or nearly the atomic proportions of the alcoate, crystallized slowly upon cooling, forming crystals upon the surface of the liquid and sides of the phial, of great regularity and beauty. The whole crystallized during a cold night, leaving no mother liquor whatever.

The injurious effect of the presence of water, in the formation of this alcoate, was evident in alcohol of the specific gravity 0.798, in which the contaminating water did not amount to 1 per cent. A solution of chloride of calcium in alcohol of this strength did not crystallize readily, and the crystals eventually deposited were small and ill formed. Chloride of calcium does not crystallize at all in alcohol of the specific gravity 0.827. The same inconvenience arises from employing chloride of calcium containing a little water.

Although the alcoate of chloride of calcium in a state of purity is entirely decomposed at a temperature not exceeding  $250^{\circ}$ , yet, when water is present, alcohol can be retained by the chloride of calcium at a much higher temperature. Thus I repeatedly found, that chloride of calcium, from which alcohol had been rectified, and which afterwards had been washed out the retort by water, gave indications of the presence of alcohol, after being exposed on the sand-bath to a heat of  $400^{\circ}$  or  $500^{\circ}$  for several hours. Transferred in a crucible to the fire, after it ceased to lose weight on the sand-bath, alcohol-vapour was emitted, which took fire and burned.

## 2. *Alcoate of Nitrate of Magnesia.*

It is difficult to expel the whole of the water with which nitrate of magnesia is combined, without driving off a portion of the acid, and decomposing the salt. For this salt may be wholly reduced in a glass tube by the heat of a spirit-lamp, and yet a sand-bath heat of  $600^{\circ}$  or  $700^{\circ}$  is not sufficient to drive off all its water of crystallization. But a partial decomposition of this salt is of no great consequence, as alcohol dissolves the undecomposed portion of the salt, while the magnesia resulting from the decomposition precipitates, and may be separated by decanting the solution, or by filtering.

Four parts alcohol at  $60^{\circ}$  dissolve one part nitrate of magnesia, and boiling alcohol dissolves more than half its weight of this salt. From the great difference between the solubility of this salt at high and low temperatures, the alcoate is obtained with facility. A hot solution,



containing a greater proportion of nitrate than one part to three parts alcohol, became, upon cooling, an irregular dry mass, which could be indented by the point of a glass-rod, but was much harder than the alcoate of chloride of calcium. In solutions considerably weaker crystals were deposited on cooling, which sometimes resembled the crystals of the former alcoate, but were much smaller, and less distinct; but more frequently the crystals were exceedingly minute, and detached, without any regular form which could be discerned. But the great mass of crystalline matter precipitated in scales of a pearly lustre and whiteness, but apparently made up of the small crystals.

Dried by pressure, in blotting-paper, this alcoate much resembled the alcoate of chloride of calcium in external characters. It sank in water, but floated on the surface of a saline solution of the specific gravity 1.1. Heated, it melted readily; boiled, and much alcohol was given off. When boiled violently, red fumes rise with the alcohol-vapour; but when dried slowly, no loss of acid takes place.

Upon cautiously heating 13.4 grains alcoate of nitrate of magnesia to dryness, there remained 3.56 grains nitrate of magnesia. This gives 9.84 alcohol to 3.56 nitrate of magnesia. But the atomic weight of anhydrous nitrate of magnesia is 9.25. Now,

$$3.56 : 9.84 :: 9.25 : 25.57.$$

In another case, 16 grains alcoate were reduced to 4.2 grains. This gives 11.8 grains alcohol to 4.2 grains nitrate of magnesia.

$$4.2 : 11.8 :: 9.25 : 25.99.$$

On the supposition that this alcoate consists of one atom nitrate of magnesia united with nine atoms alcohol, the alcohol should amount to 25.875, a number intermediate between the two results. This alcoate will be thus represented:—

One atom nitrate of magnesia, .	9.25
Nine atoms alcohol, . . .	25.875
	<hr/>
	35.125

### 3. *Alcoate of the Nitrate of Lime.*

Nitrate of lime may be obtained anhydrous with much greater facility than nitrate of magnesia, as, after being dried on the sand-bath, it may be heated in a glass capsule by the spirit-lamp without decomposition, although it partially fuses. Boiling alcohol saturated with this salt formed a solution, which became very viscid on cooling, and remained without crystallizing for a whole day. But during a frosty night it was resolved into an amorphous solid, slightly moist, but with-



out any appearance of crystallization. This substance was carefully dried in the usual way.

14.8 grains were reduced by heat to 8.8 grains. This gives 6 grains alcohol to 8.8 grains nitrate of lime. The atomic weight of anhydrous nitrate of lime is 10.25. Now,

$$8.8 : 6 :: 10.25 : 6.98.$$

In another case, 15.6 grains were reduced to 9.2, which gives 6.4 alcohol to 9.2 nitrate of lime. But,

$$9.2 : 6.4 :: 10.25 : 7.13.$$

This approaches 7.1875, or two and a half equivalent proportions of alcohol. The composition of the alcoate of nitrate of lime would be represented on this view, by

Two atoms nitrate of lime,	.	20.5
Five atoms alcohol,	.	14.375
		<hr/> 34.875

In another strong alcoholic solution of nitrate of lime, a few irregular crystals were deposited, but the quantity was not sufficient to admit of examination, although they proved that this alcoate is capable of crystallizing.

#### 4. *Alcoate of Protochloride of Manganese.*

The protochloride of manganese, dried in a glass tube, at a red heat, was light, friable, and of a reddish colour. Alcohol dissolved a very large quantity of it. When the solution was made at a high temperature, the alcoate crystallized readily upon cooling in plates with ragged edges. 14.6 grains of this alcoate, carefully dried by pressure in blotting-paper, were reduced by heat to 7 grains. The alcoate, therefore, consisted of 7 grains protochloride of manganese, and 7.6 grains alcohol. The atomic weight of protochloride of manganese is 8. Now,

$$7 : 7.6 :: 8 : 8.686.$$

This slightly exceeds three atoms alcohol = 8.625, but the approximation to the theoretical number is as close as could be expected. The composition of this alcoate may therefore be expressed by

One atom protochloride of manganese,	.	8.
Three atoms alcohol,	.	8.625
		<hr/> 16.625



5. *Alcoate of Chloride of Zinc.*

Alcohol dissolves chloride of zinc with great facility, and the solution when filtered is of a light amber colour. This solution may be concentrated to a very great extent without injury, and becomes so viscid when cold, that it may be inverted without flowing perceptibly. It is not till so concentrated that it begins to deposit crystals, which are small and independent, but apparently of no regular shape. A viscid solution, in which crystals formed, was found to be composed of 20 parts chloride of zinc, and 7 parts alcohol. The small proportion of alcohol is astonishing; yet no more alcohol was given out when the chloride was heated nearly to redness, and began to volatilize; nor did a portion of the chloride thus heated take fire when exposed directly to the flame of a candle.

The crystalline matter was dried with difficulty by pressure in blotting-paper. When dry, it possessed the usual waxy softness of the alcoates, and was of a yellowish colour. Heated, it entered into a state of semifusion, and gave off its alcohol. Nine grains alcoate were reduced by the application of sufficient heat to 7.65 grains. Hence the alcoate consisted of 7.65 chloride of zinc, and 1.35 alcohol. But the atomic weight of chloride of zinc is 8.75.

$$7.65 : 1.35 :: 8.75 : 1.544.$$

1.544 slightly exceeds 1.4375, or half an atomic proportion of alcohol. It is probable that the excess was owing to the difficulty of freeing the alcoate completely from the viscid solution. According to this view, the alcoate of zinc consists of

Two atoms chloride of zinc,	.	17.5
One atom alcohol,	. . .	2.875
		<hr/> 20.375

Besides these alcoates, similar compounds of chloride of magnesium and of protochloride of iron and alcohol were formed, although in quantities too minute to enable me to ascertain their proportions. Alcohol is retained with great force by chloride of iron, and is partially decomposed when heated, as is the case with many metallic chlorides.

As I had it only in my power to present the fixed alkalies to absolute alcohol in the state of hydrates, no alcoate appeared to be formed. The same was the case with the vegetable acids soluble in alcohol.

It is probable that many more alcoates of salts may be formed, particularly of the metallic chlorides. The great obstacle to their formation is the difficulty, and frequently the impossibility, of rendering the salts perfectly anhydrous, before their solution in alcohol is attempted.



I am not aware of any other compounds in the solid form of the same class as the hydrates and alcoates. But there is an oxide, classed by Dr. Thomson, in his *System of Chemistry*, with water and other neutral and unsalifiable oxides, the habitudes of which with certain salts are exceedingly remarkable, and have been looked upon as anomalous, but on which the established properties of hydrates and alcoates appear to me to throw some light. I refer to the deutoxide of azote or nitrous gas. 100 volumes pure water are capable of absorbing only 5 volumes of this gas, according to the experiments of Dr. Henry. But Dr. Priestley and Sir H. Davy ascertained that certain metallic salts, particularly the protosalts of iron, are capable of absorbing this gas in large quantities; and again emit the greater part of it unaltered, on being heated. That the absorption of deutoxide of azote by these salts is not dependent upon the oxygen of their bases, or the water which they contain, I have proved in two ways, in the case of protomuriate of iron. By heating this salt to redness in a glass tube, it is reduced to the state of protochloride of iron. Now, I find that this chloride in the dry state absorbs deutoxide of azote, although in a comparatively small proportion. And the alcoholic solution of the chloride, where neither oxygen nor water interferes, appears to exceed the aqueous solution of the protomuriate in its capacity for deutoxide of azote.

Deutoxide of azote, formed by the action of dilute nitric acid on copper, was conducted into a globular receiver surrounded by cold water, and thence through a glass tube of two feet in length, filled with small fragments of chloride of calcium. Thus dried, the deutoxide of azote was passed slowly over carefully prepared protochloride of iron in the state of powder, and contained in a glass tube of small diameter. The protochloride immediately became darker in colour; and upon being withdrawn, after exposure to the current of gas for some time, was found to retain the smell of nitrous gas, and to have increased in weight. In one case, 30 grains chloride had increased to 31.1 grains; and in another case, 25 grains chloride to 25.5 grains. On being gently heated, the deutoxide of azote was evolved, and the chloride restored to its former colour.

The solution of protochloride of iron in absolute alcohol absorbed a much greater quantity of deutoxide of azote, and became nearly black. A solution saturated with gas began to boil at  $100^{\circ}$ , evolving gas in great abundance, which, being collected in the pneumatic trough, proved to be pure deutoxide of azote. The greater part of the gas was expelled before the alcohol rose to its boiling point, and after the solution was in the state of ebullition for a few seconds gas ceased to rise, and the alcoholic solution recovered its original colour, which was generally a chocolate-brown, from the presence of a little bichloride of iron. The



quantity of gas evolved from a solution of one part protochloride of iron in five parts absolute alcohol, amounted to 23 times the volume of the alcohol.

I think it probable that the absorption of deutoxide of azote by protochloride of iron, is analogous to the absorption of alcoholic and aqueous vapours by the same body. For I find that protochloride of iron absorbs alcohol-vapour as well as the vapour of water. The absorption of deutoxide of azote may depend upon a tendency of chloride of iron to *deliquesce* in like manner, in an atmosphere of that neutral oxide. At a very low temperature, which it is perhaps out of our power to reach, protochloride of iron would probably absorb this gas in sufficient quantity to exhibit the appearance of deliquescence, and might form with it a neutral compound similar to its alcoate or hydrate.

A reason can also be given for the superiority of the aqueous and alcoholic solutions of this chloride over the dry chloride itself, in absorbing deutoxide of azote. We formerly saw that the alcohol of the alcoate of chloride of calcium was completely expelled by a heat of  $250^{\circ}$ , when no water was present; but that, when a considerable quantity of water was present, alcohol was retained by that chloride at the temperature of  $400^{\circ}$  or  $500^{\circ}$ . Now chloride of iron might be enabled to retain deutoxide of azote more powerfully, by the assistance of alcohol or water, in the same manner. But the *retaining* power we have formerly found in a similar case to be an index of the *absorbing* power. Hence solutions of protochloride of iron might absorb deutoxide of azote more powerfully than the chloride itself.

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### III.

## RESEARCHES ON THE ARSENIATES, PHOSPHATES, AND MODIFICATIONS OF PHOSPHORIC ACID.

COMMUNICATED BY EDWARD TURNER, M.D., F.R.S., &c.<sup>1</sup>

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### I. OF THE SUBSALTS.

No classes of salts have more liberally rewarded investigation than the arseniates and the phosphates. Witness the discovery of the extraordinary phosphates of lime by Berzelius; the observation of the identity of form of the corresponding arseniates and phosphates by Mitscherlich, and the doctrine of isomorphism to which that observation

<sup>1</sup> Received January 29,—Read June 19, 1833.



led; the discovery by the same chemist of two biphosphates of soda, agreeing in composition but differing in form; and lastly, the discovery of the pyrophosphates by my friend and townsman Mr. Clark. Much, however, still remains to be done to complete the history of these interesting salts.

### 1. *Subarsenate and Subphosphate of Soda.*

The extraordinary disposition of arsenic and phosphoric acids to form subesquisalts—such as the brown arseniate and the yellow phosphate of silver, the common subarsenates of lime, lead, etc.—is well known. Corresponding alkaline salts exist, which merit the consideration of chemists.

To a strong solution of arseniate or phosphate of soda add a solution of caustic soda till the liquor feels soapy between the fingers. At least half as much soda as already in the salt must be added, but an excess of alkali is not injurious. Concentrate the liquor till a pellicle forms on its surface, and then allow the solution to cool. At the temperature of  $150^{\circ}$ , tufts of slender prismatic crystals appear in it; these rapidly increase in quantity, and finally fill the vessel. The crystals must be drained as well as possible, and the mother-liquor may be thrown away, as it contains little else than the excess of caustic soda and the soluble impurities of the salts. It is necessary, without loss of time, to redissolve the crystals in twice their weight of hot water, to filter the solution through paper, and to recrystallize.

Both salts crystallize readily, as their solutions cool, in the form of six-sided prisms, which are generally slender. The prism is often terminated by a flat surface, which appears to be a right section. The angles of the crystals were not measured, but two of them are much more obtuse than the remaining four. The subarsenate may be procured in crystals of larger size than the subphosphate, but of the same form. These salts in the crystalline form are not altered by exposure to the air, but in solution they absorb carbonic acid; and when again crystallized, a portion of carbonate is found to adhere pertinaciously to the crystals. It is easy, however, to produce fine crystals by the process described, free from carbonic acid, and apparently pure.

A solution of the subarsenate is precipitated exactly neutral, by an excess of fused nitrate of silver, the brown subarsenate of silver falling down, which proves the alkaline subarsenate to be in the same state of neutrality as the metallic subarsenate, and consequently of a similar constitution. The subphosphate gives, with the same reagent, the yellow subphosphate of silver, and leaves a liquid either neutral or very faintly alkaline by the most sensible cudbear paper. The alkalinity, how-



ever, must be accidental, as it disappears on the addition of the smallest quantity of acetic acid. These salts, therefore, rank as subsesquisalts, containing one proportion and a half of base to one of acid.<sup>1</sup> They are interesting as the only known soluble salts of that constitution. The subphosphate had been previously crystallized by Dr. Dalton and recommended as a reagent;<sup>2</sup> but it was supposed to contain twice as much soda as the common phosphate. Mitscherlich also infers the existence of a subsesquiphosphate of soda, from the quantity of carbonic acid expelled, when phosphate of soda is calcined with carbonate of soda.<sup>3</sup> The same salt appears likewise to have fallen into the hands of Dr. Thomson, as an accidental product, but is described as a carbonophosphate of soda, being probably impure.<sup>4</sup>

In regard to the properties of these salts. They are strongly alkaline to the taste, and act upon chlorine and iodine like free alkalies. Indeed, the excess of their alkali is separated by the weakest acids, even by carbonic acid, and the common rhomboidal phosphate or arseniate afterwards appears on crystallizing. When the pure crystals are thrown into neutral nitrate of ammonia, the volatile alkali is disengaged. At 60° Fahr. 100 parts water dissolve 28 crystallized subarseniate of soda; and the crystals by themselves melt at 186°.

At 60°, 100 parts water dissolve 19.6 crystallized subphosphate of soda, and the crystals melt at 170°. Hence, although more fusible, they are less soluble than the crystals of subarseniate.

It is a fact of extraordinary interest, that the acid of this subphosphate is not convertible into pyrophosphoric acid by the action of heat upon the salt, like the acid of the common phosphate of soda. Indeed, when the pyrophosphate of soda itself is calcined with an excess of carbonate of soda, carbonic acid is expelled, and the former salt passes entirely into subphosphate of soda, which crystallizes in the usual form, and contains not pyrophosphoric but phosphoric acid. This change takes place equally well although both the carbonate and pyrophosphate be made anhydrous before being calcined; and we can obtain consequently an anhydrous subphosphate of soda. A solution of pyrophosphate of soda, to which sufficient caustic soda or carbonate of soda has been added, cannot be evaporated to dryness without becoming subphosphate. But pyrophosphate of soda may be boiled with caustic soda for hours without sensible alteration, provided the solution is not evaporated to dryness; and it crystallizes afterwards in its original form, exhibiting no disposition whatever to form a subpyrophosphate.

<sup>1</sup> Three atoms oxygen in the base for five atoms oxygen in the acid.

<sup>2</sup> *Manchester Memoirs*, N.S., vol. iii. p. 12.

<sup>3</sup> *Annales de Chimie et de Physique*, tom. xix. p. 363.

<sup>4</sup> *First Principles*, etc., vol. ii. p. 451.



I may premise thus early, that the preceding facts, and many others to be afterwards enumerated, appear to be most easily explained on the hypothesis that phosphoric acid, in contradistinction to pyrophosphoric, is characterized by a disposition to unite with three atoms of base;—that common phosphate of soda, for instance, is a phosphate of soda

and of water, and that its symbol is  $\text{Na}^2\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{H}}}\overset{\cdot\cdot}{\text{P}}$ . Now for this basic water an atom of any of the usual bases may be substituted; an atom of soda,

for instance, as in our subphosphate, of which the symbol is  $\text{Na}^3\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{P}}}$ ; an atom of oxide of silver, as in the yellow subphosphate of silver; and so in the other subphosphates. We have here a clew also to the disposition of phosphoric acid to form such subsesquisalts; for the common phosphate of soda which we use as a precipitant exchanges its basic water for a fixed base. Hence, although a phosphate of neutral composition, such as the common phosphate of soda, cannot be made anhydrous without becoming pyrophosphate, the subphosphates, having an excess of fixed base, may be anhydrous, as was observed by Stromeyer; and indeed they are not convertible into pyrosalts.

The pyrophosphoric acid of Clark, which exists in the pyrophosphate of soda, appears to unite with only two atoms of base.

Phosphoric acid, produced in white flakes on burning phosphorus in air or oxygen gas, or the acid heated to redness by itself, constitutes, we shall afterwards find, a third modification of phosphoric acid. This third variety is characterized by alone coagulating albumen; by producing precipitates, even when free, in muriate of barytes, lime, etc.

Much time and attention were devoted to the determination of the water of combination of the foregoing subsalts. Both salts, when dried by heat, act upon glass with as much violence as the caustic alkalies, absorb carbonic acid with avidity, and retain a small but notable quantity of water under the most intense heat. The problem is therefore environed by difficulties.

(1.) Excellent hard crystals of subarsenate of soda lost nothing when reduced to powder and exposed to a dry atmosphere. Dried most cautiously in a platinum flask, on a sand bath,

				Water.	
In Exp.	1.	42.42 grs. crystallized salt lost	21.13 . . .	49.81	per cent.
"	2.	26.04 "	12.94 . . .	49.69	"
"	3.	41. "	20.40 . . .	49.76	"
Mean . . .				49.75	

These results exhibit the entire quantity of water which the salt abandons by the action of heat alone; for an adopter being applied to the flask and made tight by luting, the salt was in each case subsequently heated for a few minutes to full redness, without any further



loss of weight. No sensible absorption of carbonic acid occurred when the experiment was conducted in this manner. The salt was not fused; indeed, it is not fused by a strong white heat.

But the calcined salt still contains water, as may be shown by fusing it with any body capable of combining with the excess of alkali. A quantity of bichromate of potash in a glass tube may easily be kept in a state of fusion by the flame of a lamp. On throwing the calcined subarsenate into that fused and anhydrous salt, a notable quantity of water was given off, which condensed in the upper part of the tube.

EXP. 1. About 50 grains of the fused bichromate of potash, as it falls to pieces in the progress of cooling, but still warm, were introduced into the platinum flask containing 13.1 grains of calcined salt of Experiment 2d above, and the whole maintained in a state of fusion for a considerable time at a low red heat, by means of a spirit-lamp. The salt lost 0.16 grain additional, and no green oxide of chromium was formed. This is an additional loss of 0.62 per cent. on the crystallized salt, and makes the entire water amount to 50.31 per cent.

EXP. 2. 25.57 grains of crystallized subarsenate were introduced, with a little water, into a crucible containing already 20 grains of pure anhydrous arsenic acid, calcined immediately before by a spirit-lamp heat which does not decompose it. The whole was cautiously dried, and finally fused by a red heat. The loss amounted to 12.8 grains, or 50.06 per cent.

EXP. 3. To 25.11 grains of binarsenate of soda previously fused in a crucible, 45.5 grains of subarsenate of soda were added, with water sufficient to dissolve the whole. Cautiously evaporated to dryness in a crucible partially covered by a watch-glass, as usual, and finally heated to redness, the subarsenate lost 22.88 grains, or 50.29 per cent. This last is certainly the preferable mode of determining the problem.

The mean of the three experiments detailed gives the entire water in the subarsenate of soda 50.22 per cent., while the proportion expelled by heat alone amounts to 49.75 per cent. Hence the quantity retained amounts to 0.47 per cent.

When the calcined salt retaining this small quantity of water is reduced to an impalpable powder, and heated afresh on the sand-bath, the whole water is expelled, with the exception of a mere trace.

Although small, the quantity of water retained in the calcined salt could not be passed over without investigation, as it may afford indication of some internal change which the subarsenate undergoes. Calcined in the open fire, this salt absorbs carbonic acid gas, and afterwards effervesces briskly with an acid. The salt becomes at the same time anhydrous. This may arise from the hydrate of soda becoming carbonate of soda.

A portion of subarsenate of soda, dried by the spirit-lamp, was



reduced to powder, and calcined anew with a mass of carbonate of ammonia in the same crucible, so that the maximum absorption of carbonic acid (as it was imagined), might take place. The salt was kept uncovered for some time, at a low red heat, after all the volatile carbonate had escaped. It was found that the quantity of carbonic acid absorbed, might be determined most exactly by disengaging the gas over mercury by means of a small quantity of muriatic acid slightly diluted.

Eleven grains of calcined salt afforded 0.49 cubic inch of carbonic acid gas, at  $60^{\circ}$ ; of which the weight is 0.23 grain, and which is equivalent to 0.56 grain of carbonate of soda. Hence, by calculation, 100 parts of the calcined salt contain 2.1 carbonic acid, or 5.1 carbonate of soda; 2.1 carbonic acid are equivalent to 0.9 water; but 50 calcined salt, it was previously shown, retain 0.47 water, and therefore 100 calcined salt retain 0.94. It would thus appear that the carbonic acid is just in quantity sufficient to occupy the place of the water. The carbonic acid is not expelled by an intense white heat.

The supposition is quite inadmissible that our salt contains the notable quantity of soda which becomes carbonate, as a casual impurity, and not essential to its composition; for the salt employed in all these experiments was in large, clear and perfect crystals. Such a supposition is also opposed by the analytic determination of the soda.

The quantity of water in the salt, namely, 50.22 per cent., is not easily reconciled with our best data for atomic weights. Adopting the atomic weight of arsenic acid, given by Berzelius, which I had an opportunity of verifying, a salt of

\*24 atomic proportions of water correspond with 50.82 per cent.

23½	„	„	50.29	„
23	„	„	49.75	„

Our experimental result agrees closely with the middle number, and is perhaps compatible with either 23 or 24 atoms of water. Chemists will probably agree with me that the last supposition is the most likely. If so, it is curious that the subarsenate differs only from the neutral arseniate, by the substitution of an atom of soda for an atom of water, for the last salt contains 25 atoms of water.

It is well known that the analytic determination of the acid in the arseniates and phosphates is attended with considerable difficulty, chiefly from unsteadiness in the proportions of the precipitates.

41.87 grains of crystallized subarsenate of soda, precipitated by an excess of pure acetate of lead, gave a neutral mother-liquor, and a

\* We are obliged to adopt the double atom of arsenic acid here ( $As = 1440.1$ ); and consider these subsalts as consisting of one proportion of arsenic acid (containing five proportions oxygen) and three proportions of base (containing three of oxygen).



quantity of subarsenate of lead, which successfully washed by decantation, without the use of a filter, and heated to redness, weighed 46.41 grains; 35.17 grains of this subarsenate of lead, freshly calcined, were dissolved entirely in water, acidulated with nitric acid; and, precipitated by sulphate of soda, gave 35.86 grains of sulphate of lead, which contain 26.38 oxide of lead. In such calculations the atomic numbers of Berzelius are adopted in this paper. Hence the portion of subarsenate of lead analysed contains 8.79 arsenic acid; and the whole 46.41 grains subarsenate of lead contain 11.62 arsenic acid, which is therefore the quantity of arsenic acid in the portion of subarsenate of soda submitted to analysis. Hence crystallized subarsenate of soda contains 27.76 per cent. arsenic acid.

The soda of the salt was determined in the usual way. The arsenic acid being precipitated by acetate of lead, and received on a filter, the excess of lead was removed by carbonate of ammonia added to the hot liquor. The solution of acetate of soda resulting, was then filtered, concentrated, and transferred into a platinum crucible, in which it was evaporated on the sand-bath to dryness with the greatest caution; partially covered by a watch-glass; and eventually decomposed by a full red heat gradually applied to the crucible still covered by the watch-glass, as from the effervescence during the decomposition of the acetates, small particles are thrown up with considerable force, and would otherwise be lost. The solution of carbonate was then filtered, evaporated to dryness in a crucible, and raised to a strong red heat. The following results were obtained after a knowledge of all the necessary precautions had been acquired.

EXP. 1. 39.98 grains of crystallized subarsenate of soda yielded 15.61 carbonate of soda, equivalent to 9.14 soda; or the salt contains 22.87 per cent. soda. Now 22.87 soda contain 5.85 oxygen, and 50.22 water contain 45.74 oxygen; or the oxygen in the water is 7.819 times that in the base. But as there are three atoms of oxygen in the base, there are  $7.819 \times 3$ , or 23.457 atomic proportions of oxygen in the water.

EXP. 2. 40.3 grains of crystallized subarsenate of soda yielded 15.73 carbonate of soda, equivalent to 9.21 soda; or the salt contains 22.85 per cent. soda.

EXP. 3. 21.62 grains of crystallized salt gave 8.41 carbonate of soda, equivalent to 4.93 soda; or 100 grains of crystallized salt contain 22.8 soda.

These experiments agree very closely among themselves; but I am doubtful whether this method gives the alkali with perfect precision in the case of the arseniates, but somewhat in excess. The general result of the analysis may be stated as follows:—



## Subarsenate of soda.

	Experiment.	Theory of 23 atoms water.
Arsenic acid, . . . .	27.76	27.69
Soda, . . . .	22.85	22.55
Water, . . . .	50.22	49.75
	<hr/> 100.83	<hr/> 100.

(2.) The crystals of subphosphate of soda submitted to analysis were smaller than the crystals of subarsenate, but well formed and remarkably pure, containing not a trace of sulphuric, muriatic, or carbonic acid.

EXP. 1. A quantity of the salt had been reduced to powder and exposed to a dry atmosphere, in which it lost a little weight; of the salt so dried, 29.12 grains lost by red heat in a platinum retort, as described in the case of the subarsenate, 16.07 grains; which is 55.19 per cent. water.

EXP. 2. 21.83 grains of crystallized salt heated in the platinum retort on the sand-bath lost 12.05 grains, or 55.2 per cent. Being heated thereafter to redness by the lamp, the loss appeared to be only 12.01 grains; but the calcined salt had acquired a little carbonic acid, notwithstanding the precautions, and now effervesced with acids. These two experiments give, therefore, the same result.

The salt still retained a little water, about twice as much as the subarsenate in the same circumstances. But when the calcined subphosphate was reduced to an impalpable powder, and heated anew, the greater portion of the water which had been retained was readily expelled.

EXP. 3. Fused with recently ignited protoxide of lead, 19.36 grains of crystallized salt lost 10.84 grains, or 55.99 per cent., which is the entire water in the salt.

EXP. 4. To 17 grains of biphosphate of soda recently fused in a crucible, 35.54 grains of crystallized subphosphate of soda were added, with a quantity of water, in which the salts were dissolved together by digestion. Evaporated to dryness, and calcined by a red heat without fusing, the salts sustained a loss of 19.92 grains. Hence 100 crystallized salt have abandoned 56.05 water.

Calcined with access of carbonic acid, the subphosphate, like the subarsenate, absorbs that gas, becoming at the same time anhydrous; but redissolved in water and evaporated, it affords crystals of the original form and composition, which retain a trace of carbonic acid.

A quantity of the subphosphate ignited in an open crucible was found to consist of



Subphosphate of soda,	.	.	.	100
Carbonic acid,	.	.	.	2.3

Another portion, calcined with a mass of dry carbonate of ammonia in the same crucible, consisted of

Subphosphate of soda,	.	.	.	100
Carbonic acid,	.	.	.	2.25

A quantity of subphosphate of soda dissolved in a solution of carbonate of ammonia, was thereby purposely contaminated by a large quantity of carbonic acid, and calcined three times in succession with alternate pulverization. It finally consisted of

Subphosphate of soda,	.	.	.	100
Carbonic acid,	.	.	.	1.7

Or of

Subphosphate of soda,	.	.	.	100
Carbonate of soda,	.	.	.	4.3

It seemed to follow from the last experiment, that, by pulverizing the salt and recalcining it, the quantity of carbonic acid may be diminished, as in the case of water in the hydrate of the same salt.

The calcined salt did not fuse at a strong white heat, but acquired a beautiful blue tint where in contact with platinum.

By the mean of two experiments detailed above, 100 crystallized subphosphate of soda contain 56.03 water. Twenty-three atoms would be 55.61 per cent. only, and twenty-four atoms water would be 56.66 per cent.<sup>1</sup>

The soda of the subphosphate was determined directly, in the same manner as the soda of the subarsenate.

EXP. 1. 41.23 grains of crystallized salt gave 17.27 carbonate of soda, equivalent to 10.12 soda. Hence 100 of crystallized salt contain 24.54 soda.

EXP. 2. 40 grains of the crystallized salt gave 16.97 carbonate of soda, equivalent to 7.03 soda, or 24.87 per cent. soda.

It was also attempted to determine the phosphoric acid directly, by precipitating with nitrate of silver, which leaves a mother-liquor either exactly neutral or feebly alkaline. The result was 18.6 per cent. phosphoric acid, which certainly approaches the truth. But the subphosphate of silver was discovered to carry down with it a portion of nitrate of silver, which comes away gradually, but which no continuance of washing is sufficient entirely to remove. The subarsenate of silver has the same

<sup>1</sup> Assuming the double atom of phosphoric acid (P) = 892.3.



property. Thus to precipitate 27.5 grains of crystallized subphosphate of soda, 38.1 grains of fused nitrate of silver were found necessary, which is more than one grain above the theoretical quantity: 25 grains of crystallized subarsenate of soda required 31.08 grains of nitrate of silver for complete precipitation, which is an equally excessive proportion of the precipitant. From these precipitates fumes of nitrous acid were evolved, on the application of heat. When nitrate of ammonia, exactly neutral, was first mixed with the solution of subarsenate of soda, a less quantity of nitrate of silver sufficed; 30.05 grains of nitrate of silver left still an excess of arsenic acid, when added to 25 grains of subarsenate of soda; but on introducing 0.06 grain of nitrate of silver additional, the liquid contained an excess of silver: but the nitrate of ammonia retains in solution a trace of subarsenate of silver. It is curious that the pure subarsenate of silver, precipitated in the way last mentioned, withdraws nothing from a solution of nitrate of silver. This shows that the subarsenate of silver carries down the soluble nitrate only at the moment of precipitation, and by the agency of some chemical affinity very different from the attraction of animal charcoal for many bodies in solution.

The addition of a little acetic acid to a solution of subarsenate of soda, occasioned a notable deficiency in the amount of the precipitate by nitrate of silver.

It may be safely concluded from the quantity of soda which it contains, that the salt under examination is a subsesquiphosphate. The crystals consist of

Subsesquiphosphate of soda,	.	.	.	43.97
Water,	.	.	.	56.03
				<hr/> 100.

## 2. *Subphosphates and Subarsenate of Potash.*

The corresponding salts of potash were formed, but I did not succeed in obtaining them in a state of purity.

When caustic potash is added in excess to phosphoric acid, the solution becomes muddy although dilute, and a precipitate partly flaky and partly in a gritty powder shows itself. This precipitate in both conditions is a diphosphate of potash according to Dr. Thomson, who examined it.<sup>1</sup> When arsenic acid was treated in the same way, with excess of caustic potash, no insoluble salt fell; but on concentrating the solution it crystallized almost entirely in the form of minute needles. These crystals I could not free from carbonate; and either of themselves, or rather from the presence of free potash, they were deliquescent in the

<sup>1</sup> *Inorganic Chemistry*, vol. ii.



extreme. There is every reason to believe that they constitute a subsalt corresponding with the subsalt of soda.

A crystallized subphosphate of potash, however, may be formed by fusing together phosphoric acid and an excess of carbonate of potash (bicarbonate was employed). A strong solution crystallizes in small needles, like the preceding subsalts. These crystals were exceedingly soluble, and retained a little carbonate of potash, but were not at all deliquescent. They precipitated the yellow subphosphate from nitrate of silver in excess, and left a neutral or slightly alkaline mother-liquor.

The soluble subarsenate and subphosphate of soda present a favourable opportunity of forming the corresponding insoluble earthy and metallic subsalts. Salts of this formula, it is well known, generally present themselves, even when the alkaline salts of arsenic and phosphoric acid, which are neutral in composition, are employed as precipitants. But the consequent and unavoidable acidity of the mother-liquor is apt to prevent complete precipitation, the phosphates, with few exceptions, being soluble in an excess of acid.

### 3. *Subarsenate and Subphosphate of Barytes.*

To a solution of subarsenate of soda, chloride of barium was gradually added till in slight excess. The precipitate first appeared gelatinous, consisting of little pellucid masses; but on the application of heat to the liquor, the precipitate immediately became small-flaky and heavy, and subsided. The mother-liquor proved strongly alkaline, and the precipitate, it was found, had taken down with it a quantity of subarsenate of soda, of which protracted washing did not entirely divest it. Berzelius has remarked that barytes is most disposed to combine with phosphoric acid in the proportion of a neutral salt, which is true also of arsenic acid, and accounts for the above derangement of precipitation, a little of the neutral salt being probably formed. The process was reversed, and into a large quantity of neutral solution of chloride of barium, a solution of 50 grains of subarsenate of soda was gradually poured with stirring. A pulverulent heavy precipitate fell easily. The filtered mother-liquor did not fully restore the blue colour of reddened litmus paper in some hours, but acted at once as an alkali on cudbear paper, although in a feeble manner. The precipitate, however, was easily washed. While still wet on the filter, it had acquired a sensible trace of carbonic acid; and when heated, it displayed, like the corresponding alkaline salts, considerable avidity for carbonic acid. 22.33 grains of this salt, heated to redness by the spirit-lamp, were found by one analysis to be composed of



Carbonic acid, . . . .	0.18		
Arsenic acid, . . . .	7.10	. . .	32.06
Barytes, . . . .	15.05	. . .	67.94
	<u>22.33</u>		<u>100.</u>

If we may trust a single analysis, the salt contains an excess of barytes; for by theory a subsesquiarsenate of barytes should be composed of

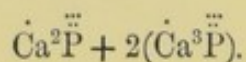
Arsenic acid, . . . .	1440.1	. . .	33.4
Barytes, . . . .	2870.6	. . .	66.6
	<u>4310.7</u>		<u>100.</u>

When a solution of subphosphate of soda is added to chloride of barium, a corresponding subphosphate of barytes subsides as a heavy, small-flaky precipitate, leaving a mother-liquor neutral or nearly so.

#### 4. *Subarsenate and Subphosphate of Lime.*

The subarsenate of lime, formed by pouring chloride of calcium into subarsenate of soda, is a bulky gelatinous body, and continues so although heated. It carries down subphosphate of soda, but to a less extent than the subarsenate of barytes prepared in the same way. Prepared by the converse process, the subarsenate precipitates in little gelatinous masses, as before; although the general aspect is flaky, particularly after the liquor has been heated. The mother-liquor from 50 grains of subarsenate of soda precipitated in this way, required several minutes to affect reddened litmus paper unequivocally, being slightly alkaline. The precipitate appears, therefore, to correspond closely with the subarsenate of soda. The properties of the subphosphate appeared to be similar. Such a phosphate occurs native, but hitherto had not been formed artificially.

Berzelius proves the existence of another subphosphate of lime, which has acquired the name of the Subphosphate of lime of bones,—a gelatinous body, formed when muriate of lime is poured into an excess of phosphate of soda; or when phosphate of lime, dissolved in muriatic acid, is precipitated by ammonia. The composition of this phosphate is singular and without parallel, consisting, on the simplest view which can be taken of it, of three proportions of phosphoric acid and four of lime. It is designated by Gay-Lussac the  $\frac{3}{4}$  phosphate, while the preceding compound is called the  $\frac{2}{3}$  phosphate. The anomaly may in some measure be removed by viewing this salt as a compound of one proportion of the neutral phosphate of lime and two proportions of the subsesquiphosphate. Its formula would be as follows:





Berzelius finds the calcined bones of the ox to be composed of such a phosphate of lime with a small quantity of carbonate of lime. His analysis may be stated thus :

Phosphate of lime,	{ Phosphoric acid, . . .	46.45	} 51.86
	{ Lime, . . . . .	49.7	
Carbonate of lime,	{ Lime, . . . . .	2.16	
	{ Carbonic acid, . . .	1.69	
		<hr/> 100.	

The only doubt we can entertain of this view arises from the circumstance, that the presence of carbonic acid in the calcined phosphate of the bones is no proof of the existence of carbonic acid in the same body previous to calcination. We know that the subphosphate of soda absorbs a variable quantity of carbonic acid when calcined. The quantity of carbonic acid which the earth of bones contains is variable. A specimen which had been calcined more than a year before, contained 1.2 per cent. As this was below the determination of Berzelius, I reduced a portion to fine powder, and kept it for some minutes in an atmosphere of carbonate of ammonia, at a heat scarcely amounting to redness. The earth, however, by this treatment, had lost carbonic acid, and now contained only 0.5 per cent. Another portion reduced to powder, and gently heated in the same way, but without the carbonate, retained 0.57 per cent. carbonic acid.

The earth of bones, although calcined at a high temperature, contains phosphoric acid and not pyrophosphoric acid, the excess of base preventing the transition. But eight ounces of earth of bones being mixed with two ounces of sulphuric acid, and calcined again, were found thereafter to contain a large proportion of an acid which precipitated silver white.

##### 5. *Subarseniate and Subphosphate of Lead.*

When the subarseniate or subphosphate is poured into a solution of acetate of lead in excess, the salt which falls was found to contain an excess of base. I therefore had recourse to the converse process. To 50 grains of subarseniate of soda in solution, 50 grains of acetate of lead in solution were gradually added with stirring, which left an excess of the first in solution. The subarseniate of lead was washed by decantation, till the water digested upon it ceased to acquire an alkaline reaction. Heated to low redness, this substance acquired a yellow tint, but became white again on cooling; it was found somewhat aggregated together by the heat, but not fused. 15.25 grains were dissolved in dilute nitric acid, and precipitated by sulphate of soda added in excess. The sulphate



of lead amounted to 15.41 grains, equivalent to 11.336 oxide of lead. The washings became of a brown tint on the addition of sulphuretted hydrogen, but the quantity of lead which they contained was too small to be appreciated. This analysis affords a striking confirmation of the atomic weight of arsenic acid, deduced by Berzelius from his analysis of arsenious acid by sulphur. I place together the results of my analysis, and the composition of the same salt calculated by that accomplished analyst from his own data.

	Analysis.	Theory of Berzelius.
Arsenic acid, . . . . .	25.67	25.61
Oxide of lead, . . . . .	74.33	74.39

In another analysis, the quantity of lead which escaped precipitation by the sulphate of soda was even more notable, from the presence of too much nitric acid. The result was 74.18 per cent. oxide of lead. This salt I believe to be most suitable of all the arseniates for determining directly the combining proportion of arsenic acid.

## II. OF THE NEUTRAL PHOSPHATES AND PYROPHOSPHATES.

It is well known that the phosphate of soda is a highly alkaline salt, although generally viewed as neutral in composition. Mitscherlich found that a solution of this salt required the addition of half as much acid as it already possesses, to deprive it of an alkaline reaction. This result I had an opportunity of confirming in a general way, although I could not ascertain the exact point of saturation, from the test-paper proving doubtful in its indications for a considerable distance on either side of the supposed point of neutrality.

Although Mr. Clark's experiments afford strong evidence that the phosphate of soda of the usual form contains twenty-five atoms water, yet it was thought proper to settle the point by a careful experiment. Pure crystals were employed, which had been formed about six months before and were dry, but possessed bright surfaces. A portion for analysis was reduced to powder in a damp day, and pressed for twenty hours between folds of dry blotting-paper. A crystal exposed to the air at the same time, beside the paper, remained perfectly bright. Carefully dried and heated to redness, 35.44 grains of the salt lost 22.29 grains of water. Hence the crystallized salt consists of

Phosphate of soda, . . . . .	37.1
Water, . . . . .	62.9
	<hr/>
	100.



Our result gives 25.22 atoms water, and therefore confirms the previous determination.

Mr. Clark has the entire merit of discovering the change which takes place upon phosphate of soda by the action of heat, and his original description of the pyrophosphate of soda is very complete.<sup>1</sup> He likewise remarked the connexion between the transition into pyrophosphate and the loss of the last atom of water of the phosphate of soda, which atom requires a much higher temperature to expel it than the other twenty-four; but he did not entertain the idea, broached in this paper, of the basic function of that atom of water in the constitution of the salt.

The phosphate of soda contains three atoms base; namely, two atoms soda and one atom water; and when added to the earthy or metallic salts, gives precipitates which uniformly contain three atoms base, namely, three atoms of the foreign oxide, as in the case of the subphosphate of silver, or one atom water and two atoms of the other oxide, as in the phosphate of barytes. These precipitations afford the strongest proof of the basic function of that atom of water which is essential to the phosphate of soda, as they can be accounted for, on the usual laws of double decomposition, on no other supposition. The pyrophosphate of soda, on the other hand, contains only two atoms soda as base, and gives, accordingly, bibasic precipitates.

In his *Traité de Chimie*, Dumas speaks in an incidental manner of a third phosphate of soda, differing from the two preceding, obtained by keeping for a long time a solution of the common phosphate at the boiling temperature; but I have been able to discover no description nor any other notice of this new salt. To investigate the point, I boiled for several hours each day during three weeks, an ounce of phosphate and the same quantity of pyrophosphate of soda, in separate flasks, with several ounces of water. A considerable heavy, flaky precipitate soon appeared in both, but was most abundant in the pyrophosphate. The flasks, on removing the liquors from them, were found strongly corroded. The solution of pyrophosphate, on being filtered and concentrated, yielded crystals of our subphosphate of soda to the last drop. It had evidently derived alkali from the glass, while a portion of its acid had also united with the oxide of lead of the glass, and formed a precipitate insoluble both in water and in acids. But the solution of the boiled phosphate of soda filtered, concentrated, and set aside in a cool place, became gradually filled with crystalline plates, which were the finest films and had a beautiful silky lustre. The mother-liquor being poured off, yielded a second, third, and fourth crop of crystals of the same singular appearance. The last drops of the liquor were still alka-

<sup>1</sup> *Edinburgh Journal of Science*, vol. vii. p. 298.



line, but I thought not so strongly so as the phosphate of soda. The crystallization in these cases was gradual, and not hurried and confused. To look at these silky films, nobody would have guessed them to be phosphate of soda. But on examining them minutely, complete rhomboidal plates of the common form of phosphate of soda were distinguished; and the water of crystallization of the salt was found to be exactly the same as that of the rhomboidal phosphate. In a dry atmosphere, too, a portion of the silky plates, and an equal quantity of pounded crystals of the common phosphate lost their water *pari passu*. It is evident, therefore, that we have nearly obtained the phosphate of soda of an unusual appearance. I shall have occasion, in the sequel of the paper, to notice other circumstances in which the phosphate presents itself of this appearance. On dissolving and recrystallizing the silky plates, the usual solid rhomboids presented themselves. It was also determined by experiment, that neither the phosphate nor pyrophosphate of soda is altered by being boiled for a week in water contained in a silver capsule, in which no decomposition can take place. There can be no doubt, therefore, that these salts undergo no change at the boiling temperature, unless they react upon the material of the containing vessel. Even at the usual temperature a solution of these alkaline salts corrodes a glass phial and becomes turbid in the course of months.

### III. OF THE SUPERPHOSPHATES.

#### 1. *Of the Biphosphate of Soda.*

This salt admits, as I shall immediately show, of so many changes in its constitution and properties, as to entitle it to be considered one of the most interesting of chemical substances. The facts which I have to communicate on this subject are certainly the most extraordinary of the paper, and were determined with care and considerable difficulty.

I had an opportunity of noticing the dimorphism of this salt, and confirmed the observation of Mitscherlich, that both forms of crystals possess the same chemical properties and the same proportion of water. Of the four atoms of water which the crystals contain, they lose, I find, two atoms at the temperature of  $212^{\circ}$ , and not a particle more till heated up to about  $375^{\circ}$ .

1st. Thus 4.96 grains of the crystals reduced to powder, when dried on the water-bath for several days, retained only 0.76 water, or consisted of

Biphosphate of soda,	.	.	.	.	100
Water,	.	.	.	.	18.09
					<hr/> 118.09



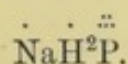
This is as nearly as possible one-half of the entire water in the crystals, which by the mean of Mitscherlich's experiments consist of

Biphosphate of soda,	.	.	.	100
Water,	.	.	.	35.57
				<hr/> 135.57

2*d.* 10.01 grains of the salt dried on the water-bath retained 1.53 water, which is 18.04 water to 100 dry salt, or the same result as in 1°.

3*d.* 50 grains of the crystals lost 6.52 grains on the water-bath; their entire water being by theory 12.77.

There is every reason to believe that the two atoms of water retained are essential to the constitution of the biphosphate of soda, and that its composition is expressed by the following formula,



It contains three atoms base, namely, one atom soda and two atoms water, united to a double atom of phosphoric acid. The salt cannot sustain the loss of any portion of this water without assuming a new train of properties. There are accordingly three atoms oxygen in the base (two in the water, and one in the base), and five in the acid. When crystallized the salt contains, besides, two atoms water of crystallization.

The crystals of biphosphate of potash contain only the two essential atoms of water, and the lustre of their surfaces is not affected by a water-bath heat, nor by any degree of heat under 400° Fahr.

A solution of either of these alkaline biphosphates, when added to nitrate of silver, occasions a copious precipitation of the yellow subphosphate of silver; and if ammonia be cautiously added, so as merely to make up the excess of nitric acid disengaged, the whole phosphoric acid falls in that state. It is to be here remarked, that the three atoms base of the alkaline biphosphate are replaced in this precipitation by three atoms of oxide of silver.

## 2. *Second variety of Biphosphate of Soda, or Bipyrophosphate of Soda.*

When a quantity of the biphosphate of soda, previously dried on the water-bath, is afterwards gradually heated on a solder-bath, it begins to lose water at about 375°, and before it is raised to 400° it has lost exactly half the water which it possessed, or one atom. The dried salt may thereafter be heated up to 450°, and maintained for an hour or more at that temperature, without sustaining any further loss. When rapidly heated in a glass tube, the salt undergoes semifusion at some point near 400°, and the same quantity of water comes off in a state of ebullition.



1st. Thus 2.62 grains of the salt dried on the water-bath, when heated in a thin glass tube, lost at once 0.2 grain water on attaining  $400^{\circ}$ , which is one-half of the water which it possessed, namely, 0.396 grain; while it was exposed again for four hours to a temperature between  $450^{\circ}$  and  $470^{\circ}$ , without losing 0.01 grain additional.

2d. In one experiment, 18.45 grains of the crystallized biphosphate lost 3.68 grains by  $400^{\circ}$  Fahr. on the solder-bath. This is 27.04 of the 35.57 parts water, which are united to 100 dry salt in the crystals. The salt has lost 3.04 atoms of water.

3d. A quantity of the salt, previously deprived of its two atoms water of crystallization, was kept for three hours at a temperature ranging between  $400^{\circ}$  and  $460^{\circ}$ . 11.19 grains of the salt so dried contained 0.9 water, or consisted of

Biphosphate of soda,	.	.	100
Water,	.	.	8.72
			<hr/> 108.72

The water retained amounts to 0.981 atom, which is a close approximation to 1 atom.

4th. A quantity of the salt which had been heated to  $400^{\circ}$  was dissolved in water, evaporated to dryness, and exposed again for some days on a solder-bath at a temperature not exceeding  $400^{\circ}$ . 13.94 grains of the salt so dried still retained 1.06 grain water, as was found by fusing the salt at a red heat; or it consisted of

Biphosphate of soda,	.	.	100
Water,	.	.	8.23
			<hr/> 108.23

This is less than one atomic proportion, which is 8.89 parts; but the temperature at which the salt loses its entire water is elevated no great number of degrees above that in which it loses the atom under consideration; and a protracted exposure to the air at  $400^{\circ}$  occasions the partial dissipation of the last atomic proportion of water, as in this experiment.

The heated salt which retains one atom water, is still very soluble and possesses an acid reaction, but it is altered essentially in properties. Added to nitrate of silver, it produces a sparing chalky white, pulverulent precipitate, and a very acid liquor. By the cautious addition of ammonia so as merely to take up the excess of nitric acid, the entire phosphoric acid is precipitated in the same state. The precipitate proved, on analysis, to be the pyrophosphate of silver, containing two atoms oxide of silver to one double atom phosphoric acid.

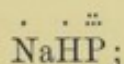


Of this precipitate, heated to redness but not fused, 18.75 grains dissolved in nitric acid and precipitated by muriatic acid, afforded 17.82 grains chloride of silver, equivalent to 14.41 oxide of silver. The composition of this phosphate and of the pyrophosphate of silver, with which it appears to correspond, is as follows:—

	Experiment.	Theory.
Oxide of silver, .	76.85	76.49
Phosphoric acid, .	23.15	23.51
	<hr/> 100	<hr/> 100

Added to acetate of lead, this altered biphosphate likewise threw down the pyrophosphate of lead. The acid of this last salt was separated by sulphuretted hydrogen, and when afterwards neutralized by carbonate of soda, it afforded crystals of pyrophosphate of soda.

Now this variety of the biphosphate of soda, which may be called the bipyrophosphate, contains one atom of basic water, and its formula is,



or it contains two atoms base like the salt of silver which it precipitates. This salt when treated with caustic soda affords the neutral pyrophosphate. It also occasions a precipitate in muriate of barytes, in which respect it differs from the proper biphosphate. I failed in all my attempts to obtain the bipyrophosphate of soda in a crystalline form. It uniformly dried up into the state of a friable white crust.

### 3. *Third variety of the Biphosphate of Soda.*

When the salt last described was exposed on the solder-bath for several days at a temperature between 400° and 470°, it lost weight; only 3.48 parts out of the entire 35.57 water were retained in one experiment, and 2.81 parts water in another. The whole water was expelled, with the exception of 0.38 to 100 dry salt, in other experiments in which the salt was heated on the sand-bath, probably at a temperature not much under 600°. The salt became in fact very nearly anhydrous. Now on pouring water upon the salt so dried, the greater part of it dissolved at once, but an inconstant quantity remained undissolved, varying from 6.57 to 18 parts in 100 salt, but increasing with the intensity of the heat to which the salt had been exposed. This insoluble matter is a fourth variety of the biphosphate, which shall immediately be noticed. As this insoluble salt may be proved to be of the same composition as the biphosphate, it follows that the soluble portion is unaltered in composition.

The insoluble portion appears a heavy dense powder; yet as a part



of it remains in suspension in the liquid for a long time, it is necessary to filter to obtain the soluble salt in a state of purity.

The preceding two varieties of biphosphate of soda have a distinct acid reaction, but the solution of this salt is exactly neutral, as was determined by very careful experiments. This property is the best distinctive character of this variety that I can mention. When a solution of the salt is concentrated, it does not deposit any of the insoluble variety, but allows rings of dry salt to form round the margin of the fluid, which are soluble. I have not succeeded in crystallizing it in the vacuum of an air-pump, or by other means which were employed. The salt always dried up into a friable white crust, which on one occasion, when dried at  $212^{\circ}$ , contained 11.56 parts water to 100 anhydrous salt. This salt occasions a precipitate in muriate of barytes like the preceding. With nitrate of silver it gives a considerable white pulverulent precipitate, and the liquid becomes strongly acid. 8.38 grains of this precipitate dried and heated to redness without fusing, were found to consist of 6.58 oxide of silver and 1.8 phosphoric acid, or 77.32 oxide of silver and 22.68 phosphoric acid = 100; while the neutral pyrophosphate of silver, containing two atoms oxide of silver, consists of 76.49 oxide of silver, and 23.51 phosphoric acid. The correspondence is sufficiently close to prove that our silver precipitate is the same neutral phosphate which presents itself when the second variety of biphosphate of soda is precipitated in the same manner. Like that variety, also, this form of the biphosphate afforded crystals of the pyrophosphate of soda when treated with caustic soda.

In regard to the exact constitution of this variety I entertain considerable doubt. We are warranted to presume that the biphosphate of soda can exist in an anhydrous condition soluble in water, and neutral in its reaction on litmus. The formula of the salt may be,



It must, however, be allowed that no confirmation of this view of the constitution of the salt can be drawn from the composition of the silver precipitate. But the precipitate that should fall by theory, is the biphosphate of silver. Now no such salt exists, the biphosphate of silver described by Berzelius containing the new modification of phosphoric acid.

#### 4. *Fourth or insoluble variety of Biphosphate of Soda.*

When any of the preceding varieties of the biphosphate of soda is heated for a few minutes at a temperature approaching but not amounting to low redness, it becomes anhydrous, if not so before, and the whole of



it becomes insoluble in water. We are apt to overheat the salt in a crucible if a lamp be employed. I found it the most convenient process to introduce a quantity of the crystallized biphosphate into a platinum crucible, to place this in sand contained in a Hessian crucible, and to place the whole in a situation in an open fire where it would not be heated with rapidity. The time was watched when the sand was red hot to within a small space of the platinum crucible, and the whole then withdrawn from the fire. The appearance of the heated salt depends entirely upon circumstances. If the heat be applied rapidly, the salt undergoes fusion on losing its two essential atoms of water, and is found of a slaggy appearance and hard. But if the heat be applied in a gradual manner, the water escapes without any fusion, the powder merely shrinks and aggregates slightly together. In both states the resulting salt is the same. It may be reduced with ease to the most impalpable powder, and in this condition is very slowly acted upon by continued digestion in a large quantity of boiling water. When it does dissolve, it appears to pass into the preceding variety. But it may be inferred analogically, that if a more intense heat could be applied to the salt under consideration without inducing another change (to be described) the salt would be rendered perfectly insoluble. The biphosphate of potash affords this analogy.

This last salt contains only the two essential atoms of water. When heated above  $400^{\circ}$ , it begins to undergo a semifusion, although the heat has been applied in a gradual manner; and becomes partially insoluble, without exhibiting the changes which precede this in the biphosphate of soda. A still higher temperature, approaching a red heat, renders the biphosphate of potash as insoluble as the biphosphate of soda. But the biphosphate of potash may be fused in a platinum crucible and heated to whiteness without undergoing any further change of state; and after being thus strongly heated, it may be reduced to powder and digested in boiling water for hours without dissolving to such an extent as to afford a solution capable of affecting nitrate of silver in a sensible manner. It may be inferred, therefore, that if the biphosphate of soda could be sufficiently heated, water would be wholly incapable of acting upon it. Dilute acids have no action upon this insoluble variety of biphosphate of soda; but alkalies by long digestion withdraw a portion of the phosphoric acid. So far as we can judge, the acid appears not to be in a modified or altered condition.

##### 5. *Fifth variety of Biphosphate of Soda, or Metaphosphate of Soda.*

When the preceding insoluble variety, or the biphosphate in any condition, is heated in a platinum crucible to low redness, it undergoes



fusion, and on cooling presents itself as a transparent glass, which deliquesces in a damp atmosphere and is highly soluble in water. But the fused salt has undergone a most extraordinary and permanent change of properties. The solution has a very feeble acid reaction when compared with crystallized biphosphate. Indeed, the addition of 4.3 anhydrous carbonate of soda to one hundred fused biphosphate of soda imparted to the latter a distinct alkaline reaction. When this salt is added to nitrate of silver, the phosphoric acid is nearly entirely thrown down in gelatinous flakes, which aggregate together as a soft solid when heated near  $212^{\circ}$ , and correspond in composition with the soda salt. This silver precipitate loses acid when washed. It agrees in properties with the biphosphate of silver described by Berzelius, which, when washed, appeared to pass into a sesquiphosphate. He formed it by adding phosphoric acid to nitrate of silver, but the phosphoric acid employed by him must have been the glacial acid recently dissolved.<sup>1</sup>

When the fused biphosphate of soda is added to muriate of barytes, nearly the whole of the phosphoric acid precipitates with the barytes as a flaky gelatinous precipitate, which contains only one atom barytes to the double atom phosphoric acid, like the soda salt. But all the new properties of this salt depend upon the acid having undergone an essential change in constitution. The acid may be separated in the usual way, namely, precipitating by acetate of lead, washing the phosphate of lead and decomposing it by a stream of sulphuretted hydrogen gas. After exposure for some hours to allow the escape of the sulphuretted hydrogen, the acid liquid, without being neutralized, uniformly produced an opal-white flaky precipitate in muriate of barytes, which appeared immediately, unless the liquors were very dilute. This is also a character, I find, of phosphoric acid recently ignited *per se*. The acid of our salt possesses also the property of coagulating albumen. In fact, this acid appears to be the glacial phosphoric acid, which had been hastily assumed by recent writers upon this subject to be the pyrophosphoric acid, but is totally different. I shall take the liberty to designate provisionally the acid of the fused biphosphate of soda, the Metaphosphoric acid, from an hypothesis of its constitution to be immediately explained; and the fused salt itself, the Metaphosphate of soda.

The metaphosphate of soda is insoluble in alcohol. Its solution in water is not altered by time; at least no change could be perceived in a solution which had been kept for several months. When exposed to a temperature not exceeding  $100^{\circ}$  Fahr., the solution becomes viscid as it concentrates, and finally dries into a transparent brittle pellicle like gum. All my attempts to crystallize this salt by slow evaporation in the atmosphere, or by means of the air-pump, have failed. It never

<sup>1</sup> *Annales de Chimie et de Physique*, tom. xlv. p. 143.



presented the slightest trace of crystallization. But many of the insoluble metaphosphates fall down in the state of hydrates, which have the fluid form; which may also be the form that the soda salt is disposed to assume.

The hydrated metaphosphate of soda dried over sulphuric acid in the vacuum of an air-pump, at the ordinary temperature of the atmosphere, was found to consist of

Metaphosphate of soda, . . . . .	100
Water, . . . . .	10.86,

by an experiment in which 11.64 grains of the hydrated salt lost 1.14 by fusion at a red heat. This is 1.22 atomic proportion of water.

When heated to  $400^{\circ}$ , the hydrated salt appears to retain 1 atom of water, and to pass into the bipyrophosphate of soda. 13.94 grains dried on the solder-bath at  $400^{\circ}$  for several days, retained 1.06 water; or the salt consisted of

Biphosphate of soda, . . . . .	100
Water, . . . . .	8.23
	<hr/>
	108.23

This is less than one proportion of water (8.89); but the additional loss of water which the salt sustained is accounted for by the length of time that it was exposed to the heat, which had the effect of converting a small portion of it into the insoluble and anhydrous variety. The dried salt when dissolved in water gave with nitrate of silver a chalky, white, heavy precipitate, which evidently was not the usual metaphosphate of silver. A portion of the salt was therefore precipitated by acetate of silver, and the acid liberated in the usual manner. The acid did not disturb albumen, nor precipitate muriate of barytes; but when neutralized with caustic soda it gave excellent crystals of the pyrophosphate of soda. There can be no doubt, therefore, that the metaphosphoric acid has returned to the condition of pyrophosphoric acid. The question arises, Is this transition the consequence of merely exposing the metaphosphate of soda to a particular temperature ( $400^{\circ}$ ), or does the water interfere and the transition arise from the affinity of phosphoric acid for water, as a base, with soda? Now, upon trial, the anhydrous fused metaphosphate of soda, as it is first formed, was found to undergo no alteration when kept for several days between  $400^{\circ}$  and  $600^{\circ}$ . The change is therefore peculiar to the hydrated salt, and effected by the interference of the water.

A solution of the metaphosphate of soda may be treated with caustic soda, and even boiled with it, without any change in the nature of the



acid; at least, the saline solution still precipitates silver white, and the acid when separated coagulates albumen. The solution may even be evaporated gently to dryness, without a change of acid; but if dried by a sharp sand-bath heat, and if the alkali be present in sufficient quantity, the common subphosphate of soda is formed.

The metaphosphate of soda forms a series of insoluble metaphosphates when added to solutions of the earthy and metallic salts.

*Metaphosphate of Barytes.*

The metaphosphate of barytes has already been alluded to. As this salt is soluble in an excess of the metaphosphate of soda, it is best prepared by adding that salt to muriate of barytes in excess. There is an abundant, white, flaky precipitate, and the mother-liquor remains acid. This precipitate washed and dried at 600° Fahr. formed brittle masses; these masses heated to redness give off water and undergo an imperfect fusion. 11·86 grains of the ignited salt were dissolved with considerable difficulty by pure nitric acid, and then precipitated by sulphate of soda. The sulphate of barytes amounted to 9·69 grains, which is equivalent to 6·36 grains barytes. The composition of this metaphosphate, and of a biphosphate of barytes, is as follows:

	Metaphosphate of Barytes.	Biphosphate of Barytes.
Barytes, . . . . .	53·62 . . . . .	51·75
Phosphoric acid, . . . . .	46·38 . . . . .	48·25
	<hr/> 100·	<hr/> 100·

Our salt is therefore 1·87 per cent. deficient in phosphoric acid. I thought that muriate of barytes had perhaps been carried down by the precipitate, but on examining a portion I found it free of muriatic acid.

But another quantity of the metaphosphate of barytes was prepared, with the precaution of having a more decided excess of muriate of barytes, and the liquors less dilute. 6·61 grains of the ignited salt yielded 5·24 grains sulphate of barytes, which is equivalent to 3·44 grains barytes. This specimen therefore consisted of

Barytes, . . . . .	52·04
Metaphosphoric acid, . . . . .	47·96
	<hr/> 100·

which will be found on comparison to correspond very closely with the biphosphate of barytes.

The metaphosphates in general precipitate with considerable difficulty from very dilute solutions, although when once precipitated they



are highly insoluble. The last washings of the metaphosphate of barytes, hot water being employed, contained no sensible trace of barytes, for they had no effect upon a sulphate. Hence the metaphosphate of barytes is an insoluble salt.

The metaphosphate of barytes may be boiled in water for two hours without sensible change; but it then begins to dissolve, and the solution proceeds at an accelerated rate, till eventually the whole disappears. The resulting solution is strongly acid, and certainly contains biphosphate of barytes, for it precipitates silver yellow. We have here, therefore, an instance of an insoluble metaphosphate passing into a soluble phosphate.

#### *Metaphosphate of Lime.*

On adding metaphosphate of soda to muriate of lime in excess, a precipitate appears like what occurs on throwing into water a solution of an essential oil in alcohol. A transparent semi-fluid body of the consistency of pitch collects at the bottom, which is a hydrate of the metaphosphate of lime in the liquid form, but insoluble in water. This salt appears to have occurred to Berzelius, and is described in his paper on the phosphates.<sup>1</sup> He formed it by precipitating muriate of lime by metaphosphoric acid, but did not observe the circumstances necessary to insure the success of the process.

### IV. OF THE MODIFICATIONS OF PHOSPHORIC ACID.

The distinctive character of phosphoric acid which exists in common phosphate of soda, as compared with the other modifications, is a disposition to form salts which contain three atoms of base to the double atom of acid. Of these salts the most remarkable is the yellow subphosphate of silver, which the soluble phosphates precipitate when added to nitrate of silver. This acid does not affect albumen; and the other modifications pass directly into the condition of this acid on keeping their aqueous solutions for some days, and more rapidly on boiling these solutions; or upon fusing the other modifications or their salts with at least three proportions of fixed base.

Pyrophosphoric acid, or the acid which exists in the fused phosphate of soda, is remarkably disposed to form salts having two atoms base, which is the constitution of the white pyrophosphate of silver, formed on testing the pyrophosphate of soda with a salt of silver. Such salts of the preceding acid as contain no more than two atoms of fixed base, pass into pyrophosphates when heated to redness. The acid under con-

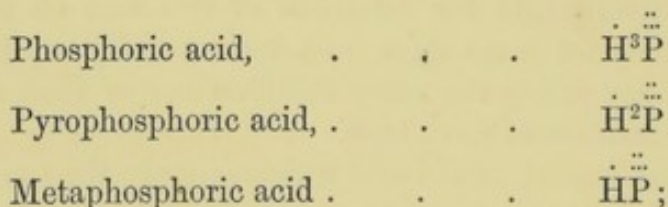
<sup>1</sup> *Annales de Chimie et de Physique*, tom. ii. p. 172.



sideration, when free, does not disturb albumen, nor produce a precipitate in muriate of barytes.

The metaphosphoric acid is disposed to form salts which contain one atom of base to the double atom of acid. The other modifications pass into metaphosphoric acid when heated to redness *per se*, or when heated to redness in contact with no more than one atomic proportion of certain fixed bases, such as soda. This acid, when free, occasions precipitates in solutions of the salts of barytes and of most of the other earths and metallic oxides, and forms an insoluble compound with albumen. The glacial or metaphosphoric acid appears to be capable of dissolving in general only about four-fifths of the quantity of carbonate of soda which it can decompose when converted into phosphoric acid. But a large quantity of the meta-acid passes into phosphoric acid on uniting with the alkali, and the solution deposits phosphate of soda in tufts composed of fine crystalline plates of a silky lustre. The salt presented itself of this appearance, it will be remembered, in the case of a solution of phosphate of soda which had been boiled for a long time in a glass vessel. The liquid about the crystals, in the present case, still contained metaphosphoric acid.

Now it is a matter of certainty that if we take one combining proportion of any modification of phosphoric acid, and fuse it with soda or its carbonate, we shall form a metaphosphate, a pyrophosphate, or a phosphate, according as we employ one, two, or three proportions of base. The acid when separated from the base will possess, and retain for some time, the characters of its peculiar modification. It would appear, therefore, that the acid is impressed with a disposition to form different classes of salts by the proportion of base to which it has been united, and that it retains this disposition even when liberated from the original compound. But I suspect that the modifications of phosphoric acid, when in what we would call a free state, are still in combination with their usual proportion of base, and that that base is water. Thus the three modifications of phosphoric acid may be composed as follows :



or they are respectively a terphosphate, a biphosphate, and phosphate of water. Now, when one of these compounds is treated with a strong base, the whole or a part of the water is supplanted, *but the amount of base in combination with the acid remains unaltered*. There are thus three sets of phosphates, in which the oxygen in the acid being five, the



oxygen in the base is three, two, and one. The constitution of the acids and of the salts of soda which they form, is exhibited in the following Table :

		Oxygen in		
		Soda.	Water.	Acid.
<i>First Class.</i>	{ Phosphoric acid, . . .	0	3	5
	{ Biphosphate of soda, . .	1	2	5
	{ Phosphate of soda, . . .	2	1	5
	{ Subphosphate of soda, . .	3	0	5
<i>Second Class.</i>	{ Pyrophosphoric acid, . .	0	2	5
	{ Bipyrophosphate of soda, .	1	1	5
	{ Pyrophosphate of soda, . .	2	0	5
<i>Third Class.</i>	{ Metaphosphoric acid, . .	0	1	5
	{ Metaphosphate of soda, . .	1	0	5

The hypothetic composition of the acid hydrates may also be stated as follows :

	Acid.	Water.
Phosphoric acid, . . .	100	37·81 = 3 atoms.
Pyrophosphoric acid, . .	100	25·21 = 2 „
Metaphosphoric acid, . .	100	12·61 = 1 atom.

By a heat of  $300^{\circ}$  a dilute solution of phosphoric acid in a platinum crucible concentrates readily till the water is reduced to the proportion of three atoms, at which stage the acid assumes a dark colour, and is of the consistence of treacle when cold, but much more fluid when hot. In this condition the acid gives an unmixed yellow precipitate with silver, and is entirely phosphoric acid. By exposure for seven days over sulphuric acid in the vacuum of an air-pump, the water was reduced to 43·5 parts, and almost the whole of the acid had crystallized in thin plates, which were deliquescent in the extreme, and which there is every reason to believe were the terhydrate. By a protracted exposure to  $300^{\circ}$  or  $320^{\circ}$ , the acid continues to lose water, but much more slowly. At  $460^{\circ}$  the water was quickly reduced to 34·4 parts, or little more than  $2\frac{2}{3}$  atoms, in an experiment conducted in an open crucible, and the acid now precipitated silver white with a trace of yellow; but when neutralized by carbonate of soda, it afforded crystalline plates of phosphate of soda, among which no crystals of pyrophosphate existed. But it may be deemed possible from this result that a hydrate of phosphoric acid exists, containing  $2\frac{2}{3}$  atoms water to 1 atom acid, which is 8 atoms base to 3 atoms acid, the proportion of base to acid in the salt termed by Berzelius, the phosphate of lime of bones. In another case in which the evaporation was conducted much more slowly in a platinum flask, the above compound was certainly not formed; but the evaporation at  $415^{\circ}$ , after



advancing for several days, seemed to cease entirely when the water was reduced to 29.9 parts, which is very nearly  $2\frac{1}{3}$  atoms of water. Acid at this degree of concentration, neutralized as usual by ammonia, gave, with silver, a chalky white precipitate without a shade of yellow, which suggests the idea that an acid hydrate of  $2\frac{1}{3}$  water may exist, having a corresponding silver salt. Acid, so far concentrated, when neutralized by carbonate of soda, afforded a mixture of crystals of phosphate and pyrophosphate of soda, in which the latter predominated. For the production of metaphosphoric acid, the concentration of a much higher temperature was requisite; but this acid was observed to appear before the proportion of water had fallen under 2 atoms, namely, when it amounted to 28.05 per cent. in one experiment. By the greatest heat of the sand-bath, which was considerably above the melting point of lead, the proportion of water was reduced a little under 2 atoms, namely, to 22.99 parts; and the acid then contained abundance of metaphosphoric acid, as evinced by its power to coagulate albumen. In the glacial phosphoric acid, Dulong found 100 acid united with 20.6 water, and Rose 100 acid with only 10.42 water. The latter determination falls short of 1 atom water, and would indicate that phosphoric acid may be rendered partially anhydrous by heat. I do not enter upon the details of my experiments on the hydrates of phosphoric acid, as the subject is difficult, and requires a much more minute investigation than I have as yet had it in my power to give it.

Although of opinion that there is only one phosphoric acid, and that the modifications are entirely due to the quantity of water combined with the acid, I have still retained the names which have come into use, and even proposed a third, *metaphosphoric acid*, implying merely that the acid to which this name is applied is phosphoric acid with something else, namely, with an atom of water. As the classes of salts which the acid hydrates form are quite distinct, these trivial names are practically convenient, and may be adopted provisionally till chemists are prepared, by an extended knowledge of the salts, to innovate upon their nomenclature with more advantage than can be done at present.

I may be allowed to state, before concluding, that the binarseniate of soda does not appear to undergo the same remarkable changes as the biphosphate; at least, after being exposed to heat of various degrees of intensity, it continued to give the usual brown subarseniate, with nitrate of silver. But arsenic acid exhibits a weaker affinity for water than phosphoric acid, and is readily made anhydrous by heat.



## IV.

ON HYDRATED SALTS AND METALLIC PEROXIDES; WITH  
OBSERVATIONS ON THE DOCTRINE OF ISOMERISM.

From *Brit. Assoc. Report*, 1834, pp. 579-582. [Liebig, *Annal.* xii. 1834, pp. 1-12 ;  
Poggend. *Annal.* xxxii. 1834, pp. 33-75.]

VARIOUS classes of salts, besides the arseniates and phosphates, contain water, which is essential to their constitution : of this the sulphates of magnesia, and the protoxides of zinc, manganese, iron, nickel, copper, and cobalt, are examples.

These salts crystallize from their aqueous solutions, either with seven or five atoms of water, one of which is in a state of much more intimate union than the other six or four. Thus, crystallized sulphate of zinc loses six atoms of water, at a temperature not exceeding  $65^{\circ}$ , when placed over sulphuric acid *in vacuo*, but retains one atom of water at  $410^{\circ}$  and all inferior temperatures. This salt may be viewed as a sulphate of oxide of zinc and water, with six atoms of water of crystallization ; a constitution which may be expressed as follows,  $\dot{H}\dot{Zn}\ddot{S} + 6\dot{H}$ . This sulphate may be made anhydrous, but when moistened always regains one atom of water, slaking with the evolution of heat. This last atom of water appears to discharge a basic function in the constitution of the salt, and affords a clew to the disposition of this sulphate to form double sulphates. Sulphate of zinc combines with sulphate of potash, and forms a well-known double salt, in which the basic water of the sulphate of zinc is replaced by sulphate of potash, without any further change. The formula of the double sulphate is  $(\dot{K}\ddot{S})\dot{Zn}\ddot{S} + 6\dot{H}$ . In the double salt, the whole six atoms of water are retained with somewhat greater force than in the simple sulphate ; but even the double sulphate becomes anhydrous below  $212^{\circ}$  *in vacuo*.

The sulphates of the other metallic oxides mentioned are quite analogous to sulphate of zinc in their habitudes with water, although the particular temperature at which they part with their water of crystallization is different in each. The analogy holds also in the double sulphates of those oxides.

Of hydrous sulphate of lime, or gypsum, the two atoms of water which it contains appear to be essential, and are retained at  $212^{\circ}$ . At a temperature not exceeding  $270^{\circ}$ , this salt becomes anhydrous, but retains the power of recombining with two atoms of water, or setting. The salt is then in a peculiar condition. It is the *débris* of the hydrate,



and not a neat chemical compound. Heated above  $300^{\circ}$  the salt becomes properly sulphate of lime, and has lost the disposition to combine with water.

The protochlorides, and corresponding cyanides of zinc, manganese, iron, etc., are disposed to combine with two atoms of water. Hence the cyanide of iron combines with *two* atoms of cyanide of potassium, to form the double cyanide of iron and potassium, commonly called the ferro-prussiate of potash.

Berzelius found the peroxide of tin formed by the action of nitric acid on metallic tin, to differ in certain properties from the same compound precipitated from a persalt of tin by an alkali, and distinguished the first under the name of the nitric acid peroxide of tin. Both peroxides combine with muriatic acid, but the muriate of the nitric acid peroxide is peculiar in being insoluble in water strongly acidulated with muriatic acid. But the precipitated peroxide of tin assumes, I find, all the properties of the other modification, when kept for some time exposed to the heat of boiling water, or even when strongly dried over sulphuric acid *in vacuo*, at the ordinary temperature of the atmosphere. The two modifications are merely different hydrates of the peroxide of tin, but it is difficult to ascertain what proportion of water is essential to each. The hydrates combine with acids, and form two sets of compounds; but absolute peroxide of tin itself (which is obtained by heating the hydrated peroxide to redness), has no disposition to combine with acids. The same is true of many other metallic peroxides; they combine as hydrates only with acids. There are at least two hydrates of peroxide of iron: the muriate of that which contains least water is red in solution, and the muriate of the other, yellow; but these muriates pass readily into each other. Mr. R. Phillips observed of the red muriate, that it is precipitated by an access of acid, which, it may be remarked, establishes an analogy between it and the muriate of the nitric acid peroxide of tin, which possesses the same property.

Metallic peroxides can in general be obtained by the application of a moderate heat to their hydrates, in a state in which they are the débris of hydrates, and not neat chemical compounds. Upon heating peroxides in this condition to redness, they generally glow or become spontaneously incandescent at a particular temperature (a phenomenon to which the attention of chemists has been particularly directed by Berzelius), and lose their solubility in acids at the same time. Till they have undergone this change, they are not absolute or proper peroxides. Various salts, such as phosphates, antimonates, etc., exhibit the same phenomenon when heated; but they all had possessed water, which is essential to their first constitution, but not to their second.

The doctrine of isomerism, or that two bodies may exist of the same



composition, but differing in properties, has been proposed by Berzelius as a sequence from such facts as the preceding. But the propriety of the inference may be doubted. Most, if not all, cases of apparent isomerism may be explained by reference to one or other of the following facts :—

1. Water is essential to the constitution of many bodies. Thus, what have been called metaphosphoric acid, pyrophosphoric acid, and common phosphoric acid, are three different phosphates of water, or compounds of one absolute phosphoric acid with three different proportions of water.

2. A particular condition of bodies must be recognised, in which they are the débris of some compound, and not proper chemical compounds of their constituents. Thus, on heating a certain borate of water and magnesia to redness, water only is expelled; but what remains is not a simple borate of magnesia, but a mixture of boracic acid and magnesia, from which the former may be dissolved out by water. Stucco in a state for setting is in this particular condition. But this is a department of corpuscular philosophy which stands much in want of further development.

3. The proximate constitution of many bodies may be widely different, of which the ultimate composition is the same. Thus the cyanic acid of Wöhler is undoubtedly an oxide of cyanogen, but we have no evidence that cyanogen exists in fulminic acid, which consists of the same proportions of carbon, nitrogen, and oxygen as cyanic acid. It is wrong, therefore, to speak of the fulminic as a second cyanic acid, and useless to couple them together as isomeric bodies. Tartaric and racemic acids are of the same ultimate composition, but they certainly contain different radicals, and probably have as little natural relation to each other as any two vegetable acids which could be named. Why, then, associate them as isomeric bodies, and call them the tartaric and paratartaric acids?

4. A minute trace of adventitious matter may sometimes affect the properties of a chemical body to a surprising degree.

Professor Rose, of Berlin, has shown that the two kinds of phosphuretted hydrogen, one of which is spontaneously inflammable in air, and the other not so, are of the same composition and specific gravity. To account for their possessing different properties, recourse is had to the doctrine of isomerism. But my observations indicate the existence of a *peculiar principle* in the spontaneously inflammable species, which principle may be withdrawn, and leaves the gas not spontaneously inflammable. Phosphuretted hydrogen gas, which is not spontaneously inflammable in air, may be made so, by the addition to it of one ten-thousandth part of its volume of nitrous acid vapour. There are grounds



for supposing that the peculiar principle of the ordinary gas is a volatile oxide of phosphorus analogous to nitrous acid, and that it is present in a minute, almost infinitesimal, proportion. Subsequently to the meeting of the Association, an account of the author's researches on phosphuretted hydrogen has been published in the number for December 1834, of the *London and Edinburgh Journal of Science*.

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V.

ON WATER AS A CONSTITUENT OF SALTS.

From *Edin. Roy. Soc. Trans.* xiii. 1836, pp. 297-314. [*Phil. Mag.* vi. 1835, pp. 327-334, 417-424; *Annal. de Chimie*, lxiii. 1836, pp. 45-64; *Edm. Journ. Prak. Chem.* v. 1835, pp. 90-109; xv. 1838, pp. 437-439; Liebig, *Annal.* xx. 1836, pp. 141-149; Poggend. *Annal.* xxxviii. 1836, pp. 123-142.]

It may be useful to distinguish some of the functions which water is already admitted to discharge in the constitution of hydrated salts.

Every amphigene ammoniacal salt contains an atom of water, and cannot exist without it. The state of combination of the water is peculiar, and has been represented by supposing that the elements of ammonia unite with the hydrogen of the water, and form a new compound radicle, to which the name Ammonium is given, while the oxygen of the water unites with this radicle, and produces oxide of ammonium. Hence nitrate of ammonia, in which there exist the elements of one atom of nitric acid, of ammonia, and of water, is viewed as anhydrous nitrate of the oxide of ammonium, and corresponds with nitre or the nitrate of the oxide of potassium. But it is not the object of this paper to discuss particularly the state of water in the ammoniacal salts.

We have it often in the crystals of salts, united by a feeble affinity, and known under the name of water of crystallization. The number of atoms of water with which some salts unite, in crystallizing from a state of solution, is affected by temperature, and other slight causes. This water is commonly viewed as a constituent of salts which is not essential, owing to the facility with which it may in general be expelled by heat, and also to the circumstance that many salts usually hydrated are likewise capable of existing in a crystalline state without water.

In the hydrates of the caustic alkalies and of the earths, water is retained by a strong affinity, and is generally supposed to be united, like an acid, to the alkali or earth. In such hydrates, water discharges an *acid* function.



In the case of hydrates of the acids, the portion of water which is found to be inseparable by heat, or to be very strongly retained, has generally been presumed to be in the place of a base to the acid, although little attention has been paid to the subject. The most highly concentrated sulphuric acid retains one atom of water, and is supposed to be a sulphate of water. In the case, too, of such a supersalt as bisulphate of potash or bitartrate of potash, the single atom of water which is known to be persistently attached to the salt, has been viewed of late, by our most enlightened chemical theorists, as essential to its constitution, and the possibility admitted that such salts may really be *double salts*; the bisulphate of potash, a sulphate of potash combined with sulphate of water, and the bitartrate of potash, a tartrate of potash combined with tartrate of water.

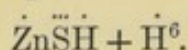
In a late publication, I have developed this view of water acting as a base in the case of phosphoric acid. That acid is capable of combining with water in three different proportions; and the number of atoms of water with which the acid combines at any time depends upon circumstances which are understood. That the water is basic in these different hydrates, follows from the fact that, on treating them with an alkali, the water is constantly replaced by a quantity of alkali chemically equivalent to the water. By nitrate of silver, the same precipitate is thrown down from any phosphate of soda and from the corresponding phosphate of water; the composition of the precipitate being determined in both cases by the same double decomposition. The peculiarity of phosphoric acid is, that it is capable of uniting with water as a base, in several proportions, while all other acids combine with water as a base in one proportion only, so far as is yet known. By these discoveries in regard to phosphoric acid and its salts, the ordinary conceptions entertained of the constitution of salts were completely deranged. The salts called biphosphate of soda, phosphate of soda, and subphosphate of soda, are all tribasic salts. The common idea of a supersalt is inapplicable to any of them.

I have subsequently found water to exist in a different state in certain salts, not possessed of a true basic function, being replaceable by a *salt*, and not by an alkaline base. To illustrate this new function of water as a constituent of salts is my principal object in the present communication.

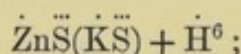
The tendency of phosphate of soda to unite with an additional dose of soda, and form a subsalt, I had traced to the existence of basic water in the former. The inquiry suggested itself, is there any analogous provision in the constitution of such salts as have a tendency to combine with other salts, and to form double salts? The salts which combine together most readily are the sulphates, and to these I therefore turned.



The result was, that in that well-known class of sulphates, consisting of sulphates of magnesia, zinc, iron, manganese, copper, nickel, and cobalt, all of which crystallize with either five or seven atoms of water, one atom proved to be much more strongly united to the salt than the other four or six, which last generally may be expelled by a heat under the boiling point of water, while the remaining atom uniformly requires a heat above 400° Fahrenheit for its expulsion, and seems to be in a manner essential to the salt. The constitution of crystallized sulphate of zinc, for instance, may be expressed thus :

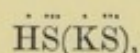


We here divide the seven atoms of water into one atom, which is essential to the constitution of the salt as we know it, and six atoms which are not so ; and to this last quantity we may restrict the application of the name "water of crystallization." Now, in the double sulphate of zinc and potash, the single atom of water in question pertaining to the sulphate of zinc is replaced by an atom of sulphate of potash, and the six atoms of water of crystallization remain. Sulphate of magnesia combines with sulphate of potash after the same manner, and so do all the other salts of the class. The constitution of the crystallized sulphate of zinc and potash, which may be taken as the type of this family of double salts, is therefore represented by the following formula,

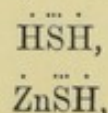


which differs only from the previous formula in having the sign of sulphate of potash (K $\ddot{\text{S}}$ ) substituted for the sign (H) of the essential atom of water.

From a contemporaneous examination of the supersulphates, the conclusion proved to be inevitable, that they also are double salts ; that the bisulphate of potash, for instance, is a sulphate of water and potash, and that its formula is as follows,



with or without water of crystallization in addition. There is likewise a provision in the constitution of hydrated sulphuric acid for the production of such a double salt, as in the case of the sulphate of zinc. Hydrated sulphuric acid of specific gravity 1.78 contains two atoms of water, and is capable of crystallizing at a temperature so high as 40° Fahrenheit. It is the only known crystallizable hydrate of sulphuric acid. It may be represented by the formula,





which may be compared with that of sulphate of zinc placed below it. This second atom of water present in hydrated sulphuric acid is replaceable by sulphate of potash, a salt; and the bisulphate of potash results from the substitution. But the first atom of water in the acid hydrate can be replaced only by an alkali or true base. The function of the first atom is *basic*, but a new term is required to distinguish the function of the second atom of water, or of the essential atom of water in the sulphate of zinc. The application of the epithet *saline* to that atom of water, may, perhaps, be permitted, to indicate that it stands in the place of a salt. The hydrate of sulphuric acid in question contains, therefore, an atom of basic, and an atom of saline water. It is "a sulphate of water with saline water," as the hydrous sulphate of zinc is "a sulphate of zinc with saline water." The bisulphate of potash also is "a sulphate of water with sulphate of potash," and corresponds with the sulphate of zinc and potash; which last is "a sulphate of zinc with sulphate of potash."

A reason could now be given why there exist no supersulphates (or indeed any supersalts) of magnesia, zinc, etc. A bisulphate of magnesia would be a compound of sulphate of water with sulphate of magnesia, on our view of supersulphates. Now sulphate of magnesia, and sulphate of water, are bodies of analogous constitution, or of the same category, and should have as little disposition to combine together, as sulphate of zinc and sulphate of magnesia have.

1. *Sulphate of Water with Saline Water*:  $\text{H}\ddot{\text{S}}\text{H}$ .

*Sulphuric Acid of sp. gr. 1.78.*

It appears, then, that in an exposition of the relations of the sulphates, we may set out from this body as our primary sulphate. Of the two atoms of water which it contains, that atom which is basic cannot be separated from the acid, unless by the agency of a stronger base. The second, or saline atom of water, may be separated by heat, but not by any degree of heat, under  $400^{\circ}$  Fahrenheit, and is re-absorbed with great avidity.

A diluted sulphuric acid may, I find, be concentrated at a temperature not exceeding  $380^{\circ}$ , without the loss of a particle of acid; and the quantity of water retained is reduced to two atoms most precisely. This in fact is an exact method of obtaining the definite sulphate of water with saline water; which may be kept at  $380^{\circ}$  or  $390^{\circ}$ , without sustaining any further loss. I have observed a close approximation to the same proportion of water, even in the case of a dilute acid concentrated at a temperature not exceeding  $300^{\circ}$ . But at  $400^{\circ}$  or  $410^{\circ}$ , this



hydrate begins to be decomposed, and a portion of it is apt to distil over with the water expelled. When, however, this hydrate is distilled *in vacuo*, at the last-mentioned temperature, it loses nothing but water for some time.

In one experiment, a small quantity of dilute sulphuric acid was found to concentrate down to three atoms of water, at a temperature not exceeding  $212^{\circ}$ , at which it was sustained *in vacuo* for not less than forty hours. It consisted of 100 parts dry acid united with 68.07 water, while three atomic proportions of water are 67.32 parts.

The concentrated acid of commerce, which is a definite sulphate of water, without the saline atom, does not freeze at a temperature so low as  $-36^{\circ}$ , according to Dr. Thomson. To sulphuric acid of sp. gr. 1.78, I added water in the proportion of two, four, and six atoms; but all these hydrates remained fluid, when kept for a short time at  $0^{\circ}$  Fahrenheit. Anhydrous sulphate of magnesia or zinc never dissolves, *as such*, in water; or exhibits any determinate chemical character. It must always combine with its saline atom of water in the first instance, or with something equivalent, and it is the compound which is soluble, etc. So it is with the sulphate of water, or concentrated sulphuric acid ( $\text{H}\ddot{\text{S}}$ ). In chemical character it is an *incomplete body*. There is a hiatus in its constitution, which must be filled up. When it dissolves in any menstruum, we may be sure that it has first acquired its second or saline atom of water, or something in its place. Hence a set of reactions of sulphuric acid, which are peculiar to its concentrated condition, upon alcohol and many organic bodies. But to this peculiar state of bodies I shall again have occasion to allude under sulphate of lime, a body which illustrates it more strikingly than the sulphate of water.

*Sulphate of Water with Sulphate of Potash:  $\text{H}\ddot{\text{S}}(\text{K}\ddot{\text{S}})$ .  
Bisulphate of Potash.*

Of all the sulphates, the acid sulphates or bisulphates of potash and soda deviate least from the primary sulphate of water. We have, in the one case, merely sulphate of potash; and, in the other, sulphate of soda, substituted for the saline atom of water of the sulphate of water. In none of the specimens of these salts which I had occasion to examine, was there any water of crystallization, and the evidence which is given of its occasional presence is of a very doubtful description. The crystals could be heated to  $300^{\circ}$ , without impairing their transparency; and they fused at a temperature not under  $600^{\circ}$ , without the loss of anything, except a trace of water, which had been mechanically retained. Upon heating a bisulphate nearly to redness, a portion of sulphate of



water is expelled. I greatly doubt whether water ever comes off in such a case unaccompanied by sulphuric acid, although Berzelius appears to be of a different opinion. It is well known that the sulphate of water is not entirely expelled from these salts by heat alone, even the most intense. Sulphate of water, however, leaves the sulphate of soda with greater facility than it leaves the sulphate of potash.

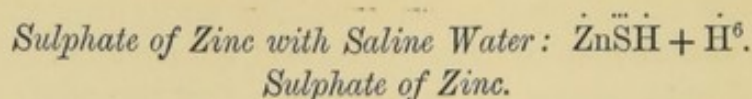
These sulphates should be crystallized from concentrated solutions at a high temperature; for their solutions are very apt to undergo decomposition at low temperatures, the neutral sulphate crystallizing, and leaving "the sulphate of water with saline water" in solution. I have often observed this decomposition to occur, even in solutions containing a great excess of sulphuric acid. At low temperatures, therefore, the affinity of sulphate of water for "saline water," prevails over its affinity for sulphate of potash. Crystals of bisulphate of soda, pounded and put under pressure in blotting-paper, are apt to undergo the same decomposition, if the air is damp, and frequently impart a large quantity of their sulphate of water to the paper in the course of twenty-four hours. This circumstance must be kept in view in preparing bisulphates for analysis. The facility with which these salts are decomposed by water, accords well with their relation to sulphate of water with saline water, which we have supposed to exist. Sulphate of zinc, sulphate of magnesia, etc., are capable of separating the sulphate of water from these salts, at a temperature approaching to redness, and take its place.

I have observed that the bisulphate of soda is more prone to decomposition, when dissolved in water, than the bisulphate of potash. The double salts of sulphate of soda with sulphate of magnesia, etc., are also much less stable than the corresponding double salts containing sulphate of potash. Indeed, I believe that the former are uniformly decomposed when dissolved in water.

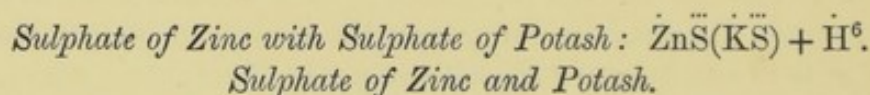
*Sulphate of Potash, Sulphate of Soda.*     $\dot{\text{K}}\ddot{\text{S}}, \dot{\text{N}}\ddot{\text{S}}.$

These salts differ from other sulphates in having no saline water. Of the ten atoms water with which sulphate of soda crystallizes, none is essential to its constitution. The whole were lost, even at a temperature not exceeding 47° Fahrenheit, when the crystals of the salt were exposed over sulphuric acid *in vacuo* for five days. From the regular progress of the desiccation of the salt, which was observed by occasionally weighing it, it was evident that no portion of the water was more strongly retained than the rest. It is well known that sulphate of soda crystallizes in an anhydrous condition from a hot solution.

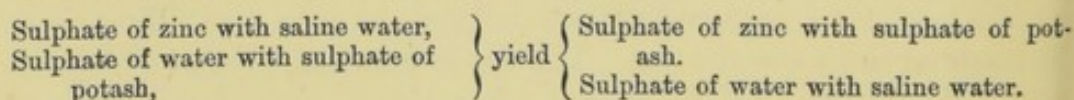




In the sulphate of zinc, we have the basic atom of water contained in sulphate of water displaced by oxide of zinc, while the saline atom remains; and to this compound six atoms of water are attached in the common crystals. These crystals, placed over sulphuric acid *in vacuo*, thermometer  $68^\circ$ , were found to lose six atoms water, retaining only one. Exposed to the air at  $212^\circ$ , the crystals likewise readily effloresced down to one atom; and the sulphate of zinc is known to be deposited from a boiling solution, in crystalline grains, containing one atom of water. On the other hand, the sulphate of zinc was found to retain this single atom of water at the high temperature of  $410^\circ$  Fahrenheit, but to lose it, and become anhydrous, at a temperature not exceeding  $460^\circ$ . In all such cases, the hydrated salt was heated in a tube receiver, by means of an oil or solder-bath, of which the temperature was observed by a thermometer. However strongly it has been heated, without being decomposed, the sulphate of zinc always regains this atom of water when moistened, slaking with the evolution of heat. Common sulphate of zinc is therefore "sulphate of zinc with saline water;" and the true or absolute sulphate of zinc is unknown to us in the crystalline form, or in a soluble state. But we may continue to designate the salt we possess as sulphate of zinc, as the name is attended with no dubiety.



In this well-known double salt, we have sulphate of potash substituted for the saline water of sulphate of zinc, and the six atoms of water of crystallization remain. It is readily formed, on mixing together solutions of sulphate of zinc and sulphate of potash, in atomic proportions. It is formed likewise, and separates by crystallization, when the sulphate of zinc is added to the bisulphate of potash; and, in that case, an interesting double decomposition occurs.



In the sulphate of zinc and potash, the whole six atoms of water are retained with considerably greater force than in the sulphate of zinc itself; but even the double salt becomes anhydrous at  $250^\circ$ , and, indeed, the water retained falls below a single atomic proportion, when the salt is dried *in vacuo* over sulphuric acid, at a temperature not exceeding



78° Fahrenheit. The sulphate of potash in the double salt has not the effect of neutralizing the acid reaction of sulphate of zinc, according to my observations; nor has it that effect in the case of any other double salt.

I subjoin a table of observations, made on the quantity of water retained by this double salt, in different circumstances. In the first two columns, the composition of the quantities actually examined is stated in grains.

	Anhydrous Salt.	Water.	Anhydrous Salt.	Water.
Dried <i>in vacuo</i> over sulphuric acid for ten days, temp. from 68° to 78°, . . . }	17.2	0.68	100	3.95
Nine hours, at 238°, . . . . . }	19.03	1.33	100	6.99
Two hours at 250°, and one hour at 270°, . }	7.79	0.	100	0.
Four hours, at 250°, . . . . . }	6.55	0.	100	0.
Composition of sulphate of zinc and potash with one atom water (by theory), . }	...	...	100	5.37

*Sulphate of Zinc with Sulphate of Soda:*  $\text{ZnS}(\text{NS}) + \text{H}^4$ .

*Sulphate of Zinc and Soda.*

This salt, I believe, has not hitherto been described. I failed in attempting to form it, by dissolving together sulphate of zinc and sulphate of soda in atomic proportions: the salts uniformly crystallized apart, either in cold or in warm weather. Each of the salts was also added in excess to the other, but with no better effect. It appears, then, that sulphate of soda does not displace the saline water of sulphate of zinc, so easily as sulphate of potash does. But the desired salt was obtained by a process of double decomposition, suggested from consideration of the relations of the sulphates. Solutions of bisulphate of soda, and of sulphate of zinc, were mixed together in atomic proportions, from which the sulphate of zinc and soda separated in a gradual manner in the course of a day or two, leaving sulphuric acid in solution.

Sulphate of zinc with saline water, } yield { Sulphate of zinc with sulphate of soda.  
Sulphate of water with sulphate of soda, } { Sulphate of water with saline water.

This salt is deposited in distinct tabular crystals, of a peculiar form, which are often associated in tufts, and is best obtained by evaporating the mixed solutions over sulphuric acid without heat. It cannot be redissolved in pure water, without undergoing decomposition, which accounts for the impossibility of forming it by the direct process. The



crystals contain four atoms of water, and are about as deliquescent as nitrate of soda, in a damp atmosphere. The anhydrous salt undergoes fusion, like all the other double sulphates, at an incipient red heat, without the evolution of acid fumes. The fused salt solidifies, on cooling, into a white and opaque mass.

*Sulphate of Copper with Saline water:*  $\text{CuSH} + \text{H}^4$ .

*Sulphate of Copper.*

The common blue rhomboidal crystals of sulphate of copper contain five atoms of water, four of which are readily expelled by drying the salt in air at  $212^\circ$ ; by which treatment the salt loses its blue colour, and becomes white, with a dirty shade of green. The sulphate of copper with one atom of water was also obtained in a crystallized state by Dr. Thomson, and called by him green sulphate of copper. Dried over sulphuric acid *in vacuo* for seven days, when it had ceased to lose, at a temperature between  $65^\circ$  and  $74^\circ$ , the common hydrated salt retained 21.67 parts water to 100 anhydrous salt, which is somewhat under two atomic proportions of water, namely 22.57 parts. At a temperature between  $430^\circ$  and  $470^\circ$ , the sulphate of copper loses its fifth, or saline, atom of water, and is found in the state of a powder, which is white without any shade of colour. When a few drops of water are thrown upon anhydrous sulphate of copper, it slakes and becomes blue, and so much heat is evolved as to occasion the ebullition of the water. In one case the temperature was observed to rise to  $276^\circ$ . This arises from the resumption of saline water by the salt.

*Sulphate of Copper with Sulphate of Potash:*  $\text{CuS}(\text{KS}) + \text{H}^6$ .

*Sulphate of Copper and Potash.*

This salt may be formed by mixing sulphate of copper with either sulphate or bisulphate of potash, in atomic proportions. Dried in the open air, it loses six atoms water, and becomes quite anhydrous at a temperature not exceeding  $270^\circ$  Fr. The following Table of the composition of this hydrated salt in different circumstances illustrates three facts,—that the salt has a disposition to retain two atoms of water when dried at  $212^\circ$  in open air,—that a greater portion of water of crystallization is withdrawn from the salt by drying it over sulphuric acid *in vacuo*, without artificial heat, than by drying it at  $212^\circ$  under the atmospheric pressure, and that the mechanical water retained by the crystals of this salt may exceed 3 per cent. of their weight.



	Anhydrous Salt.	Water.	Anhydrous Salt.	Water.
Dried on water-bath at 212°, for three days, } or till it ceased to lose weight, . . . }	19·6	2·21	100	11·27
Dried on nitre-bath at 238°, for three days, } Dried <i>in vacuo</i> over sulphuric acid for seven } days, or till it ceased to lose weight; } therm. from 65° to 74°, . . . }	22·06	2·37	100	10·74
Crystals pounded, and slightly dried at 80°, } so as not to injure the lustre of an entire } crystal, . . . }	22·97	1·61	100	7·09
Same crystals not deprived of mechanical } water by the above treatment, . . . }	13·94	3·4	100	32·25
Composition of sulphate of copper and } potash with two atoms of water (by } theory), . . . }	23·79	8·64	100	36·22
Composition of do. with six atoms of water } (by theory), . . . }	...	...	100	10·77
	...	...	100	32·33

I have confirmed the observation of Berzelius, that a concentrated solution of this salt, when boiled, deposits an insoluble subsalt, containing sulphate of potash, but which is decomposed by washing, and cannot be had in a proper state for analysis. But the crystals of the double salt are quite soluble after being heated to 212°, so that they do not undergo the same change as their solution does at that temperature.

This double salt retains its blue colour after being fused at a red heat and cooled, and does not become white like the sulphate of copper. Indeed, it appears that, to be coloured, the salts of the oxide of copper require the addition of some other constituent, such as saline water, sulphate of potash, or ammonia. Hence, if the absolute sulphate of copper could be obtained in a crystallized state, it would be a colourless salt.

*Sulphate of Copper with Sulphate of Soda:*  $\text{CuS}(\text{NS}) + \text{H}^2$ .

*Sulphate of Copper and Soda.*

Like the other double salts of sulphate of soda, this salt cannot be formed directly, being decomposed by water. Even when it is attempted to form it by double decomposition from the bisulphate of soda, in general a large quantity of sulphate of soda and of sulphate of copper are separately deposited before the double salt appears. It is then deposited in a crust, consisting of small but distinct crystals, which are slightly deliquescent, and appear to contain two proportions of water. This salt is easily made anhydrous, and thereafter fuses at an incipient red heat without loss of acid, and remains of a blue colour when cool. The fused salt does not split into thin scales in the progress of cooling, as the corresponding sulphate of copper and potash does.



*Sulphate of Manganese with Saline Water*:  $\text{MnSH} + \text{H}^4$ .

*Sulphate of Manganese.*

The water in this salt was found to be reduced from five atomic proportions to little more than one, by drying the crystals in open air at  $238^\circ$ , while one entire atomic proportion was retained at  $410^\circ$ . Flesh-coloured crystals, dried *in vacuo* in warm summer weather, without artificial heat, lost somewhat more than three proportions of water.

	Anhydrous Salt.	Water.	Anhydrous Salt.	Water.
Flesh-coloured crystals of salt, . . .	28.42	17.07	100	60.06
Do. dried at $238^\circ$ , . . .	21.53	2.92	100	13.05
A portion of last, afterwards dried for one hour between $380^\circ$ and $410^\circ$ , . . .	9.54	1.12	100	11.74
A portion of same, dried for one hour between $415^\circ$ and $468^\circ$ , . . .	10.90	0.56	100	5.14
Crystals dried for nine days <i>in vacuo</i> over sulphuric acid, thermometer $64^\circ$ to $72^\circ$ , but had lost nothing the last two days, . . .	8.62	11	100	20.88
Composition of sulphate of manganese with one atom of water (by theory), . . .	...	...	100	11.88
Composition of do. with five atoms of water, . . .	...	...	100	59.4

A crystalline crust of sulphate of manganese, deposited from a warm solution, was found to contain three atoms of water. It is likewise known to be deposited from a boiling solution with only one atom of water, namely, the saline atom. We have, therefore, sulphates of this class with no water of crystallization, and with two, four, and six atoms.

The sulphate of manganese and potash did not crystallize on mixing the solutions of its constituents. The sulphate of manganese and soda was obtained in analogous circumstances with the sulphate of copper and soda, but was not examined.

*Sulphate of Iron with Saline Water*:  $\text{FeSH} + \text{H}^6$ . *Sulphate of Iron.*

Of the seven atomic proportions of water which the crystals contain, 5.48 proportions were lost *in vacuo* over sulphuric acid; and six proportions at  $238^\circ$ , and probably at lower temperatures. The saline atom of water is retained by this salt at so high a temperature as  $535^\circ$ . But the salt can be made perfectly anhydrous, with proper caution, without appreciable loss of acid.



*Sulphate of Iron with Sulphate of Potash:*  $\text{Fe}\ddot{\text{S}}(\text{K}\ddot{\text{S}}) + \text{H}^6$ .

*Sulphate of Iron and Potash.*

A specimen of this salt was made anhydrous by a sandbath heat, which was found not to affect the saline atom of water of the preceding compound.

Sulphate of nickel was found to correspond closely with sulphate of iron in the temperatures at which it lost its water of crystallization, and also its saline water. And in the case of both of the compounds of these salts with sulphate of potash, a considerably higher temperature was required to render them perfectly anhydrous, than in the case of the corresponding double salt of zinc.

*Sulphate of Magnesia with Saline Water:*  $\text{Mg}\ddot{\text{S}}\text{H} + \text{H}^6$ .

*Sulphate of Magnesia.*

One atom of water is retained by sulphate of magnesia at  $460^\circ$ , but the other six are not entirely expelled under  $270^\circ$  in open air. Indeed, this sulphate is remarkable for a disposition to retain two atoms of water, in which respect it resembles the sulphate of lime. Dried at  $212^\circ$  in open air, the crystals of sulphate of magnesia were found in several experiments to retain somewhat more than two atomic proportions of water. When dried at the same temperature *in vacuo* over sulphuric acid, the water was reduced to two proportions. Crystals placed over sulphuric acid *in vacuo*, without heat, were found to retain only two and a quarter atomic proportions of water.

	Anhydrous Salt.	Water.	Anhydrous Salt.	Water.
Crystallized salt, dried <i>in vacuo</i> at $70^\circ$ for } six days, or till it ceased to lose, . . . }	12.34	4.13	100	33.46
Do. <i>in vacuo</i> at $212^\circ$ , . . . . . }	21.8	6.24	100	28.62
Do. heated between $410^\circ$ and $460^\circ$ for one } hour, being previously dried at $238^\circ$ , . . }	4.9	0.74	100	15.1
Relative composition of the anhydrous salt } with one atom of water (by theory), . . }	...	...	100	14.81

The sulphate of magnesia and ammonia lost its six atoms of water of crystallization and became anhydrous, when exposed to a temperature not exceeding  $270^\circ$ , for one hour, having previously been dried at  $212^\circ$ . It retained of course the atom of water which is essential to the ammoniacal salts. A somewhat higher temperature was required to deprive the sulphate of magnesia and potash of its whole water of crystallization.



*Hydrated Sulphate of Lime:*  $\text{CaSH} + \text{H}$ .

The only crystalline hydrate of sulphate of lime, which is known, contains two atoms of water. It occurs native in gypsum and selenite. Pounded selenite loses little or nothing in the open air at  $212^\circ$ . Water begins to escape at a temperature not much higher, but is not completely expelled by any degree of heat under  $270^\circ$ . That hydrated sulphate of lime may contain an atom of saline water, is indicated by the existence of a double salt of sulphate of lime with sulphate of soda, constituting the mineral Glauberite. I succeeded in obtaining a definite compound of sulphate of lime with one atom of water, by drying pounded selenite, at  $212^\circ$ , *in vacuo* over sulphuric acid.<sup>1</sup> The salt which had been so dried at  $212^\circ$  did not form a coherent mass, like stucco, when made into a paste with water. The affinity of sulphate of lime for the saline atom of water appears to be feeble, as the salt can be made quite anhydrous under  $300^\circ$ ; and consequently the sulphate of lime has much less disposition to form double salts than the sulphates of magnesia, zinc, etc.

	Anhydrous Salt.	Water.	Anhydrous Salt.	Water.
Selenite, dried for ten days in open air at $212^\circ$ , . . . . . }	17.07	4.27	100	25.01
Do. dried <i>in vacuo</i> at $212^\circ$ , . . . . . }	17.61	3.04	100	14.72
Sulphate of lime with one atom of water (by theory), . . . . . }	...	...	100	13.13
Do. with two atoms of water (by theory), . . . . . }	...	...	100	26.26

In drying gypsum, to make plaster of Paris, a third or a fourth of the water of the salt is allowed to remain, by which it sets more strongly. But the salt may be made quite anhydrous, I find, and yet retain the power of recombining with two atoms of water, if dried at a temperature not exceeding  $270^\circ$  F.; although the hydrate which results on slaking in the last case is rather pulverulent. When gypsum has been dried at a higher temperature, as at  $300^\circ$  or  $400^\circ$  F., it refuses entirely to combine with water, and is technically called *burnt stucco*. The anhydrous sulphate of lime which occurs in nature exhibits the same indifference to water. In Anhydrite we have, I believe, the true or absolute sulphate of lime in a crystallized state. The body which results from exposing hydrated sulphate of lime to  $270^\circ$ , although composed of nothing but sulphuric acid and lime, should be viewed as the *débris* of the hydrated sulphate of lime, and not confounded with the absolute sulphate of lime, which last has no disposition to combine with water. The first, which

<sup>1</sup> It has subsequently been observed, that the water is reduced under one atomic proportion, by a protracted exposure to the same temperature.



we may call "anhydrous gypsum," is an *imperfect* body. We know sulphate of lime in four states, which may be expressed symbolically as follows :

Gypsum,	.	.	.	.	.	$\dot{\text{Ca}}\ddot{\text{S}}\ddot{\text{H}} + \dot{\text{H}}$
Gypsum dried at 212°,	.	.	.	.	.	$\dot{\text{Ca}}\ddot{\text{S}}\ddot{\text{H}}$
Anhydrous gypsum (dried at 270°),	.	.	.	.	.	$\dot{\text{Ca}}\ddot{\text{S}}-$
Anhydrite,	.	.	.	.	.	$\dot{\text{Ca}}\ddot{\text{S}}$ .

Here we distinguish the imperfect body, anhydrous gypsum, from anhydrite, by placing the minus sign after the former. In the same manner, concentrated sulphuric acid, or oil of vitriol, may be represented by  $\dot{\text{H}}\ddot{\text{S}}-$ ; anhydrous sulphate of magnesia, sulphate of zinc, etc., by  $\dot{\text{Mg}}\ddot{\text{S}}-$ ,  $\dot{\text{Zn}}\ddot{\text{S}}-$ , etc.; the absolute sulphates of water, magnesia, zinc, etc.,  $\dot{\text{H}}\ddot{\text{S}}$ ,  $\dot{\text{Mg}}\ddot{\text{S}}$ ,  $\dot{\text{Zn}}\ddot{\text{S}}$ , etc., being unknown to us.

The view which is given in this paper of the constitution of the sulphates, must not be hastily generalized and applied to other classes of salts. From investigations not yet completed, I am satisfied that each class of salts has its peculiarities, which must be studied before the law of the class can be laid down.

## VI.

### ON THE WATER OF CRYSTALLIZATION OF SODA-ALUM.<sup>1</sup>

From *Phil. Mag.* ix. 1836, pp. 26-32. [Liebig, *Annal.* xxiii. 1837, pp. 269, 270; Poggend. *Annal.* xxxix. 1836, pp. 582-585.]

THE double sulphate of alumina and soda crystallizes in the form of the regular octohedron, like the sulphate of alumina and potash, while the former salt is supposed to contain twenty-six atoms of water, and the latter contains only twenty-four. The coincidence in form of these two salts is most interesting, for in no other corresponding salts of potash and soda has such a relation been observed from which any inference in respect to isomorphism could properly be drawn. Yet if the soda-salt contains two atoms more of water than the potash-salt, the conclusion which follows is, not that soda and potash are isomorphous bodies, but that soda *plus* two atoms water is isomorphous with potash, as ammonia *plus* one atom of water is isomorphous with the same body. But the last analogy is superficial and likely to prove illusory.

<sup>1</sup> Communicated by the Author.



The exact determination of the water of crystallization of a salt is often a problem of no inconsiderable difficulty, as many precautions must be taken which are by no means obvious. To have alumina free from potash or ammonia, it was precipitated from pure potash-alum by means of carbonate of soda. A solution of sulphate of alumina was formed by dissolving the precipitated alumina in the proper quantity of sulphuric acid, and the requisite proportion of sulphate of soda was added. A considerable crop of crystals of soda-alum were obtained from the above solution allowed to evaporate spontaneously in air.

Like most very soluble salts the crystals of soda-alum, when newly prepared, retain hygrometrically a notable quantity of the saline liquor in which they have been formed. But the crystals of this salt cannot be dried easily, as after they lose their hygrometric water they are nearly as efflorescent as sulphate of soda itself. Before being submitted to analysis the crystals had been kept for five months of cold weather in a large phial stoppt by a cork. Their surfaces remained perfectly bright, and not in the slightest degree effloresced; but the crystals had lost, from the escape of their hygrometric water, that extreme and watery clearness which we have in the crystal newly removed from its mother-liquor. From my experience in respect to such salts, I had reason to believe that the crystals of soda-alum were now in a most suitable condition for analysis.

Upon a very damp day the crystals were reduced to powder and pressed in blotting-paper. A large crystal exposed to the air at the same time lost nothing. 20·35 grs. of the salt so prepared were exposed on a sand-bath to a heat, which was gradually raised so as to effloresce the salt without melting it or causing vesicular swelling. In eight hours the salt had been heated above the melting point of tin, and had lost 8·98 grains. It was thereafter heated, in a gradual and cautious manner, to low redness by the spirit-lamp, and the loss became 9·65 grains. By a continued exposure to the same heat for half an hour more, the salt lost only one hundredth of a grain additional. Supposing it now to have lost all its water, the salt will consist of

			Theory of 24 atoms of water.
Sulphate of alumina and soda,	10·69	100·	100·
Water, . . . . .	9·66	90·37	88·9
	<hr/> 20·35	<hr/> 190·37	188·9

The calcined salt dissolved slowly but completely in boiling water. By precipitation with muriate of barytes it afforded 21·22 grains sulphate of barytes, equivalent to 7·37 grains sulphuric acid. Or the crystallized salt contains 34·73 per cent. of sulphuric acid, while the theory of



twenty-four atoms of water supposes it to contain 34·93 per cent. sulphuric acid.

It follows from this analysis that soda-alum contains twenty-four atoms of water and not twenty-six.

There is no reason to question the perfect accuracy of the analysis of potash-alum by Berzelius, which gives to it likewise twenty-four atoms of water. Dried in the manner described for soda-alum, I found it to consist of

		Theory of 24 atoms of water.
Sulphate of alumina and potash,	100·	100·
Water,	84·8	83·4
	<hr/> 184·8	<hr/> 183·4

In such analysis there is imminent danger of the water carrying off a little acid with it, unless it is expelled in the most slow and cautious manner. It is probably from this cause that the water has come to be over-estimated in the case of the alums. But they stand a low red heat without decomposition, if first made quite anhydrous.

## VII.

### INQUIRIES RESPECTING THE CONSTITUTION OF SALTS. OF OXALATES, NITRATES, PHOSPHATES, SULPHATES, AND CHLORIDES.<sup>1</sup>

From *Phil. Trans.* 1837, pp. 47-74. [*Liebig, Annal.* xxix. 1839, pp. 1-35.]

FROM the results obtained in a former paper upon water as a constituent of sulphates, it seemed likely that a close analogy would generally be found to exist between any hydrated acid and the magnesian salt of that acid. The sulphate of water is constituted like the sulphate of magnesia; and so do I now find the oxalate of water to resemble the oxalate of magnesia, and the nitrate of water to resemble the nitrate of magnesia. Indeed, it appears probable that the correspondence between water and the magnesian class of oxides (as we may call the metallic oxides isomorphous with magnesia) extends beyond their character as *bases*,—that in certain subsalts of the magnesian class of oxides we have the metallic oxide replacing the water of crystallization of the neutral salt, or discharging a function which was thought peculiar to water.

<sup>1</sup> Received June 23,—Read November 24, 1836.

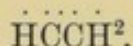


In the formation of a double sulphate a certain kind of substitution or displacement was observed, such as the displacement of an atom of water pertaining to the sulphate of magnesia, by an atom of sulphate of potash, to form the double sulphate of magnesia and potash. The same kind of displacement appears to occur likewise in the construction of double oxalates; and the tracing of it enables us to form an idea of the constitution both of the double and of the superoxalates, and to explain their derivation, as in the case of the sulphates.

## I. OF THE OXALATES.

The oxalates promised ample scope for investigation from their number and variety. For we have not only neutral oxalates, double oxalates, and binoxalates, but likewise an unparalleled combination, the quadroxalate of potash, of which the true constitution or proximate composition is a most interesting subject of inquiry.

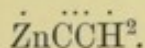
### 1. *Oxalate of Water, or Hydrated Oxalic Acid.*



The recent and accurate experiments of Berzelius, Gay-Lussac, and Turner, leave no doubt that the crystals of oxalic acid contain three atoms of water. I find the acid to crystallize with this proportion of water in a variety of circumstances, and believe that it is never deposited from its aqueous solution in any other state. Of these three atoms of water one atom is basic, which is expressed in the formula by placing its symbol *before* that of the acid; while the other two atoms of water are attached to this oxalate of water, and may be termed the *constitutional* water of the oxalate of water. These two atoms of water are found in the oxalate of magnesia, the oxalate of zinc, and the other oxalates of the magnesian class, as well as in the oxalate of water.

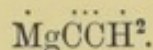
It is well known that oxalic acid can likewise exist in combination with no more than one atom of water (its basic water), and is obtained in that state by drying it at a temperature a little above 212° Fahr., or on subliming the hydrated acid by a higher temperature. I have made many experiments in order to discover whether, in the case of the other two atoms of water, one is retained more strongly than the other, or whether an oxalate of water with one additional atom of water, instead of two, could be obtained. The common crystals were dried at various temperatures, both in air and *in vacuo*, but either none of the water was lost, or the entire two atomic proportions. There is certainly no intermediate hydrate.



2. *Oxalate of Zinc.*

In the oxalate of water we observe a contracted solubility, and all the oxalates of the magnesian class of oxides are very sparingly soluble in water. They may be obtained by precipitation, on mixing a solution of oxalate of potash with sulphate of zinc, etc. Cold solutions of the salts were always made use of in our experiments; and the precipitates, which were always granular and more or less distinctly crystalline, were washed with cold water, and dried by exposure to the air for a week or two, without the application of artificial heat.

The oxalate of zinc is admitted to possess two atoms of water, and these I find are retained pretty strongly, as in the case of oxalate of water. It was observed that 24.95 grains of the salt lost only 0.44 grain by three days' exposure to 212° Fahr.; but by a few hours at 315° Fahr. the salt lost in all 4.87 grains of water, and appears to have become anhydrous.

3. *Oxalate of Magnesia.*

The oxalate of magnesia retains its two atoms of constitutional water very strongly, and it is doubtful whether they can be expelled without decomposing the salt; 13.74 grains of the salt lost only 0.32 grain by an exposure to 212°, protracted for several days; and by two days at 300° Fahr. the whole loss amounted only to 0.47 grain. 22.36 grains of the same salt, ignited, left 5.94 grains of caustic magnesia, or one part of the salt contains 0.2656 magnesia. A salt constituted with two atoms of water should contain 0.2759 magnesia, of which the specimen analysed falls a little short, probably from containing some hygrometric moisture.

The *oxalate of manganese* lost nothing at 212°, and was found by analysis to contain 0.2416 water, which approaches very closely the quantity equivalent to two atoms, namely, 0.2474 water in one hydrated oxalate of manganese.

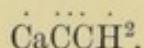
In regard to several other oxalates of this class, namely, the oxalate of the protoxide of iron, of oxide of nickel, of oxide of cobalt, and of oxide of copper, I believe it is impossible to obtain them in a state of sufficient purity for analysis. They appear to carry down with them portions of the precipitating salts; and they alter manifestly in appearance and composition during the progress of the washing, to which they must be submitted for the purpose of purification. In the case of oxalate of copper, which was examined most particularly, the results were so anomalous that no inference whatever could be drawn from them.



It will appear, however, that a neutral oxalate of copper with two atoms of water can exist but in combination with oxalate of potash, or with oxalate of ammonia, as a double salt.

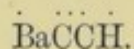
None of the oxalates of the magnesian class of oxides is more soluble in oxalic acid than in water, and none of them combines with that acid to form a binoxalate. The crystals, which are obtained on mixing together solutions of binoxalate of potash and sulphate of magnesia, and which have been supposed to be a binoxalate of magnesia, are really a mixture of oxalate of magnesia and of quadroxalate of potash. Hence there is no combination of oxalate of magnesia with oxalate of water; which illustrates the fact that bodies of the same class, such as these two oxalates are, have no disposition to enter into union and form a new compound.

#### 4. *Oxalate of Lime.*



The oxalate of lime contains two atoms of water, like the oxalate of magnesia, but parts with its water more freely than that salt. Thus 12.06 grains of the hydrated oxalate of lime were found to lose 1.6 grain of water at 212° Fahr. in the course of two days, 1.68 grain in three days, 1.84 grain in six days, and nothing more in nine days. The salt originally consisted of 100 oxalate of lime united to 27.85 water, of which last it has lost 19.53 parts, and retained 8.32 at 212°. It is probable therefore that the constitution of hydrated oxalate of lime is the same as that of hydrated oxalate of magnesia, that oxalate of lime forms only one definite hydrate, containing two atoms of water, but that it parts with the whole of its constitutional water at a moderate temperature.

#### 5. *Oxalate of Barytes.*



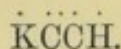
This oxalate differs from all the preceding, and contains only one atom of water. It was formed by digesting an excess of oxalic acid upon carbonate of barytes, and afterwards washing the resulting oxalate with cold water. 20.60 grains of the oxalate, calcined by a low red heat, left 16.45 grains carbonate of barytes, equivalent to 12.77 barytes. Hence it follows that the oxalate consisted of

		Composition of $\text{Ba}\ddot{\text{C}}\ddot{\text{H}}$ .
Barytes,	100	100
Volatile matter,	61.32	59.08
	<hr/> 161.32	<hr/> 159.08



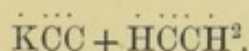
Before being washed this oxalate had a sour taste, and the volatile portion of it amounted to 67.01 parts instead of 61.32; but it was evidently the neutral oxalate with a little free oxalic acid. It was not a binoxalate; nor did such a salt present itself on digesting the neutral oxalate in oxalic acid, so that I am constrained to deny the existence of a binoxalate of barytes. Indeed, it is scarcely a matter of doubt that no supersalt whatever exists of barytes, strontian, lime, or of the magnesian class of oxides.

#### 6. *Oxalate of Potash.*



Oxalate of potash is known to crystallize from solution with one atom of water, and with no other proportion. The crystals speedily become white and opake at 212° Fahr., from the loss of water, but cannot, I believe, be made quite anhydrous at that temperature; at least a portion of the salt, which had been exposed to 212° for four days, still retained water, consisting of 100 oxalate of potash and 3.4 water, which is rather less than a third of the water which the salt originally contained (10.8 parts). The oxalate of potash becomes quite anhydrous when dried at 300°. Of salts so dried 100 parts reabsorbed 10.63 water in a damp atmosphere with the greatest avidity. The oxalate of potash has therefore a certain attraction for a single atom of water, and this is an important feature of the salt.

#### 7. *Bincoxalate of Potash.*



This salt has hitherto been supposed to contain only two, but it certainly contains three atoms of water.

21.37 grains of the salt, calcined by a full red heat, which is necessary for complete decomposition, left 10.14 grains of carbonate of potash. Allowing the potash an equivalent proportion of oxalic acid, the salt must consist by this experiment of

Potash,	.	.	.	.	32.23
Oxalic acid,	.	.	.	.	49.38
Water,	.	.	.	.	18.39
					<hr/> 100.

The water almost coincides with three atoms, which would amount to 18.42 per cent. of the salt.

In the formation of the bincoxalate of potash, the constitutional atom of water of the neutral oxalate of potash appears to be displaced



by an atom of hydrated oxalic acid; so that the formula of binoxalate of potash represents anhydrous oxalate of potash, followed by oxalate of water with two atoms of water, as given above. The same principle of derivation applies most happily to that anomalous salt, the quadroxalate of potash.

#### 8. *Quadroxalate of Potash.*

Analitic formula, .  $\dot{\text{K}}(\ddot{\text{C}}\ddot{\text{C}})^4\dot{\text{H}}^7.$

Rational formula, .  $\dot{\text{K}}(\ddot{\text{C}}\ddot{\text{C}}) + \dot{\text{H}}\ddot{\text{C}}\ddot{\text{C}} + 2(\dot{\text{H}}\ddot{\text{C}}\ddot{\text{C}}\dot{\text{H}}^2)$

The formula of the preceding salt is terminated by two atoms of water: let us replace them by two atoms of hydrated oxalic acid, and we have the quadroxalate of potash. We thus derive the quadroxalate from the binoxalate, in the same way that the binoxalate itself is derived from the oxalate.

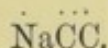
There can be no doubt, from the accurate analysis of Berzelius, that this salt contains seven atoms of water. He found 100 parts of the quadroxalate of potash to yield by ignition 27.225 carbonate of potash. In an experiment in which 17.3 grains of the salt were ignited by us, there resulted 4.7 carbonate of potash; which is 27.11 carbonate of potash from 100 quadroxalate. Berzelius determined the water directly by igniting the salt with oxide of copper, and found it to amount to 24.8 per cent. of the salt. Calculated from our experiment, the water comes out 25.05 per cent., while the theory of seven atoms of water in the salt requires 24.72 per cent.

10.87 grains of this salt, dried by a nitre-bath, of which the temperature was 240°, lost eventually 1.46 grains; or 100 salt lost 13.43. Four atoms of water amount to 14.12 per cent. of the salt, to which the experimental result approximates sufficiently to prove that this salt parts readily with four of its seven atoms of water. These four atoms of water are evidently the constitutional water of the two atoms of hydrated oxalic acid, which the quadroxalate contains. When the salt is still more strongly heated, oxalic acid itself goes off, partly as a sublimate and partly in a decomposed state.

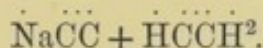
#### 9. *Oxalates of Ammonia.*

The oxalate and the binoxalate of ammonia agree exactly in composition with the corresponding salts of potash, the hypothetic oxide of ammonium being substituted for potash. It has been supposed that no quadroxalate of ammonia exists; but this is a mistake. Such a salt is formed, on dissolving together equal weights of binoxalate of ammonia and hydrated oxalic acid, and is analogous in form and composition to the quadroxalate of potash.



10. *Oxalate of Soda.*

This salt is perhaps the least soluble of the salts of soda, and presents itself as a granular precipitate on saturating carbonate of soda with oxalic acid. Of the oxalate of soda dried in air without the application of heat, 23.44 grains left 18.52 carbonate of soda when strongly ignited, or 100 oxalate yield 79.01 carbonate of soda. Now 100 anhydrous oxalate of soda should yield 79.09 carbonate of soda. Hence the oxalate of soda is correctly stated to be anhydrous. It nevertheless combines with hydrated oxalic acid, and forms a binoxalate. In this compound we have simply the attachment of an atom of the oxalate of water, to the atom of oxalate of soda, without the displacement of an atom of water, as in the formation of the binoxalate of potash. Probably the absence of the atom of water in the oxalate of soda indicates an indifference on the part of this salt to enter into further combination. There is certainly a binoxalate of soda; but this binoxalate cannot support the further attachment to it of two atoms of hydrated oxalic acid, and there is no quadroxalate of soda.

11. *Binoxalate of Soda.*

This salt I find to resemble the binoxalate of potash, in containing three atoms of water. 22.11 grains, strongly ignited, left 8.05 grains fused carbonate of soda; or 100 binoxalate leave 40.67 carbonate of soda, equivalent to 23.84 soda; while a binoxalate with three atoms of water should yield 23.95 per cent. soda, or almost exactly the experimental result. The binoxalate of soda lost little more than 1 per cent. of its weight when kept at 212° Fahr. over sulphuric acid *in vacuo*. But by a heat approaching 300° Fahr. the salt lost 14.64 per cent. of water, which is a little more than two atomic proportions, namely, 13.78 per cent. Hence this salt retains the whole of its constitutional water at 212°, but loses two atoms of it at a higher temperature, retaining strongly the third atom of water, which is basic.

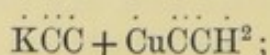
*Double Oxalates.*

The number of double oxalates is not so great as is generally supposed. On mixing a solution of binoxalate of potash either with the muriate or the sulphate of magnesia, zinc, etc., the oxalate of magnesia

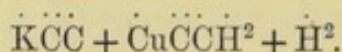


or of zinc precipitates, while the quadroxalate of potash is formed, and remains in solution or crystallizes, being very sparingly soluble, according to circumstances. When binoxalate of potash is digested upon magnesia or upon oxide of zinc, a portion of the oxide is dissolved, but is quickly deposited again as an insoluble oxalate, and no double salt formed. But one member at least of the magnesian class of oxides, namely, oxide of copper, is dissolved by the binoxalates of the alkalies, and forms double salts, which were discovered and carefully examined by M. Vogel of Bayreuth.

12. *Oxalate of Copper and Potash.*



and also



The binoxalate of potash, when considerably diluted, and digested with heat upon the oxide of copper, dissolves it easily, and a double salt of sparing solubility crystallizes, presenting itself generally in two forms, one of which contains two and the other four atoms of water, according to the analyses of M. Vogel, which I have repeated and confirmed so far as the water is concerned. The crystals containing four atoms of water soon become opake by exposure to the air, and lose two atoms of water by efflorescence.

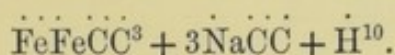
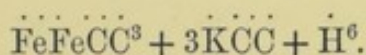
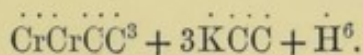
Binoxalate of ammonia likewise dissolves oxide of copper, and does so still more readily than the binoxalate of potash, which may depend upon the circumstance that the resulting double salt of ammonia is considerably more soluble in water than the double salt of potash. The oxalate of copper and ammonia crystallized in plates of a blue colour, and seemed to affect one form only. Of these plates, 9.38 grains were readily decomposed by heat, and left 2.37 grains black oxide of copper, or 25.27 per cent., which is almost exactly the proportion of that of the oxide of copper, which a salt of two atoms water should contain, namely, 25.37 per cent. This salt loses water readily at 212° Fahr.; and of the 11.52 per cent. which it is supposed to have on the theory of its containing two atoms of water, 11.46 per cent. escaped by the exposure of the salt to that temperature. M. Vogel describes two other double oxalates of copper and ammonia; but it is evident that they contain ammonia and not oxide of ammonium; so that they do not come under our consideration at present.

It is to be remarked that the oxalate of copper and potash is represented above by a formula quite analogous to that of binoxalate of potash, oxide of copper being simply substituted for basic water. We



have oxalate of potash in both cases, to which there is attached oxalate of copper with two atoms of water in the one formula, and oxalate of water with two atoms of water in the other. It is to be remembered that in the case of the sulphates, the double sulphate of copper and potash was shown to have a similar analogy in constitution to the bisulphate of potash.

*Oxalate of Chromium and Potash, of Peroxide of Iron and Potash, of Peroxide of Iron and Soda, etc.*



This group of salts has not hitherto been submitted to analysis, although they occupy the same important position among the oxalates which the alums do among the sulphates.

### 13. *Oxalate of Chromium and Potash.*

This remarkable salt was first described by Dr. Gregory, and its optical properties have been made the subject of a memoir by Sir David Brewster.<sup>1</sup> It is easily prepared by the following process, which is Dr. Gregory's, with the proportions slightly altered, from a knowledge of the composition of the salt. One part of bichromate of potash, two parts binoxalate of potash, and two parts hydrated oxalic acid, are dissolved together in hot water. There is a copious evolution of carbonic acid gas, arising from the deoxidation of the chromic acid, and nothing fixed remains except the salt in question; of which a pretty concentrated solution crystallizes upon cooling in prismatic crystals, which are black by reflected light, but of a splendid blue colour by transmitted light, when sufficiently thin to be translucent.

This salt, strongly dried without decomposition, was found to lose 11.67 per cent. of water.

The oxide of chromium cannot be precipitated from it completely by means of an alkaline carbonate, and it is very remarkable that only a small portion of the oxalic acid is thrown down from this salt by chloride of calcium.

To determine the proportion of oxalic acid, the salt was heated in strong sulphuric acid, and the gases allowed to escape through a tube containing chloride of calcium. 15.19 grains of the crystals lost 6.71

<sup>1</sup> *Philosophical Transactions*, 1835.



grains by this treatment, which loss is the weight of the oxalic acid. Hence this salt contains 44·17 per cent. of oxalic acid.

When this double oxalate is ignited, carbonic oxide escapes, and the residuary salt is a mixture of chromate and carbonate of potash, which is entirely soluble in water, and contains no oxide of chromium. In four experiments the fused residuary salt amounted to 0·5458, 0·5411, 0·5454, and 0·5425 of the weight of the crystals operated upon, while it should be 0·5433, provided this residuary salt is a mixture of two atoms chromate and one atom carbonate of potash, and that the composition of the crystals is as follows :

One atom oxide of chromium, $\ddot{\text{Cr}}\ddot{\text{Cr}}$ , . . . . .	1003·6	16·28
Three atoms potash, $3\ddot{\text{K}}$ , . . . . .	1769·7	28·70
Six atoms oxalic acid, $6\ddot{\text{C}}\ddot{\text{C}}$ , . . . . .	2717·4	44·07
Six atoms water, $6\ddot{\text{H}}$ , . . . . .	675·	10·95
	<hr/>	<hr/>
	6165·7	100·

The results in regard to the water and oxalic acid narrated above, agree completely with this view, and so does the determination of the oxide of chromium. 26·01 grains of the crystals left, when ignited, 14·08 grains of the mixed chromate and carbonate of potash, which were dissolved in water, and being acidulated with acetic acid, the chromic acid was precipitated by acetate of lead, and gave 17·45 grains chromate of lead, equivalent to 4·28 grains oxide of chromium. Hence by this experiment the crystals contain 16·46 per cent. of oxide of chromium, which approaches very nearly to the theoretical result. The fused residuary chromate and carbonate of potash amounted to 0·5425 of the weight of the crystals, which is so near the theoretical result, namely, 0·5433, that we may safely conclude that the quantity of potash in the salt agrees with our theoretical estimate.

This salt is clearly, therefore, a compound of one atom oxalate of chromium, containing three atoms oxygen in the oxide and nine atoms oxygen in the acid, with three atoms oxalate of potash ; and the salt has six atoms of water of crystallization. The oxygen in the oxide of chromium being 1, that in the potash is also 1, that in the water 2, and that in the oxalic acid 6.

I made several attempts to crystallize the oxalate of chromium itself, but without success, so that I had no opportunity of studying its constitution in relation to the constitution of the preceding double salt.



14. *Oxalate of Peroxide of Iron and Potash.*

This salt, which has not hitherto been described, is formed by dissolving the hydrated peroxide of iron to saturation in binoxalate of potash. There is no effervescence, but a sap-green solution results, which, when concentrated, deposits the salt in question in tabular crystals, of which the form has no resemblance to that of the corresponding oxalate of chromium and potash, and which are of a beautiful grass-green colour. These crystals are permanent in the air, unless it is very dry, when they lose water by efflorescence and become brown and opake. The solution of the salt is decomposed by ammonia, and the peroxide of iron completely thrown down. The salt, when ignited, leaves peroxide of iron and carbonate of potash. It loses 10·56 per cent. of water at a temperature not exceeding 230° Fahr., but is partially decomposed at 300°. Below, the theoretical composition of this salt is placed in juxtaposition with the results of an analysis.

	Theory.	Experiment.
One atom peroxide of iron, . . .	15·93	16·13
Three atoms potash, . . .	28·82	29·07
Six atoms oxalic acid, . . .	44·25	43·74
Six atoms water, . . .	11·00	10·56
	<hr/> 100·	<hr/> 99·50

Hence its composition is the same as that of the preceding salt, iron being substituted for chromium.

15. *Oxalate of Peroxide of Iron and Soda.*

This salt is formed by dissolving the hydrated peroxide of iron in binoxalate of soda. It crystallizes in solid green crystals. It is composed as follows, the water being calculated from the loss on the analysis :

	Theory.	Experiment.
One atom peroxide of iron, . . .	16·32	16·56
Three atoms soda, . . .	19·57	19·66
Six atoms oxalic acid, . . .	45·34	45·51
Ten atoms water, . . .	18·77	18·27
	<hr/> 100·	<hr/> 100·

Of the ten atoms water which this salt contains it readily loses six at 212° Fahr., and retains four atoms water at that temperature. It differs, therefore, in composition, and it does so also in form, from either of the preceding double oxalates.

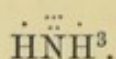


A corresponding oxalate of chromium and soda was produced by a similar process, and crystallized with some difficulty in solid dark crystals, which appeared to have the same form as the preceding soda-salt, and were found, like it, to contain ten atoms of water.

There is also a double oxalate of alumina and potash, which may be made by dissolving hydrated alumina in binoxalate of potash, and crystallizes in white tables of a pearly lustre, which have the same form as the oxalate of iron and potash.

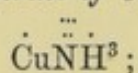
## II. OF NITRATES.

### 1. *Hydrated Nitric Acid, the Nitrate of Water.*

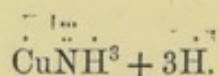


Nitric acid combines with one atom of water as base, and with three atoms more by a less powerful affinity. The well-defined character of the combination containing four atoms water, which is the acid of specific gravity 1.42, is evinced in its high boiling point and in an appearance of saturation which it exhibits. The true and complete nitrate of water has therefore three atoms of constitutional water attached to it. And in the case of the nitrates of those metallic oxides which correspond with water in their basic character, we find the water of crystallization likewise to be three atoms, or a multiple of three, and no other number.

### 2. *Nitrate of Copper.*



and also



There are two nitrates of copper, one of which crystallizes in prisms, and the other in rhomboidal plates of a lighter blue colour than the prisms; the first of which I find to contain three and the other six atoms of water. Both are deliquescent to a certain degree, the salt which contains the large proportion of water being more so than the other.

(1.) Of the dark blue prisms, 28.12 grains carefully calcined left 8.98 grains black oxide, or 31.94 per cent. In a second experiment, 22.9 grains left 7.34 grains oxide, or 32.05 per cent. The salt being neutral in composition, the quantity of nitric acid may be inferred from the oxide of copper, and the difference between their sum and the weight of the salt operated upon is the water. By the first analysis the water



amounts to 3.38, and by the second to 3.28 atomic proportions. The excess above three atoms is probably hygrometric moisture, to remove which from this salt we cannot employ the ordinary means. In a third experiment upon a portion of the same salt, which has been dried over sulphuric acid till it began to effloresce, 33.19 grains of nitrate left 11.04 grains oxide, which gives 2.83 atomic proportions of water to the salt, or the result is a little below the three atoms. Hence this nitrate may safely be supposed to possess three atoms of water.

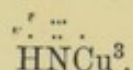
(2.) Of the lighter coloured crystals in plates, 10.60 grains left 2.78 grains oxide of copper when ignited, or 27.36 per cent. Hence the salt is composed of

				With six atoms water.
Nitrate of copper, . . .	6.57	100.		100.
Water, . . . . .	4.03	61.33		57.54
	<hr/> 10.6	<hr/> 161.33		<hr/> 157.54

The experimental determination is a little above the theoretical estimate, as might be expected from the deliquescent nature of the salt.

The crystals speedily became opaque over sulphuric acid *in vacuo*, and 10.6 grains lost 2.18 grains water in a night, retaining 1.85 water; which is 28.16 water retained to 100 anhydrous salt, or almost exactly three atoms of water. Hence this salt parts easily with half its water. The other three atoms of water are retained more strongly; for by a second day's exposure over sulphuric acid there was an additional loss of only 0.15 grain water; or the water retained was reduced to 25.87 parts united to 100 anhydrous salt.

### 3. Subnitrate of Copper.



It is well known that when the nitrate of copper is heated to the temperature of 400° or 500° Fahr. it is decomposed, nitric acid and water being expelled, and a subnitrate remaining, which consists of one atom of nitric acid, one atom of water, and three atoms of oxide of copper. This decomposition I find to take place and be completed at a very moderate temperature, not exceeding 150° Fahr.; and it appears, besides, that none of the three constitutional atoms of water of the nitrate of copper can be expelled without a certain corresponding loss of acid: that on heating the salt in question, nitric acid and water go off together, in the form of nitrate of water with its three atoms water. Thus, three atoms of crystallized nitrate of copper, containing three atoms acid, three atoms oxide, and nine atoms of water, are resolved into two atoms nitrate of water, each containing one atom acid and four water; and one atom of



subnitrate of copper, which contains one atom acid, one water, and three oxide of copper.

*Experiment.*—In a stove of which the temperature never exceeded  $150^{\circ}$  Fahr., 27.54 grains crystallized nitrate of copper, containing three atoms of water, exposed on a capsule, suffered the following gradual reduction of weight: a loss of 2.59 grains in one day, of 9.62 in six days, of 11.1 in seven days, of 13.35 in eleven days, of 13.47 in twelve days, of 13.58 in sixteen days, of 13.60 in eighteen days, and nothing more afterwards by a heat of  $300^{\circ}$  Fahr., continued for several hours. Of the crystallized nitrate, 27.54 grains have left 13.94 grains subnitrate; or we have 0.5062 subnitrate from 1 nitrate. By calculation the residuary subnitrate should be 0.5026, with which the experimental result closely corresponds.

Another portion of the same nitrate of copper, dried exactly in the same way, lost 1 per cent. of its weight when afterwards heated to  $400^{\circ}$  Fahr.; and thereafter, being ignited, was found to consist of

	Experiment.	Theory.
Oxide of copper, . . .	100.	100.
Volatile matter, . . .	53.19	53.1
	<hr/> 153.19	<hr/> 153.1

I am satisfied that no other subnitrate except the preceding, which contains three atoms of oxide of copper, can be obtained by the decomposition of the neutral nitrate by means of heat. For a quantity of the subnitrate of copper of the first experiment narrated above being gradually exposed in a platinum crucible to a heat above the melting point of lead, by means of a sand-bath, so as actually to reduce a portion of the subsalt in contact with the bottom of the crucible to the state of black oxide, yet the major portion of the subsalt, which still retained its green colour, was found to be little altered in composition. After this extreme heating the subsalt consisted of

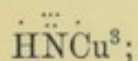
Oxide of copper, . . .	100.
Volatile matter, . . .	50.6
	<hr/> 150.6

Or the proportion of volatile matter in the subsalt has suffered only a small reduction, namely, from 53.1 to 50.6 parts. This last subnitrate afforded drops of nitric acid with fumes of nitrous acid when heated in a tube, so that the subnitrate of copper retains water even at a temperature above the melting point of lead.

The subnitrate of copper merits a careful consideration; for the subsalts of the magnesian class of oxides, which can be had



of a definite composition, are really much fewer in number than is generally supposed. What constitution ought to be assigned to this salt? It will be observed that I have represented it by the singular formula



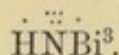
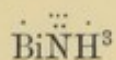
implying that the single atom of water which it contains is really the base of the salt, and that the three atoms of oxide of copper are in the place of the constitutional water of this nitrate of water. This opens a new view of the constitution of subsalts. The excess of metallic oxide which they contain may not be basic at all in certain cases like the present, but discharge a function in the constitution of the salt which has hitherto been recognised only as executed by water. For if we find water and oxide of copper strongly resembling each other as bases, why may not the analogy between them extend further, and oxide of copper be capable of discharging the function of constitutional water or water of crystallization in the composition of a salt? Indeed, the speculation that all salts whatever are neutral in composition is highly probable. Where the metallic oxide is in excess, as in what are called subsalts, we can attribute another function than that of base to the whole or a portion of the metallic oxide, and thus preserve the salt neutral in composition, or according to its formula. To this subject I shall again recur.

The following observation is particularly favourable to the view which we are taking of the constitution of subnitrate of copper. When the black oxide of copper is drenched with the strongest nitric acid, it is a subnitrate of copper which is formed, although the nitric acid may be in great excess. The black oxide is converted into a green powder, from which the excess of nitric acid should be drained off as well as possible, and the powder will be found to be in great part insoluble in water. The explanation seems to be, that the concentrated nitric acid employed does not contain the constitutional water which the neutral nitrate of copper requires, and accordingly that salt is not formed; but the nitrate of water supplies itself with oxide of copper in the place of its deficient constitutional water; so that the result is a nitrate of water with three atoms of oxide of copper attached. But when nitric acid of a specific gravity not exceeding 1.42 is digested upon the same black oxide of copper, the neutral nitrate of copper only is formed, and no subnitrate.

This view seems likewise to be necessary to account for the great force with which the single atom of water is retained by the subnitrate of copper. The water cannot be expelled without decomposing the salt, notwithstanding the great excess of oxide of copper present.



## 4. Nitrate and Subnitrate of Bismuth.



The neutral nitrate is admitted to contain three atoms of water, like the nitrate of copper, and its constitution appears to be similar.

No portion of the constitutional water of this salt can be expelled without decomposing the salt. Indeed, this salt loses acid by exposure to dry air at a temperature not exceeding 80° Fahr. The crystals of the salt are resolved by a heat of 212° into a solid and fluid portion, the first of which is probably the subnitrate, while the last is hydrated nitric acid, containing much nitrate of bismuth in solution, and not a supernitrate of bismuth. But the fluid portion fixes so readily upon cooling that the solid product cannot be obtained in a definite state.

*Experiment.*—28·61 grains of nitrate of bismuth in good crystals, being exposed to a gradual ignition, left 14·16 grains of fused oxide of bismuth. This result accords with the view which is taken above of the composition of this salt :

		Experiment.	Theory.
Oxide of bismuth, .	14·16	100·	100·
Nitric acid and water,	14·45	102·04	102·72
	<hr/> 28·61	<hr/> 202·04	<hr/> 202·72

It appears likewise that three atoms of the hydrated nitrate of bismuth are resolved, when dried at a high temperature, into two atoms hydrated nitrate of water and one atom subnitrate of bismuth, which last is of the same constitution as the subnitrate of copper.

*Experiment 1.*—Dried on the sand-bath at a temperature above the melting point of tin, 28·61 grains of nitrate of bismuth lost 9·29 grains, and retained 5·16 grains of volatile matter, or consisted of

		Experiment.	Subnitrate by theory.
Oxide of bismuth, .	14·16	100·	100·
Volatile matter, .	5·16	36·44	34·24
	<hr/> 19·32	<hr/> 136·44	<hr/> 134·24

*Experiment 2.*—A portion of nitrate dried in a stove at a temperature not exceeding 180° Fahr., till it ceased to lose weight, was thereafter found to consist of

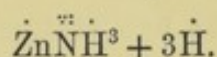
Oxide of bismuth, . . .	21·24	100·
Volatile matter, . . .	7·57	35·64
	<hr/> 28·81	<hr/> 135·64



It appears from the second of these experiments that the subnitrate of bismuth may be produced at a temperature so low as 180° Fahr., and from the first experiment that the subnitrate may be exposed to a temperature of 500° Fahr. without decomposition.

Several experiments were made to produce another definite subnitrate, containing a greater proportion of oxide of bismuth, by the action of heat upon this subnitrate, but without success. The salt was partially decomposed at various temperatures under redness, but no definite compound resulted. Hence the subnitrate described is probably the only definite subnitrate of bismuth that can exist. The small pearly crystals obtained on throwing the neutral nitrate of bismuth into a moderate quantity of water, are of the same composition as the subnitrate obtained by heat.

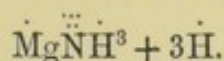
#### 5. Nitrate of Zinc.



This salt is easily obtained by dissolving zinc in nitric acid. It is very soluble in water, and moderately deliquescent.

*Experiment.*—29·17 grains of the crystals ignited, left 7·86 grains oxide of zinc. In this experiment we have 0·2694 oxide from one salt, which is very near 0·2713 oxide, the proportion which should be left, supposing the salt to contain six atoms of water. By efflorescence at 212° one part of this salt loses 0·18 water, which is one-half of the whole water which the salt is assumed to contain, namely, 0·3639 water. It loses no acid at 212°. Hence this salt is of the same constitution as the nitrate of copper, but is not decomposed at so low a temperature. The proportion of water, however, cannot be reduced below three atoms without a loss of acid, and there appears to be a subnitrate of zinc resembling the subnitrate of copper.

#### 6. Nitrate of Magnesia.



*Experiment.*—27·12 grains of crystals of nitrate of magnesia, when calcined, left 4·3 grains caustic magnesia; a result which indicates 6·17 atomic proportions of water in the salt, or the salt contains six atoms of water.

The nitrate of magnesia stands exposure to a heat which would melt lead without losing acid. At that high temperature the proportion of water is reduced to one atom, which cannot be expelled without loss of



acid. The salt remains in a fused state and transparent, and dissolves afterwards completely in water.

*Experiment.*—18·40 grains of the crystals, containing 7·71 grains water, lost 6·60 grains by a strong sand-bath heat continued till the salt ceased to lose weight. This is a loss of exactly five-sixths of the water contained in the salt.

*Experiment.*—19·76 grains, containing 8·28 water, by similar treatment lost 6·77, which approaches very closely to 6·90 grains, the number representing five atomic proportions of water.

This single atom of water retained by the nitrate of magnesia, is not displaced and expelled upon heating the salt, together with an atomic proportion of nitrate of potash to 600° or 700° Fahr., so that the retention of an atom of water does not indicate a disposition, upon the part of nitrate of magnesia, to form a double salt. It is probable that this peculiar and intimate combination of nitrate of magnesia with one atom water does not exist in the crystals or ordinary hydrate of nitrate of magnesia, but is the result of a new arrangement of the constituents of the salt at a high temperature. There are indications of the existence of a similar nitrate of water.

There does not appear to be a subnitrate of magnesia like the subnitrate of copper.

#### *Supposed Double Nitrates and Supernitrates.*

As double nitrates are said to exist, I have repeatedly attempted to form them; but when nitrate of magnesia, nitrate of zinc, or nitrate of copper was mixed with nitrate of potash or with nitrate of ammonia, the salts uniformly separated again in crystallizing. There is no proof of the existence of a single supernitrate.

Most of the nitrates of oxides not belonging to the magnesian class are anhydrous salts, such as the nitrates of potash, soda, barytes, strontian, lead, etc., and do not suggest any new subject-matter of inquiry.

### III. OF PHOSPHATES.

In the present state of our knowledge phosphoric acid is quite peculiar in being capable of combining with bases in three different proportions, forming, besides the usual class of salts containing one atom of acid to one atom of protoxide as base, two other anormal classes of salts, in which two or three atoms of base are united to one atom of acid, namely, the pyrophosphates and the common phosphates. Arsenic acid forms only one class of salts, but that class is anormal, every member of it containing three atoms of base to one atom of acid, like the common



phosphates. These anormal classes of phosphates and arseniates, with perhaps the phosphites, are, I believe, the only known salts to which the ordinary idea of a subsalt is truly applicable; or in the formulæ of these salts only, ought more than one atom of any protoxide to appear in a basic relation to one atom of acid. All other reputed subsalts are probably neutral in composition, as I have endeavoured to show in the case of the subnitrate of copper; for to this salt they all bear an analogy in their small solubility and other properties, while they exhibit little resemblance to those classes of phosphates and arseniates which really possess more than one atom of base. The following Table contains the formulæ of the most important phosphates, with a new nomenclature of these salts, which I offer for consideration.

*First Class.*

Monobasic phosphate of water (metaphosphate of water), . . . . .	$\text{H}\ddot{\text{P}}.$
Monobasic phosphate of soda (metaphosphate of soda), . . . . .	$\text{Na}\ddot{\text{P}}.$

*Second Class.*

Bibasic phosphate of water (pyrophosphate of water), . . . . .	$\text{H}^2\ddot{\text{P}}.$
Bibasic phosphate of soda and water (bipyrophosphate of soda), . . . . .	$\text{NaH}\ddot{\text{P}}.$
Bibasic phosphate of soda (pyrophosphate of soda), . . . . .	$\text{Na}^2\ddot{\text{P}} + 10\text{H}.$

*Third Class.*

Tribasic phosphate of water (common phosphate of water), . . . . .	$\text{H}^3\ddot{\text{P}}.$
Tribasic phosphate of water and soda (biphosphate of soda), . . . . .	$\text{NaH}^2\ddot{\text{P}} + 2\text{H}.$
Tribasic phosphate of soda and water (phosphate of soda), . . . . .	$\text{Na}^2\text{H}\ddot{\text{P}} + 24\text{H}.$
Tribasic phosphate of soda (subphosphate of soda), . . . . .	$\text{Na}^3\ddot{\text{P}} + 24\text{H}.$
Tribasic phosphate of soda, ammonia, and water (microcosmic salt), . . . . .	$\text{NaNH}^4\ddot{\text{P}} + 8\text{H}.$
Tribasic phosphate of magnesia and water (phosphate of magnesia), . . . . .	$\text{Mg}^2\text{H}\ddot{\text{P}} + 2\text{H} + 12\text{H}.$
Tribasic phosphate of magnesia and ammonia (ammoniac-magnesian phosphate), . . . . .	$\text{Mg}^2\text{NH}^4\ddot{\text{P}} + 2\text{H} + 10\text{H}.$



It is my object to get rid of the trivial names pyrophosphates, metaphosphates, and common phosphates, which have tended to keep up an erroneous impression that the phosphoric acid is of a different nature in these classes of salts, or is modified in some way unknown. This notion has arisen from the pertinacity with which phosphoric acid continues combined with a constant number of atoms of base, whether it be one, two, or three, although the base itself be repeatedly changed by decomposing the original combination. But this is an occurrence quite analogous to the formation of different sets of sulphurets or of chlorides, when we decompose two or more different oxides of the same metal, such as the oxide and suboxide of mercury, by sulphuretted hydrogen or by muriatic acid. The metal continues in the same relative state of saturation throughout a series of such decompositions; and so does the phosphoric acid, because in both cases the decomposition is effected by an equivalent substitution.

A difficulty occurs in naming two members of the tribasic class, so as to distinguish them from each other, namely, the biphosphate of soda and phosphate of soda, both of which contain soda and water as base. But this difficulty is obviated by placing first in the name that base of which two atoms are present. Thus the biphosphate of soda is "the phosphate of water and soda," and the phosphate of soda is the phosphate of soda and water, both being at the same time characterized as "tribasic."

What I have to add at present in regard to the phosphates relates chiefly to the last three salts, of which formulæ are given in the preceding Table, which belong to classes of tribasic phosphates that were not examined in my former paper upon the phosphates.<sup>1</sup> But I may premise a few observations, which are more strictly supplementary to the results of that paper.

1. The bibasic phosphate of water (pyrophosphate of water) is possessed of very considerable stability. Both weak and concentrated solutions of this salt have been kept for five or six months without any sensible change or production of the tribasic phosphate of water.

2. It appears to be impossible to crystallize any bibasic phosphate (pyrophosphate) of potash. Such salts can exist in solution, but not in the dry state. The same observation applies to the bibasic phosphates of ammonia, or we have no pyrophosphates of ammonia except in solution. Indeed, the solution of the bibasic phosphate of water and ammonia assumes another atom of basic water when the evaporation is carried far, and crystallizes as the tribasic phosphate of water and ammonia (biphosphate of ammonia).

3. In the case of tribasic phosphates containing potash, I have suc-

<sup>1</sup> *Philosophical Transactions*, 1833.

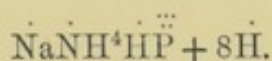


ceeded in crystallizing the tribasic phosphate of potash, and the tribasic phosphate of water and potash, but not the tribasic phosphate of potash and water, or what would be considered on the old view as the neutral phosphate of potash.

4. Both the bibasic and tribasic phosphates of water may be treated with an excess of caustic potash in solution without the formation of any precipitate or sparingly soluble combination. It is only in the monobasic phosphate of water that a sparingly soluble combination is formed by potash, such as that which is described by Dr. Thomson under the name of diphosphate of potash.

1. *Tribasic Phosphate of Soda, Ammonia, and Water.*

(*Phosphate of Soda and Ammonia: Microcosmic Salt.*)



I have repeated more than once the analysis of this salt, and obtained the same result as M. Mitscherlich. It appeared to contain 0.5094 of volatile matter: and there may be derived from an atom of this salt one atom of phosphoric acid, of soda and of ammonia respectively, and ten atoms of water. It has hitherto been viewed as a double phosphate or combination of phosphate of soda with phosphate of ammonia; but no reason can be assigned why these particular salts should combine together, and combinations of salts of soda and ammonia are exceedingly unusual. The view expressed above in the formula is much more likely to be true, namely, that this salt is simply a tribasic phosphate, of which the three atoms of base are all different: they are soda, oxide of ammonium, and water; and the salt possesses eight atoms of water of crystallization. By a graduated heat it is possible to expel the water of crystallization of this salt, and likewise the ammonia of its oxide of ammonium; and the water of the last remaining as base, the salt

$\text{NaH}^2\text{P}$  is produced.

M. Mitscherlich now admits that there is no tribasic phosphate corresponding with this, but containing potash instead of oxide of ammonium, a conclusion of which I have ascertained the accuracy.

I endeavoured to form a tribasic phosphate to contain two atoms soda and one atom of oxide of ammonium, but such a salt appears to have no existence. For when ammoniacal gas was passed into a strong and hot solution of the common phosphate of soda, a slight deposition of the tribasic phosphate of soda took place, followed by the rhomboidal crystals of the common phosphate unchanged.

It likewise appears that when the bibasic phosphate of soda and the



bibasic phosphate of potash (pyrophosphates) are mixed together, no new salt is produced; but the former may be crystallized out, and the latter remains uncrystallizable.

2. *Tribasic Phosphates containing Oxides of the Magnesian Class.*

(1.) *Tribasic Phosphate of Zinc and Water. (Phosphate of Zinc.)*



This salt, which is nearly insoluble, is obtained in minute silvery plates, by mixing three ounces of sulphate of magnesia with four ounces of phosphate of soda, each dissolved in two pounds of cold water. These crystalline plates consist of

		Theory of $\text{Zn}^2\ddot{\text{H}}\ddot{\text{P}} + 2\ddot{\text{H}}.$
Anhydrous salt, .	100·	100·
Water, . .	19·63	17·77
	<hr/> 119·63	<hr/> 117·77

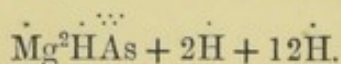
Dried above the melting point of tin the crystals still retained a glistening appearance, but had lost two-thirds of their water; for they now consisted of

		Theory of $\text{Zn}^2\ddot{\text{H}}\ddot{\text{P}}.$
Anhydrous salt, .	100·	100·
Water, . .	6·08	5·92
	<hr/> 106·08	<hr/> 105·92

The two atoms of water which are expelled in the above experiment are, notwithstanding, pretty strongly attached to the salt, being retained at the boiling point of water. Indeed, these two atoms of water are highly constitutional, and are found in all the phosphates of this class.

This phosphate fuses at a red heat, after it becomes anhydrous, but it continues soluble in dilute acids.

(2.) *Tribasic Arseniate of Magnesia and Water. (Arseniate of Magnesia.)*



This salt precipitated on mixing dilute solutions of 500 grains of arseniate of soda and 300 grains of sulphate of magnesia. It consisted of



		Theory of $\text{Mg}^2\text{H}\ddot{\text{A}}\text{s} + 14\text{H}$ .	
Anhydrous salt,	.	100·	100·
Water,	.	86·58	86·25
		<hr/>	<hr/>
		186·58	186·25

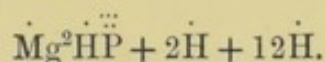
This salt contains in all fifteen atoms of water, of which three are retained and twelve expelled at the boiling point of water. Dried at  $212^\circ$  it consisted of

		Theory of $\text{Mg}^2\text{H}\ddot{\text{A}}\text{s} + 2\text{H}$ .	
Anhydrous salt,	.	100·	100·
Water,	.	17·17	17·25
		<hr/>	<hr/>
		117·17	117·25

It therefore retains pretty strongly two atoms of water besides its basic atom, resembling the preceding salt in this respect.

This arseniate and the corresponding phosphate are rendered insoluble in dilute acids by the effect of a strong red heat.

(3.) *Tribasic Phosphate of Magnesia and Water. (Phosphate of Magnesia.)*



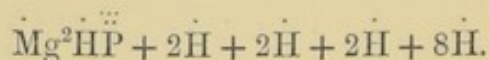
This salt appears in distinct prismatic crystals in the course of twenty-four hours, upon mixing two ounces of sulphate of magnesia with three ounces phosphate of soda, each dissolved in two pounds of water. Cold water is capable of dissolving about one thousandth part of its weight of these crystals. They have been stated erroneously to be much more soluble. The proportion of water which they contain has hitherto been stated at fourteen atoms instead of fifteen, which is the truth. By analysis the crystals were found to consist of

		Theory of $\text{Mg}^2\text{H}\ddot{\text{P}} + 14\text{H}$ .	
Anhydrous salt,	.	100·	100·
Water,	.	121·7	119·76
		<hr/>	<hr/>
		221·7	219·76

I find that the proportion of water retained by this salt is readily reduced at  $212^\circ$ , from fifteen atoms to seven, by the escape of eight atoms of water. Of the seven atoms retained one is basic, and therefore expelled with difficulty; but from a variety of experiments which I have performed it appears probable (although I have never attained very precise results) that the other six atoms go off in pairs at different temperatures between  $212^\circ$  and  $350^\circ$  Fahr. But even at  $410^\circ$  the quantity of water retained by this salt was sensibly above one atomic



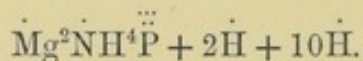
proportion. We may with considerable probability represent the consecutive combinations of this salt with water by such a formula as the following :



Besides the preceding salt there is a tribasic phosphate of magnesia, which is obtained as an insoluble precipitate on mixing tribasic phosphate of soda with sulphate of magnesia. Of this salt the whole three atoms of base are magnesia, as its name implies. Dried at  $212^{\circ}$  it retains five atoms of water. At a red heat it glows, but it continues soluble in acids even after exposure to a white heat. But I did not succeed in forming the other tribasic salt, containing two atoms of water and one atom of magnesia as bases, which is wanted to complete the series. Such a salt does not appear to exist.

It may be mentioned here in reference to the monobasic phosphate of magnesia (metaphosphate of magnesia), that although this salt does not present itself on mixing the monobasic phosphate of soda with the sulphate of magnesia, yet it is readily precipitated in the form of a soft viscid body, on using the acetate of magnesia instead of the sulphate.

(4.) *Tribasic Phosphate of Magnesia and Ammonia.* (*Ammoniaco-magnesian Phosphate.*)



This salt is the well-known granular precipitate formed on adding a salt of magnesia to any soluble tribasic phosphate with which ammonia or a salt of ammonia has been mixed. I was much interested in ascertaining the true constitution of this salt, and have carefully analysed seven or eight different specimens of it, prepared with and without free ammonia in the liquors. The result is that only one tribasic salt of these constituents exists, although two have often been admitted ; while in this compound there exists only one atom of ammonia instead of two, as M. Riffault has supposed. I subjoin the preparation and analysis of one specimen of this salt. 350 grains of crystallized phosphate of soda, 100 grains of chloride of ammonium, and 200 grains of *aqua ammoniæ* were dissolved together in four pounds of cold water, and 200 grains of crystallized sulphate of magnesia were added to that mixture. The precipitation was gradual, and the liquor remained alkaline. The precipitate was slightly washed with cold water, and afterwards dried in the air for ten days, the thermometer being  $65^{\circ}$  Fahr., without artificial heat. The true proportions of water, which this and many other precipitates affect, have often been mistaken, and definite hydrates not



obtained, from using hot solutions in their preparation. Of this precipitate 26·8 grains lost by ignition 14·5 grains, or one part of the precipitate contains 0·541 volatile matter. For the ammonia, the volatile matter from 9·65 grains of the precipitate was sent over quicklime contained in a tube, so as to arrest the water. The loss, or the ammonia, amounted to 0·67 grain, or to 0·0695 of the precipitate. Hence this precipitate consists of

		Theory of $\text{Mg}^2\text{NH}_4^{\text{III}}\text{P} + 2\text{H} + 10\text{H}.$
Anhydrous salt, . . .	45·90	45·85
Ammonia, . . . . .	6·95	6·98
Water, . . . . .	47·15	47·17
	<hr/> 100·	<hr/> 100·

From the manner in which this specimen of the salt was prepared, it should contain the maximum proportion of ammonia of which the salt admits, and yet that proportion is one atom only, and not two, as it was estimated by Riffault. A salt of the same composition was obtained from the same materials, omitting the caustic ammonia. In that case the product was not so abundant, and the mother liquor remained acid from the production of tribasic phosphate of water and soda, which has an acid reaction. When this salt, contained in a little retort, is heated in a very gradual manner to  $212^\circ$  by means of a water-bath, it is possible to distil over ten atomic proportions of the water without any ammonia whatever. Of the three atoms of water which remain (the whole quantity originally present in the salt being thirteen atoms), one appears to be combined with the ammonia in the formation of oxide of ammonium, while the other two are the constitutional water of the tribasic phosphate of magnesia and water.

It appears, then, that this salt is not a double phosphate, or combination of two phosphates, but that it is formed from the tribasic phosphate of magnesia and water, by the substitution of oxide of ammonium for the basic water of that salt; and it is a tribasic phosphate of magnesia and oxide of ammonium. The oxygen in the magnesia is double that in the oxide of ammonium.

This salt is the type of a class of tribasic phosphates, in which the magnesia is replaced by the other oxides, which are isomorphous with that base. Two of these salts were discovered and carefully examined by Dr. Otto of Brunswick.<sup>1</sup>

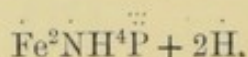
Dr. Otto's analysis of what we may call the tribasic arseniate of manganese and ammonia corresponds exactly with the analysis given above of the magnesian salt, except that he derives only twelve instead of thirteen atoms of water from his salt. The deficiency in the propor-

<sup>1</sup> *Journal für Praktische Chemie*, von Erdman und Schweigger-Seidel, 1834, p. 499.



tion of water found by him, I attribute to the use which he made of hot water in washing his salt.

His analysis of the tribasic phosphate of the protoxide of iron and ammonia is particularly interesting, as it proves that this salt is precipitated, containing no more than three atoms of water, or exactly of the composition of the magnesian salt dried at  $212^{\circ}$ , as we have described. The constitution of this salt of iron I would therefore represent by the formula



In the same paper Dr. Otto describes another extraordinary phosphate, under the name of paraphosphate of soda, ammonia, and oxide of manganese, which does not belong to any class of phosphates that I have examined, but may possibly be a combination of two bibasic phosphates.

Its constituents are  $2\ddot{\text{P}}$ ,  $2\dot{\text{Mn}}$ ,  $\dot{\text{N}}\text{H}^4$  and  $6\text{H}$ . It is prepared from bibasic phosphates, and would be said in the old language to contain pyrophosphoric acid.

#### IV. OF SULPHATES.

In a former paper upon water as a constituent of sulphates,<sup>1</sup> I examined particularly the constitution of hydrated sulphuric acid and of the sulphates of the magnesian class of oxides. All these salts contain one atom of constitutional water, which is displaced in the formation of the double sulphates by an atom of an alkaline sulphate. This view is illustrated by the following formulæ:

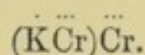
Sulphate of water (acid of sp. gr. 1.78), . . .	$\text{HSH}$
Sulphate of magnesia, . . . . .	$\text{MgSH} + 6\text{H}$
Sulphate of magnesia and potash, . . . . .	$\text{MgS}(\text{KS}) + 6\text{H}$
Sulphate of water and potash (bisulphate of potash), . . . . .	$\text{HS}(\text{KS}).$

It will be found upon experiment that the salts sulphate of magnesia and sulphate of zinc become anhydrous at much lower temperatures when mixed with sulphate of potash than by themselves, the sulphate of potash displacing the constitutional water of the other salt at a very moderate heat, although the salts are mixed in the state of dry powders.

<sup>1</sup> *Edinburgh Transactions*, vol. xiii. p. 297; or *London and Edinburgh Philosophical Magazine*, 3d series, vol. vi. pp. 327, 417.



In that paper the opinion was supported, originally suggested I believe by M. Mitscherlich, that the bisulphate of potash is a double sulphate of water and potash, and therefore really neutral in composition. The only difficulty which stood in the way of generalizing this result, and maintaining that *all* the salts usually considered as bisalts are really neutral in composition, was the composition of the bichromate or red chromate of potash, a salt which unquestionably is anhydrous. Here, it might be said, is a true bisalt. But M. H. Rose has lately published some observations in regard to anhydrous sulphuric acid, which, I think, afford a clew to the discovery of the true constitution of the red chromate of potash. It appears that the vapour of anhydrous sulphuric acid is absorbed by sulphate of potash and by chloride of potassium, without decomposition, and definite compounds formed; which, however, are destroyed by solution in water. Here we appear to have a class of combinations of sulphuric acid *with salts*. Chromic acid, which is isomorphous with sulphuric, forms combinations which I consider as analogous to these. With the neutral or yellow chromate of potash it forms the red chromate of potash, and with chloride of potassium it forms M. Peligot's salt; which differ only from M. Rose's corresponding combinations of sulphuric acid, in being more permanent. The superior stability of these chromic acid combinations unquestionably depends upon the little affinity for water which their acid possesses, while the affinity of sulphuric acid for water is very great. Hence we may suppose that the red chromate of potash is not a direct combination of two atoms of chromic acid with one atom of potash, but a combination of one atom of chromic acid with one atom of yellow chromate of potash; and it may be represented as follows:



The red chromate of potash will thus belong to a new order of combinations, differing essentially from proper salts, which contain an oxide as base. This salt, therefore, cannot be adduced as militating against the law that "all salts are neutral in composition;" the only known exceptions to which law are, I believe, afforded by the anomalous classes of phosphates, phosphites, and arseniates.

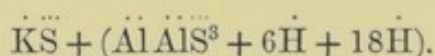
I have devoted much time to the examination of *subsulphates* of the magnesian class of oxides, particularly of the subsulphate of zinc and the subsulphate of copper. These salts were generally formed by the partial precipitation of sulphate of zinc or sulphate of copper by means of caustic potash. They have both a disposition to carry down sulphate of potash, which is never entirely removed from them by washing; while one of them, the subsulphate of zinc, is itself decomposed by washing. When most successfully prepared, they were found to contain four atoms of



metallic oxide to one atom of acid (instead of three atoms oxide, as M. Berzelius supposed), together with four atoms of water. I have not hitherto been able to form a distinct idea of their constitution, or to decide between different views which may be taken of it. But the force with which water is retained in these subsalts is very remarkable. The subsulphate of copper loses no portion of its four atoms of water at  $212^{\circ}$ , and I have not been able to reduce the quantity of water retained by this salt so low as one atomic proportion, even at the melting point of lead.

The constitution of the subsulphate of copper appears to be changed when it is made anhydrous by heat. In the progress of the desiccation of the salt, its colour passes from a dull blue to an olive green, and it finally becomes of a chocolate brown, and is then anhydrous. Water poured upon the brown matter comes off of a blue colour, dissolving out a considerable portion of the soluble sulphate of copper. It appears, therefore, that the water originally present in the subsulphate must discharge some important function in its constitution, the subsalt being obviously decomposed when made anhydrous.

The *Alums* form a most important class of the sulphates, but I have never had it in my power to compare their constitution with that of the sulphate of alumina itself, which is not easily obtained in a crystallized state. The salt, however, is described as containing eighteen atoms of water, while the alums have twenty-four. At present I would merely throw out the conjecture, that in the alums we may have simply an alkaline sulphate with the sulphate of alumina attached, that salt carrying along with it its whole water of crystallization, and acquiring six atoms more. The quantity of water in potash alum may be reduced by efflorescence to six atoms in a stove of the temperature of  $150^{\circ}$  Fahr. Hence potash alum may perhaps be represented as follows :



I have shown by an analysis conducted in very favourable circumstances, that soda-alum contains, like potash-alum, twenty-four, and not twenty-six atoms of water.

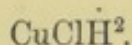
## V. OF CHLORIDES.

The affinity which the hydracids exhibit for water is weak. Of the lower hydrates of muriatic acid we know nothing, the volatility of the acid putting it out of our power to form and examine such hydrates; but it is likely that they will correspond with the hydrates of the chloride of magnesium, etc., which can be examined.



The law in the case of the chlorides of the magnesian class of metals appears to be, that they have two atoms of water pretty strongly attached to them, and which we may consider as constitutional. Thus chloride of copper crystallizes with two atoms of water, and with no lower proportion; but several chlorides of this class have two or four atoms more, the proportion of water advancing by a multiple of two atoms.

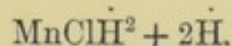
### 1. Chloride of Copper.



The blue prismatic crystals of chloride of copper become brown and lose the greater proportion of their water at a temperature not exceeding the boiling point of water. Fifteen grains of the crystals, exposed to a much higher temperature, lost 3.23 grains of water, leaving 11.77 grains of chloride of copper; and when this quantity of chloride of copper was exposed to the atmosphere, it quickly recovered 3.16 grains of water, and resumed the blue colour of the crystallized salt. I believe this method of reabsorption, in the case of constitutional water, often to give hydrates of which the composition is even more exact than if they had been obtained from solution, owing to the absence of that water, which is often mechanically interposed between the plates of crystals. The hydrated chloride of copper obtained in this way consisted of

			Theory of $\text{CuClH}^2$ .
Chloride of copper, .	11.77	100.	100.
Water, . . . .	3.16	26.85	26.84
	<hr/> 14.93	<hr/> 126.85	<hr/> 126.84

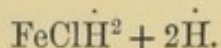
### 2. Chloride of Manganese.



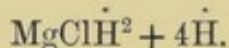
*Experiment.*—Of the flesh-coloured crystals, 15.53 grains, precipitated by nitrate of silver, gave 22.57 grains of chloride of silver, equivalent to 5.56 chlorine, or to 9.92 chloride of manganese, which leaves 5.61 grains water in the salt, or 36.12 per cent. of water. Now a chloride of manganese with four atoms of water would contain 36.33 per cent. of water.

This salt readily lost half its water when dried at  $212^\circ$  in open air, or when dried over sulphuric acid in the vacuum of an air-pump at the ordinary temperature. But when the exposure of the salt in such circumstances was long protracted, a little of the constitutional water also was lost.

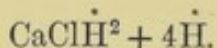


3. *Protochloride of Iron.*

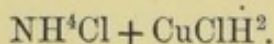
In three experiments made upon different specimens of crystallized protochloride of iron, all newly and very carefully prepared, 13.69 grains chloride of silver were precipitated from 9.72 salt, 17.20 chloride of silver from 12.44 salt, and 15.75 chloride of silver from 11.21 salt. These experiments almost coincide in their results, which are, that 1 part of the salt contains 0.3466, 0.3463, and 0.3461 of chlorine. But such proportions of chlorine are decidedly under the proportion which a neutral salt with four atoms of water should contain, namely, 0.3593 chlorine. Indeed, the quantity of water in the salt is indicated by these experiments to be four and a half atomic proportions almost exactly. By crystallizing from an acid solution Bonsdorff has lately obtained this salt in a state of purity, and containing four atoms of water.

4. *Chloride of Magnesium.*

Of the crystals of this salt, which are decidedly deliquescent, 12.65 grains were found to contain 4.29 chlorine; or the salt contains 33.91 per cent. of chlorine, which approaches sufficiently near to the theoretical proportion 34.69 per cent., supposing the salt to contain six atoms of water.

5. *Chloride of Calcium.*

The crystals of this deliquescent salt, dried *in vacuo* till they began to effloresce, were found to contain six atoms of water, the proportion usually allotted to them; but it is remarkable, that, continued *in vacuo* over sulphuric acid for ten days during the heat of summer, the crystals became opaque and of a talky lustre, without being disintegrated, and their proportion of water was reduced to two atoms.

6. *Double Chloride of Copper and Ammonium.*

Hydrated chloride of copper dissolved with chloride of ammonium, in the proportion of eleven of the first to seven of the last, readily affords



a double salt, in which we appear to have an atom of chloride of ammonium with an atom of the hydrated chloride of copper attached. This double salt is less soluble than the chloride of copper itself, and retains more strongly the two constitutional atoms of water of that salt; illustrating in both of these points what appear to be two very general occurrences: namely, 1st, the reduced solubility of double salts; and, 2d, the closer attachment which constitutional water exhibits for a salt when that salt itself enters into combination.

	Analysis.	Theory of $\text{NH}_4\text{Cl} + \text{CuClH}_2$ .
Chlorine, . . . .	51.03	51.08
Copper, . . . .	23.35	22.83
Ammonium ( $\text{NH}_4$ ), . .	13.20	13.10
Water, . . . .	12.09	12.99
	<hr/> 100.67	<hr/> 100.

The water cannot be entirely expelled without risking the sublimation of chloride of ammonium, and hence the quantity of water obtained is under the truth. The copper is above the truth, from having been precipitated by caustic potash in the state of oxide, which last when so obtained always retains a little potash.

There is a corresponding chloride of copper and potassium, but I did not succeed in forming analogous double salts with chloride of magnesium or with any other chloride of the class in the place of the chloride of copper.

The chlorides have probably their analogues in the cyanides, but with the single cyanides of iron, copper, etc., we are less acquainted. It is worthy of remark, however, that the disposition of the protocyanide of iron and of the cyanide of copper to combine with two atoms of cyanide of potassium may depend upon the cyanides of iron and of copper possessing two atoms of constitutional water (like the corresponding chlorides), which are displaced by two atoms of the alkaline cyanide in the formation of the double cyanides. In "ferrocyanic acid" we have the protocyanide of iron combined with two atoms of hydrocyanic acid, in the place of the same two atoms of water.

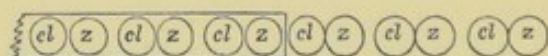


## VIII.

## ON THE THEORY OF THE VOLTAIC CIRCLE.

From *Brit. Assoc. Report*, 1839 (Pt. ii.), pp. 29-31.

PROFESSOR GRAHAM explained the views now received of the propagation of electrical induction through the fluid and solid elements of the voltaic circle, by the formation of chains of polar molecules, each of which has a positive and negative side, and in which no circulation of the electricities is supposed, but merely their displacement and separation from each other in each polar molecule. These electricities in the polar molecule of hydrochloric acid, for instance, are displaced, when the acid acts as an exciting fluid, and the positive electricity is located in the chlorine atom, and the negative electricity in the hydrogen atom. The electricities are, at the same time, made the depositories of the chemical affinities of the chlorine and hydrogen respectively. Mr. Graham proposed to modify this hypothesis so far as to abandon the idea of electricities being actually possessed by these bodies, and to refer the phenomena at once to the proper chemical affinities of the bodies. He assigned similarly polar molecules to the exciting fluid and metals; and taking hydrochloric acid as a type of exciting fluids, he gave to each molecule a pole, having an affinity resembling that of chlorine, or *chlorous* affinity, instead of negative electricity, and another pole, having an affinity resembling that of zinc or hydrogen, or *zincous* affinity, instead of positive electricity. When zinc and acid are in contact, the polar state of a single chain of molecules might be represented as in the figure.



The particle of acid B, next the zinc, has its chlorine atom in contact with the metal and its hydrogen atom distant from it, marked respectively *cl* and *z* in the figure. Part of the affinity of *cl* being engaged by the zinc, the hydrogen is so far received from that affinity, and thus attracts the *cl* of C. Thus, by a sort of induction, the *z* of B causes the *cl* of C to be chlorous, or the molecule of acid C to become polar, and that again the molecule D. In the zinc (the molecule being supposed to contain two chemical atoms), while the external atom of A becomes zincous, from its contact with the acid, the other atom becomes chlorous; so that these atoms of this molecule may be marked *cl* and *z*, and so also the molecules E and I of the zinc, which become polar by induction.



In another diagram Professor Graham showed how this chemico-polar condition is propagated round a voltaic circle. The molecules of the zinc and acid being polar by contact, which is sufficient to develop their affinities, an induction one way through the zinc, and in the opposite direction through the acid, conspire to produce the same polar condition in the molecules. The result is, that the molecule *z* of A is zincous both primarily and by induction, and its affinity for the atom *cl* of B greatly increased; and, consequently, combination can take place between these atoms when the circuit is completed, but not otherwise.

If the connecting wire be broken, and a decomposable liquid, such as hydriodic acid, be interposed between the extremities, a chain of polar molecules comes also to be established in that liquid, the iodine (which is the analogue of chlorine) being the seat of the chlorous affinity, and the hydrogen the seat of the zincous affinity. The extremity of the wire connected with the copper plate is zincous, or has zincous affinity, and consequently attracts the iodine which appears there, when decomposition occurs. The extremity of the wire connected with the copper plate is chlorous, or has the affinity of chlorine; and consequently, the hydrogen of the hydriodic acid is eliminated there when decomposition occurs. These poles in the decomposing cell of the voltaic circle have, from their importance, always received peculiar appellations, which, with two other terms, Mr. Graham changes as follows:—

Chlorous = Negative.

Zincous = Positive.

Chloroid = The negative pole, the cathode, the platinode.

Zincoid = The positive pole, the anode, the zincode.

Mr. Graham afterwards endeavoured to show, that electrolytes were bodies which, like hydrochloric acid, possessed a salt radical and basyle element, which might be the seat of the chlorous and zincous affinities, and which might, indeed, be called the chlorous and zincous elements of the electrolyte; so that the same view was applicable to electrolytes in general.<sup>1</sup>

<sup>1</sup> Mr. Graham has since developed his views more fully in the Third Part of his *Elements of Chemistry*, pp. 197-241.



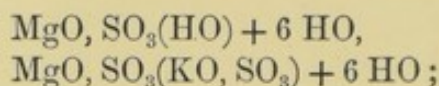
## IX.

ON THE CONSTITUTION OF THE SULPHATES AS ILLUSTRATED BY LATE THERMOMETRICAL RESEARCHES.<sup>1</sup>

From *Chem. Soc. Mem.* i. 1841-43, pp. 82-84. [*Phil. Mag.* xx. 1842, pp. 539-541.]

PROF. HESS and Dr. Andrews both apply the results of their late inquiries respecting the heat evolved in combination<sup>2</sup> to test the accuracy of a view of the constitution of double and acid salts which was published by myself, and arrive, it is remarkable, at opposite conclusions.

The view in question, I may first state, taking the example of double and acid sulphates. Crystallized sulphate of magnesia, and the double sulphate of magnesia and potash, I have represented thus:—



considering the latter salt to be derived from the former, by the substitution of sulphate of potash for that single atom of water, which is found to be much more strongly attached to the sulphate of magnesia than the other six. This atom of water, which is not basic water, was formerly named *saline* water, to indicate that it is replaceable by a salt; its presence being considered a provision in sulphate of magnesia for the formation of double salts. The water and sulphate of potash are therefore looked upon as equivalent in the construction of the two salts; and the substitution of the salt for the water might therefore be reasonably expected to occur without the evolution of heat.

In accordance with that statement, Dr. Andrews finds that no heat is evolved on mixing solutions of sulphates of magnesia and potash, nor in the formation of any other double salt. On repeating the experiment I found also no heat nor change of temperature on mixing the solutions, although a change of  $\frac{1}{100}$ th of a degree Fahr. would have been distinctly indicated by my thermometer.

Possibly, however, the double salt may not immediately be formed, and hence no change of temperature at the moment of mixing the two solutions, nor for some time afterwards. To meet this objection, solutions of sulphate of magnesia and of sulphate of ammonia (the last, from its greater solubility, being preferred to sulphate of potash) were made of such a strength that they might be mixed without the precipitation

<sup>1</sup> Read January 18, 1842.

<sup>2</sup> *Phil. Mag.* Jan. 1842.



of the double salt immediately occurring, but strong enough to allow a large quantity of the double salt to fall upon stirring the liquid strongly. The solutions were 1546·88 grains of cr. sulphate of magnesia dissolved in so much water as to form 8000 water grain measures, and 613·5 grains oil of vitriol, neutralized with ammonia and made up to 4000 water grain measures. On mixing one ounce measure of the first with half an ounce measure of the second, both exactly at  $50^{\circ}$ , not the smallest change of temperature could be observed; but as soon as the double salt began to deposit, the temperature rose, and on stirring strongly much salt was deposited, and the temperature rose  $5^{\circ}40$  Fahr. On re-dissolving this salt, however, by substituting for the mother-liquor an equal bulk of water, the temperature instantly fell  $5^{\circ}85$ . Hence the heat which first appeared was produced by the solidification of the double salt, and disappears upon its liquefaction. There is no heat referable to combination of the two salts. The cold on dissolving was always somewhat greater than the heat on precipitating the double salt, in repetitions of this experiment, chiefly, I believe, from the slowness of the precipitation, which requires a minute or two, so that a portion of the heat is lost from contact with the atmosphere, and the whole not observed, while the subsequent solution of the salt being almost instantaneous, the whole fall of temperature is observed. The same experiment was made with a solution of sulphate of zinc, of the same strength as the sulphate of magnesia, and with similar results, only that the fall of temperature, on solution, was somewhat less than that on solidification, namely, as  $9^{\circ}22$  to  $9^{\circ}67$ , difference  $0^{\circ}45$  Fahr. This was principally owing to the time required in re-dissolving this double salt being greater than that occupied in precipitating it, three applications of water being required to re-dissolve the double salt completely, owing to its sparing solubility.

M. Hess's objection is made to the analogous constitution which I have assigned to the bisulphate of potash:—

Sulphuric acid of specific gravity, 1·78, .	HO, SO <sub>3</sub> (HO).
Bisulphate of potash, . . . . .	HO, SO <sub>3</sub> (KO, SO <sub>3</sub> ).

He maintains that heat is evolved in the formation of a bisulphate, and therefore that the combination is not effected by the equivalent substitution supposed. He mixed sulphate of potash with HO, SO<sub>3</sub> + HO, and found heat evolved, but allows that the result here is fallacious, a portion only of the sulphuric acid being converted into bisulphate, while the other portion is diluted by the displaced water of the first portion, and thus heat evolved.

On performing the direct experiment, which M. Hess appears to have neglected, using a saturated solution of sulphate of ammonia, and



sulphuric acid of specific gravity 1.256, I obtained, on mixing 5°·4 of cold instead of any heat. But on diluting the sulphate of ammonia with a volume of water equal to that of the dilute acid, a fall of 1°·12 occurred. Deducting this from the former, there remains a fall of 3°·88 due to the combination of the two salts, sulphate of water with sulphate of ammonia. But this may be explained. The bisulphate of ammonia formed is an anhydrous salt, unlike the double sulphate of magnesia and ammonia, which carries along with it all the water of crystallization of the sulphate of magnesia. But the sulphate of water itself, as it exists in diluted sulphuric acid, is a largely hydrated salt, like sulphate of magnesia. The water of the former, on being set free in the last experiment, absorbs heat, because heat was evolved originally in the combining of this water with the sulphuric acid.

Although certain small corrections on these experiments for changes in capacity for heat of the liquids have been neglected, yet they are sufficient to demonstrate that no heat is evolved in the formation of double sulphates, and also, as appears by the last experiment, that these compounds are formed at once on mixing the solutions of their constituent salts, whether precipitation occurs or not. Sulphate of potash and water are therefore equivalent in the constitution of such salts, or *equicalorous*, if a term may be coined to express this relation.

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## X.

### EXPERIMENTS ON THE HEAT DISENGAGED IN COMBINATIONS.<sup>1</sup>

From *Chem. Soc. Mem.* i. 1841-43, pp. 106-126; ii. 1843-45, pp. 51-70. [*Annal. de Chimie*, viii. 1843, pp. 151-180; xiii. 1845, pp. 188-216; *Erdm. Journ. Prak. Chem.* xxx. 1843, pp. 152-183; *Phil. Mag.* xxii. 1843, pp. 329-352; xxiv. 1844, pp. 401-420.]

#### PART I.

THE observations, of which an account shall be given in the present paper, are exclusively confined to the heat disengaged in combinations formed in the humid way. The heat disengaged in such combinations is in general easily collected and measured, as it is immediately communicated to a mass of fluid, of which the temperature may be observed with accuracy. The elevation of temperature in an experiment may

<sup>1</sup> Read November 1, 1842.



often, however, be greatly affected by incidental circumstances; such as the liquefaction of the product of the combination, arising from its solution in the water, or other menstruum employed; or the hydration of the compound formed, which so generally occurs with a salt formed by uniting an acid and base; and can rarely, therefore, be taken as the expression of the heat disengaged from the combination without considerable correction.

Thus in a few preliminary experiments to ascertain whether, as has been anticipated, different bases of the same class evolve equal quantities of heat on combining with the same acid, it was found that equivalents of oxides of copper and zinc, and the equivalent of magnesia on dissolving in highly diluted sulphuric acid, evolved respectively  $4^{\circ}20$ ,  $5^{\circ}18$ , and  $11^{\circ}70$ . But the sulphates formed are all hydrated salts, and a large portion of the heat was found to be due to the combination of this water, namely  $3^{\circ}49$  in the sulphate of copper,  $3^{\circ}90$  in the sulphate of zinc, and  $4^{\circ}12$  in the sulphate of magnesia. Again, the salts are obtained in solution; now the liquefaction or solution of salts is attended with the absorption of a certain quantity of heat or fall of temperature, namely by a fall of  $0^{\circ}66$  in the hydrated sulphate of copper,  $0^{\circ}93$  in the hydrated sulphate of zinc, and  $0^{\circ}83$  in the hydrated sulphate of magnesia. The last quantities being added to the heat first observed in the solution of the oxides, and the preceding quantities being subtracted from the same heat first observed, we obtain as the corrected determinations of the heat evolved from the combination with sulphuric acid of the oxides enumerated (or rather from the substitution of these metallic oxides for the basic water of the sulphate of water), by oxide of copper  $1^{\circ}37$ , by oxide of zinc  $2^{\circ}21$ , by magnesia  $8^{\circ}41$ ; quantities which, so far from being equal, are nearly in the ratio of the numbers 2, 3, and 12. It is obvious, therefore, that experiments to determine both the heat absorbed in the solution of salts, and that evolved in their hydration, must precede inquiries respecting the heat disengaged in the formation of the salts themselves by the combination of their essential constituents, when the salts are formed in the humid way.

The apparatus employed consisted of a delicate thermometer of small bulb, namely, that used in the wet-bulb hygrometer, as prepared by Greiner of Berlin. Every degree was divided into five parts, each part again was divisible by the eye into five parts, so that observations were made to  $\frac{1}{25}$ th of a degree. The degree is that of Réaumur's scale. After trying glass jars and various other vessels, it was found that nothing answered better than a large platinum crucible, which weighed 1201.9 grains, and was capable of containing 5 ounces of water. The thermometer and crucible, with a hollow cylinder of palladium, weighing 207.6 grains, employed as a stirrer, were all the apparatus necessary. Of the



salt or other substance experimented upon, a quantity corresponding with its atomic weight, and representing a single equivalent, was always used; and the quantity of water was constant, namely 1000 grains, and relatively large, so as to render the change of the specific heat of the fluid insensible.

The water, crucible, stirrer, and thermometer, being the same in all the experiments, the results are strictly comparable. The numbers express the relative quantities of heat disengaged from atomic equivalents of the bodies.

### I. HYDRATION OF OIL OF VITRIOL.

1.  $\text{HO}, \text{SO}_3$ . The protohydrate of sulphuric acid employed was pure, and of density 1.848. The quantity used of this and other substances was always one-twentieth of the number expressing the equivalent taken in grains; that is 30.68 grains of oil of vitriol, the equivalent of the protohydrate being 613.5. It was weighed in an exceedingly thin and light glass spherule, which was afterwards broken in the water, and the acid diffused through the latter. The greater portion of the heat is disengaged in the first two or three seconds after mixture, or its evolution is almost instantaneous. To avoid the loss of heat by communication to the air, during the short time that must elapse before the thermometer in the liquid becomes stationary, the crucible, water, and stirrer were previously cooled down so far below the temperature of the air, as the liquid was expected, from a preliminary experiment, to rise on the addition of the acid. The crucible was also placed within a glass jar containing tow, to impede the passage of heat by conduction. I am indebted for several valuable hints on the mode of conducting such experiments, to the papers of Dr. Andrews and Professor Hess, who have preceded me in similar investigations.

The rise of temperature in a preliminary experiment, in which the water and crucible were not previously cooled, was  $3^{\circ}.78 \text{ R.}$  In two other experiments in which the crucible and water were previously cooled before the addition of the acid, the rise was  $3^{\circ}.88$  and  $3^{\circ}.85$ . The mean of the last results, or  $3^{\circ}.86$ , may therefore be taken as the heat disengaged in the hydration of an equivalent of the protohydrate of sulphuric acid. No perceptible change of temperature occurred on diluting further with water the products of these experiments.

2.  $\text{HO}, \text{SO}_3 + \text{HO}$ . This is the crystallizable hydrate of sulphuric acid, of density 1.78. 36.3 grains, the equivalent quantity, were mixed with 1000 grains of water, as in the preceding case. The rise of temperature in three experiments was  $2^{\circ}.40$ ,  $2^{\circ}.36$  and  $2^{\circ}.40$ ; of which the mean is  $2^{\circ}.39$ .



The dilution of this hydrate gives occasion to the disengagement of  $1^{\circ}47$  less heat than the preceding hydrate. It appears, therefore, that in the dilution of the first hydrate or of sulphate of water,  $1^{\circ}47$  is due to the combination of the first atom of water, with which it forms the crystallizable hydrate, and  $2^{\circ}39$  to combination with all the rest, making together  $3^{\circ}86$ .

3.  $\text{HO}, \text{SO}_3 + 2 \text{HO}$ . This is the hydrate of sulphuric acid in the formation of which the greatest contraction is observed to occur. With 41.93 grains, or one equivalent, the rise of temperature on dilution was in three experiments conducted as before,  $1^{\circ}88$ ,  $1^{\circ}86$ , and  $1^{\circ}85$ , of which the mean is  $1^{\circ}86$ . The difference between the heat evolved by the present and the immediately preceding hydrate is  $0^{\circ}53$ , which is therefore the heat evolved by the addition of the second atom of water to the sulphate of water. It is scarcely one-third of  $1^{\circ}47$ , the quantity evolved by the first atom.

4.  $\text{HO}, \text{SO}_3 + 3 \text{HO}$ . With 47.55 grains, or one equivalent of this hydrate, the rise by dilution was in three experiments  $1^{\circ}31$ ,  $1^{\circ}31$ , and  $1^{\circ}27$ , of which the mean is  $1^{\circ}30$ . The difference between the heat evolved by this and the preceding hydrate is  $0^{\circ}56$ , which is therefore the heat evolved by the addition of the third atom of water to the sulphate of water. Now the second atom evolved  $0^{\circ}53$ , so that the second and the third atoms of water appear to evolve sensibly the same quantity of heat. This curious result favours the conclusion that the second and third atoms of water go together; or that the hydration of the sulphate of water here advances by two atoms at a time, and that no intermediate hydrate exists, in a state of solution at least, between  $\text{HO}, \text{SO}_3 + \text{HO}$  and  $\text{HO}, \text{SO}_3 + 3\text{HO}$ . The last may be represented as  $\text{HO}, \text{SO}_3, \text{HO} + 2 \text{HO}$ .

5.  $\text{HO}, \text{SO}_3 + 4 \text{HO}$ . With 53.18 grains, or one equivalent of this hydrate, the rise of temperature on dilution was  $1^{\circ}05$ ,  $1^{\circ}07$ , and  $1^{\circ}05$ ; mean  $1^{\circ}06$ . The difference between this and the preceding hydrate, namely,  $0^{\circ}24$ , is therefore the heat evolved by the combination of the fourth atom of water with sulphate of water.

6.  $\text{HO}, \text{SO}_3 + 5 \text{HO}$ . With 58.8 grains, or one equivalent of this hydrate, the rise of temperature on dilution was  $0^{\circ}88$ ,  $0^{\circ}88$ , and  $0^{\circ}85$ ; mean  $0^{\circ}87$ . The heat from the combination of the fifth atom of water is  $0^{\circ}19$ . It is not impossible that the heat evolved from the fifth is the same in quantity as that evolved from the fourth atom of water, and that these two atoms go together like the second and third. The present hydrate of sulphate of water corresponds with crystallized sulphate of copper.

7.  $\text{HO}, \text{SO}_3 + 7 \text{HO}$ . With 70.05 grains, or one equivalent, the rise was  $0^{\circ}68$ ,  $0^{\circ}71$ , and  $0^{\circ}65$ ; mean  $0^{\circ}68$ . The difference between the



effect of this and the preceding hydrate is  $0^{\circ}\cdot 19$ , which is therefore the heat evolved by the combination of the last two atoms of water, namely the sixth and seventh atoms. This hydrate of sulphate of water corresponds with crystallized sulphate of magnesia.

By the continued hydration of the sulphate of water, the quantities of heat evolved are therefore as follows :—

	Heat evolved.	Hydrate formed.
By first atom of water,	$1^{\circ}\cdot 47$	$\text{HO}, \text{SO}_3 + \text{HO}.$
By second and third atoms together,	$1^{\circ}\cdot 09$	$\text{HO}, \text{SO}_3 + 3 \text{HO}.$
By fourth and fifth atoms together,	$0^{\circ}\cdot 43$	$\text{HO}, \text{SO}_3 + 5 \text{HO}.$
By sixth and seventh atoms together,	$0^{\circ}\cdot 19$	$\text{HO}, \text{SO}_3 + 7 \text{HO}.$
By an additional excess of water,	$0^{\circ}\cdot 68$	$\text{HO}, \text{SO}_3 + 7 \text{HO} + x\text{HO}.$

It will be observed that the heat evolved by the first atom is sensibly the same as that evolved by the four following atoms, the quantities being  $1^{\circ}\cdot 47$  and  $1^{\circ}\cdot 52$ ; the difference between these numbers being within the limits of errors of observation. The same conclusion is drawn from his experiments on the hydration of oil of vitriol by Professor Hess. Supposing the whole heat disengaged in the hydration of sulphate of water to be divided into 23 parts, 9 are evolved by the first atom of water, 9 by the next four atoms, 1 by the following two atoms, and 4 by the remaining excess.

Although the experiments detailed above agree with those of M. Hess in bringing out one curious result, they yet differ from them to an extent which it is difficult to account for in other respects. Thus reducing my results to the same scale as those of M. Hess, the comparison is as follows. In the hydration of the sulphate of water,

	Hess.	Graham.
Heat from the first atom of water,	2	2
„ second atom of water,	1	0·72
„ next three atoms of water,	1	1·35
„ additional excess of water,	1	1·18
	<hr/> 5	<hr/> 5·25

8.  $\text{HO}, \text{SO}_3, \text{HO} + 10 \text{HO}.$  An equivalent quantity of this hydrate, or 92·55 grains, was mixed with 969·3 grains of water, the quantity of the latter being diminished so as to make up 1000 grains with the water already in the acid hydrate. The rise of temperature in two experiments was  $0^{\circ}\cdot 37$  and  $0^{\circ}\cdot 41$ , of which the mean is  $0^{\circ}\cdot 39$ . This hydrate contains four atoms more of water than the last operated upon, and disengages  $0^{\circ}\cdot 29$  less heat. The heat, therefore, due to the combination of the additional four atoms of water is  $0^{\circ}\cdot 29$ .

9.  $\text{HO}, \text{SO}_3, \text{HO} + 14 \text{HO}.$  Of this hydrate the equivalent, or 115·05



grains, was mixed with 915·6 grains of water, and occasioned a rise of temperature in two experiments of  $0^{\circ}\cdot23$  and  $0^{\circ}\cdot20$ , of which the last was believed to be the most trustworthy result. Hence the four atoms of water last added evolve  $0^{\circ}\cdot09$ , or about one-third of the quantity evolved by the preceding four atoms of water.

10.  $\text{HO}, \text{SO}_3, \text{HO} + 24 \text{HO}$ . The equivalent of this hydrate, or 171·3 grains, was mixed with 859·4 grains of water, and produced in one experiment a rise of  $0^{\circ}\cdot15$ . The hydrate was kept for three days before it was diluted in the experiment; for immediately after its preparation the heat which this hydrate yielded on dilution was considerably less than the quantity assigned above to it; indeed, not more than  $0^{\circ}\cdot06$  in one experiment.

11.  $\text{HO}, \text{SO}_3, \text{HO} + 36 \text{HO}$ . The equivalent quantity of this diluted acid, or 238·8 grains, was mixed within an hour of its preparation with 792 grains of water; the rise of temperature was  $0^{\circ}\cdot11$ .

12.  $\text{HO}, \text{SO}_3, \text{HO} + 48 \text{HO}$ . The equivalent quantity, or 306·3 grains, was mixed about three hours after its preparation with 724·4 grains of water; a rise occurred of  $0^{\circ}\cdot08$ . The dilution of the same hydrate twenty-four hours after its preparation was attended with a rise of  $0^{\circ}\cdot13$ .

The last hydrate is oil of vitriol diluted with nine times its weight of water, yet it was still capable of evolving a sensible quantity of heat by further dilution. The term at which the mixture of acid and water ceases to disengage heat on a further addition of water was not observed, but the effect was insensible in a mixture formed of one part of the concentrated acid and thirty parts of water.

## II. HYDRATION OF OTHER MAGNESIAN SULPHATES.

The heat produced in the hydration of different anhydrous sulphates, compared with oil of vitriol, appears in the following results; equivalent quantities of the anhydrous salts in the solid state being thrown into the same quantity of water, and the rise of temperature observed after the hydration and complete solution of the salts.

Protosulphate of manganese,	.	.	$3^{\circ}\cdot22$
Sulphate of copper,	.	.	$3^{\circ}\cdot73$
Sulphate of water,	.	.	$3^{\circ}\cdot86$
Sulphate of zinc,	.	.	$4^{\circ}\cdot17$
Sulphate of magnesia,	.	.	$4^{\circ}\cdot33$

The most material difference in the circumferences of the experiments is, that while the oil of vitriol was liquid, the salts with which it is compared were necessarily applied in the solid form. The liquefaction



of the latter during the experiment would therefore occasion an absorption of heat of unknown amount, which does not occur in the latter.

1. *Sulphate of Magnesia*.—The same mode of experimenting was followed and apparatus used as in the preceding experiments with oil of vitriol. On dissolving the equivalent quantity, 77.35 grains (one-twentieth of 1547.02), of the crystallized salts in 960.6 grains of water, a fall occurred in three experiments of  $0^{\circ}.96$ ,  $0^{\circ}.90$ , and  $0^{\circ}.89$ , of which the mean is  $0^{\circ}.92$ . In these experiments, the water contained in the crystals, which amounts to 39.4 grains, was deducted from the 1000 grains of water usually employed to dissolve the salt; but if this quantity of water is supposed to be added, the mean result would become  $0^{\circ}.88$ .

The salt was made certainly anhydrous by exposure to an incipient red heat for a considerable time, and the equivalent quantity, 37.98 grains, in the state of a fine powder, was thrown into 1000 grains of water. It did not cake, and was dissolved completely by stirring in about one minute and a half. The rise of temperature in two experiments was  $4^{\circ}.30$  and  $4^{\circ}.36$ , of which the mean is  $4^{\circ}.33$ . To this must be added the heat lost by the liquefaction and solution of the hydrate formed.

Rise on solution of $\text{MgO}, \text{SO}_3$ , . . .	$4^{\circ}.33$
Fall from solution of $\text{MgO}, \text{SO}_3 + 7 \text{HO}$ , . .	$0^{\circ}.92$
Whole heat disengaged by $\text{MgO}, \text{SO}_3$ , . . .	$5^{\circ}.25$

$\text{MgO}, \text{SO}_3, \text{HO}$ . It is not easy to obtain the sulphate of magnesia with exactly one atom of water. The salt first operated upon retained, after being dried by an oil-bath, at  $400^{\circ}$  to 100 sulphate of magnesia only 14.14 water, instead of 14.81, the single equivalent. The hydrate was therefore  $\frac{21}{22} \text{HO}$ . The heat evolved by the solution of 43.35 grains, an equivalent quantity of this hydrate in two experiments, was  $3^{\circ}.06$  and  $3^{\circ}.9$ , of which  $3^{\circ}.08$  may be taken as the mean.

Another portion of the same sulphate, less strongly dried, retained to 100 sulphate of magnesia 15.75 water, which is  $1\frac{1}{7} \text{HO}$ . The results from the solution of 43.93 grains, the equivalent of this hydrate, were  $3^{\circ}.03$ ,  $2^{\circ}.98$ , and  $2^{\circ}.93$ , of which the mean is  $2^{\circ}.98$ . The mean of the two sets of experiments, or  $3^{\circ}.03$ , probably does not differ far from the truth.

Rise on solution of $\text{MgO}, \text{SO}_3, \text{HO}$ , . . .	$3^{\circ}.03$
Fall on solution of $\text{MgO}, \text{SO}_3 + 7 \text{HO}$ , . . .	$0^{\circ}.92$
Whole heat disengaged by $\text{MgO}, \text{SO}_3, \text{HO}$ , . .	$3^{\circ}.95$

The anhydrous salt disengaged  $5^{\circ}.25$ , while the protohydrate disengages  $3^{\circ}.95$ ; the difference, or  $1^{\circ}.30$ , is therefore the heat disengaged by the



combination of the first atom of water with sulphate of magnesia. It thus appears that of the whole heat evolved in the complete hydration of sulphate of magnesia, as nearly as possible one-fourth is due to the combination of the first atom of water, one-fourth of  $5^{\circ}25$  being  $1^{\circ}31$ .

2. *Sulphate of Zinc*.—The equivalent quantity of the crystallized salt, 89.59 grains, contains 39.38 water, and was therefore dissolved in 960.6 water. The fall of temperature in two experiments was  $1^{\circ}01$  and  $0^{\circ}98$ , of which the mean is  $1^{\circ}00$ . This sensibly exceeds the cold produced by the solution of crystallized sulphate of magnesia, which is  $0^{\circ}92$ . The difference has a real foundation, and is not the consequence of errors in experiment; for in two other sets of observations on the same salts made in glass, and which may be compared with each other, although not with the preceding experiments, the results were for sulphate of magnesia  $0^{\circ}85$ ,  $0^{\circ}80$ , and  $0^{\circ}83$ , of which the mean is  $0^{\circ}83$ ; for sulphate of zinc  $0^{\circ}97$ ,  $0^{\circ}91$ ,  $0^{\circ}92$ , of which the mean is  $0^{\circ}93$ : greater cold occasioned by the solution of sulphate of zinc than of sulphate of magnesia, by the first experiments  $0^{\circ}08$ , by the last experiments  $0^{\circ}10$ .

Of sulphate of zinc, carefully dried and made perfectly anhydrous, the equivalent quantity, 50.22 grains, was dissolved in 1000 grains of water, with the exception of a mere trace of flaky matter. The rise in one experiment was  $4^{\circ}20$ ; in another  $4^{\circ}15$ ; mean  $4^{\circ}17$ . The results then are,—

Rise on solution of $\text{ZnO}, \text{SO}_3$ , . . .	$4^{\circ}17$
Fall on solution of $\text{ZnO}, \text{SO}_3 + 7 \text{HO}$ , . .	$1^{\circ}00$
Whole heat disengaged by $\text{ZnO}, \text{SO}_3$ , . .	$5^{\circ}17$

There is the same difficulty in obtaining the protohydrate of sulphate of zinc exactly definite, as the corresponding hydrate of sulphate of magnesia. The hydrate operated upon contained to 100 sulphate of zinc 11.99 water, instead of 11.207, which is a single equivalent. The equivalent quantity, 56.21 grains, was dissolved in 1000 grains of water, and occasioned a rise of temperature in two experiments of  $2^{\circ}34$  and  $2^{\circ}33$ . As the rise for the anhydrous salt was  $4^{\circ}17$ , the deficiency from the hydrate,  $4^{\circ}17 - 2^{\circ}34 = 1^{\circ}83$ , is due to the quantity of water already combined in the salt of the experiment. But this deficiency cannot be entirely ascribed to a single atom of water, as the combined water exceeded that proportion as 11.99 to 11.21. It is difficult to find proper elements for the necessary correction, but we may probably reduce the amount of deficient heat to  $1^{\circ}71$ , that is, as 11.99 to 11.21, without any considerable error. Hence

Rise on solution of $\text{ZnO}, \text{SO}_3, \text{HO}$ , . . .	$2^{\circ}45$
Fall on solution of $\text{ZnO}, \text{SO}_3 + 7 \text{HO}$ , . .	$1^{\circ}00$
Whole heat disengaged by $\text{ZnO}, \text{SO}_3, \text{HO}$ , . .	$3^{\circ}45$



The difference between the heat disengaged by the protohydrate and the anhydrous salt, or the heat due to the combination of the first atom of water, namely  $1^{\circ}71$ , is almost exactly one-third of the whole heat disengaged in the hydration of sulphate of zinc; one-third of  $5^{\circ}17$  being  $1^{\circ}72$ . The quantities of heat disengaged by sulphate of zinc in the two conditions specified, are therefore as 4 to 6.

3. *Sulphate of Copper*.—The equivalent quantity of the ordinary crystallized salt, containing 5 HO, namely 77.97 grains, was dissolved in 1000 grains of water, with a fall of temperature in three experiments of  $0^{\circ}67$ ,  $0^{\circ}65$ , and  $0^{\circ}68$ , of which the mean is  $0^{\circ}67$ . This and other more sparingly soluble salts were pounded fine and sifted; the solution took place with stirring within one minute.

Of the anhydrous salt, 49.84 grains, the equivalent quantity, were dissolved in 1000 grains of water, with a rise in two experiments of  $3^{\circ}72$  and  $3^{\circ}74$ . Hence the results for the anhydrous salt are,—

Rise on solution of $\text{CuO}, \text{SO}_3$ , . . . .	$3^{\circ}73$
Fall on solution of $\text{CuO}, \text{SO}_3 + 5 \text{HO}$ , . . . .	$0^{\circ}67$
Whole heat disengaged by $\text{CuO}, \text{SO}_3$ , . . . .	$4^{\circ}40$

The protohydrate was prepared by drying the crystallized salt by a nitre-bath; it retained to 100 sulphate of copper 11.83 water, instead of 11.29 water, the single equivalent. The equivalent quantity, 55.72 grains, was dissolved in 1000 grains of water, with a rise in two experiments of  $2^{\circ}15$  and  $2^{\circ}13$ . The result is  $3.73 - 2.14 = 1^{\circ}59$  for the combined water. This hydrate contained  $1\frac{1}{2}$  HO.

After being dried still further on an oil-bath at  $370^{\circ}$ , it consisted of 100 sulphate of copper and 11.44 water, or was  $1\frac{1}{2}$  HO; the salt was now almost white, the green tint being barely perceptible. The equivalent quantity of the last salt, 55.54 grains, was dissolved in 1000 grains of water, but somewhat more slowly, and with greater difficulty than the preceding salt. The heat evolved in two experiments was  $2^{\circ}09$  and  $2^{\circ}07$ , which instead of exceeding falls short of the preceding results. The deficiency of heat in the last experiments is remarkable, and is in some measure, but I believe not fully, accounted for by the slowness of the solution. Giving a preference to the first results, and deducting  $\frac{1}{2}$  part for the excess of water above one atom already combined with the salt, there remains  $1^{\circ}47$  for the heat due to the combination of the first atom of water. The result for the protohydrate is,—

Rise on solution of $\text{CuO}, \text{SO}_3, \text{HO}$ , . . . .	$2^{\circ}26$
Fall on solution of $\text{CuO}, \text{SO}_3 + 5 \text{HO}$ , . . . .	$0^{\circ}67$
Whole heat disengaged by $\text{CuO}, \text{SO}_3, \text{HO}$ , . . . .	$2^{\circ}93$

One-third of  $4^{\circ}40$ , the whole heat evolved in the hydration of sulphate



of copper, is  $1^{\circ}466$ , which is as nearly as possible the result obtained above for the first atom of water. The ratio is the same as in the sulphate of zinc, while in the hydration of the sulphate of magnesia the heat evolved by the first atom of water was one-fourth of that evolved by the whole. It may be inferred from the experiments on oil of vitriol, that it approaches more closely to the former salts than to sulphate of magnesia in this character, although a rigid comparison cannot be made, as we are unacquainted with the fully hydrated sulphate of water in a crystalline form, and cannot therefore estimate its heat of liquefaction.

4. *Protosulphate of Iron*.—Of the crystallized salt containing seven atoms of water, the equivalent quantity, 86.39 grains, dissolved in 1000 grains of water in two experiments with a fall of  $1^{\circ}$  and  $1^{\circ}04$ . Allowing for the 39.38 grains of water introduced by the salt in addition to the thousand grains employed, these results become  $1^{\circ}04$  and  $1^{\circ}08$ , of which the mean is  $1^{\circ}06$ .

Fall on the solution of  $\text{FeO}, \text{SO}_3 + 7 \text{HO}$ , . . .  $1^{\circ}06$

The protohydrate of sulphate of iron, formed by drying the crystallized salt in air at a temperature approaching  $400^{\circ}$ , was found to be nearly insoluble in cold water. The anhydrous sulphate was more soluble, but not sufficiently so for the determination of its thermal relations.

5. *Protosulphate of Manganese*.—The crystallized salt employed contained five atoms of water. The equivalent quantity, 75.47 grains, of the crystallized salt was dissolved in 972 grains of water at  $59^{\circ}$  Fahr., with a fall of temperature in two experiments of  $0^{\circ}11$  and  $0^{\circ}13$  R., of which the mean is  $0^{\circ}12$ .

Of the same salt made anhydrous by heat, the equivalent quantity, 47.35 grains, was dissolved in 1000 grains of water at  $60^{\circ}$  Fahr., with a rise in two experiments of  $3^{\circ}20$  and  $3^{\circ}24$  R.; mean rise  $3^{\circ}22$ .

Rise on solution of  $\text{MnO}, \text{SO}_3$ , . . . . .  $3^{\circ}22$

Fall on solution of  $\text{MnO}, \text{SO}_3 + 5 \text{HO}$ , . . . . .  $0^{\circ}12$

Whole heat disengaged by  $\text{MnO}, \text{SO}_3$ , . . . . .  $3^{\circ}34$

The crystallized salt being well dried at a temperature not exceeding  $400^{\circ}$  Fahr., was found to retain a quantity of water in combination, which slightly exceeded a single equivalent, namely in the proportion of 5.82 grains to 5.62 grains, in 52.97 grains of the hydrated salt. The heat evolved in the solution of the equivalent quantity, 52.97 grains, of this protohydrate by 1000 grains of water was in two experiments  $1^{\circ}80$  and  $1^{\circ}78$ , of which the mean is  $1^{\circ}79$ .

Rise on solution of  $\text{MnO}, \text{SO}_3, \text{HO}$ , . . . . .  $1^{\circ}79$

Fall on solution of  $\text{MnO}, \text{SO}_3 + 5 \text{HO}$ , . . . . .  $0^{\circ}12$

$1^{\circ}91$



It follows that the heat evolved by the combination of the first atom of water with sulphate of manganese is  $3^{\circ}34 - 1^{\circ}91 = 1^{\circ}43$ . This result approaches to  $1^{\circ}47$ , the heat evolved by the combination of the first atom of water with sulphate of copper. The small depression of temperature produced by the solution of crystallized protosulphate of manganese is remarkable, and distinguishes this salt from the other magnesian sulphates. This salt alone of the class forms a thick solution, when highly concentrated, and crystallizes with difficulty. It was also observed that the protohydrate of sulphate of manganese does not dissolve easily in cold water; the quantity of the protohydrate employed in the experiments narrated above requiring to be agitated with the water for two and a half minutes, before the liquid ceased to be turbid and the salt was entirely dissolved. The anhydrous sulphate of manganese was dissolved quickly and with ease.

### III. SULPHATES AND CHROMATES OF THE POTASH FAMILY.

1. *Sulphate of Potash*.—Good crystals of this salt were reduced to powder and sifted. The solution of the equivalent quantity, 54.55 grains, in 1000 grains of water, which took place in thirty seconds, was attended by a fall of temperature in two experiments of  $1^{\circ}50$  and  $1^{\circ}52$ , of which the mean is  $1^{\circ}51$ .

Fall on solution of  $\text{KO}, \text{SO}_3$ , . . . . .  $1^{\circ}51$

The same quantity of sulphate of potash was dissolved in a mixture of 300 water-grain measures of dilute sulphuric acid of density 1.1 mixed with 700 grains of water. The dry acid in the mixture amounted to 36 grains; a single equivalent is represented by 25 grains. The solution was quite as rapid, or more so, than in pure water; the fall of temperature  $2^{\circ}04$ ; the difference of  $0^{\circ}53$  is probably connected with the formation of bisulphate of potash.

2. *Chromate of Potash*.—The solution of the equivalent quantity, 62.09 grains, of this salt in 1000 grains of water, was attended with a fall of  $1^{\circ}18$  in water.

Fall on solution of  $\text{KO}, \text{CrO}_3$ , . . . . .  $1^{\circ}18$

When dissolved in an equal quantity of the same dilute sulphuric acid as was used with sulphate of potash, the solution became red from the formation of bichromate, and only a very slight change of temperature occurred, namely a fall of  $0^{\circ}08$ .

3. *Bichromate of Potash*.—The fused salt was used, as it is easily reduced to a fine powder, and half the equivalent quantity used, as the whole equivalent is not dissolved by 1000 grains of water at  $57^{\circ}$  Fahr.,



the temperature of the experiments. The solution of 47·34 grains, half the equivalent quantity, was attended with the same fall of  $1^{\circ}98$  in two experiments. No sensible change of temperature occurred on diluting this solution. In the dilute sulphuric acid used with the two preceding salts, the fall on the solution of half an equivalent of bichromate of potash was  $2^{\circ}00$ , or sensibly the same as in pure water. The fall of temperature for a whole equivalent of bichromate of potash will therefore be  $3^{\circ}96$ .

Fall on solution of  $\text{KO}$ ,  $2 \text{CrO}_3$ , . . .  $3^{\circ}96$

The heat of liquefaction of bichromate of potash is therefore very considerable. It appears to be the same in quantity as that of *nitrate of potash*. The equivalent quantity of the latter salt, 63·25 grains, was dissolved in 1000 grains of water, with a fall of  $3^{\circ}86$ . The temperature of this solution was further reduced  $0^{\circ}10$ , by dilution with another 1000 grains of water; so that by the solution of an equivalent quantity of this salt in the same proportion of water as was employed for the solution of an equivalent of bichromate of potash, a fall of temperature of  $3^{\circ}96$  is produced. In a second experiment the whole fall of temperature on the solution of an equivalent of nitrate of potash was  $3^{\circ}95$ .

Fall on solution of  $\text{KO}$ ,  $\text{NO}_5$ , . . .  $3^{\circ}96$

It is possible that this coincidence is not accidental, but depends on a thermal equivalency of  $\text{NO}_5$ , and  $\text{Cr}_2\text{O}_6$ , the acids united with potash in these two salts. If the single equivalent of nitrogen in nitric acid be divided by three, or considered three atoms instead of one, as has been inferred on other grounds, then the acid constituents of both salts will contain the same number of atoms, namely eight; and the bichromate of potash, which has hitherto appeared so anomalous among salts, be assimilated to the nitrate of potash.

4. *Terchromate of Potash*.—Of this salt 63·63 grains, or one-half of the equivalent quantity, were dissolved easily and entirely by 1000 grains of water, with a fall of  $1^{\circ}63$ . But the terchromate of potash changes colour when thrown into water from decomposition, being resolved in a great measure into bichromate of potash and chromic acid, both of which are soon dissolved, the last more rapidly than the first.

Half an equivalent of this salt was dissolved, with a fall of  $1^{\circ}28$ , in 1000 water grain measures of dilute nitric acid, of specific gravity 1·1453. But in this menstruum also, the terchromate appeared to be decomposed with separation of chromic acid, although to a much less extent than in the preceding experiment. In a liquid, however, already charged with the salt, like the last, an additional quantity may be dis-



solved without further decomposition. Half an equivalent of the salt was dissolved in that liquid with a fall of  $1^{\circ}\cdot14$ , which is a fall of  $2^{\circ}\cdot28$  for a whole equivalent of the salt. The capacity for heat of the solution in question does not (I believe) differ materially from that of 1000 grains of water.

Fall from solution of  $\text{KO}, 3 \text{CrO}_3$ , . . .  $2^{\circ}\cdot28$

Half an equivalent of the crystallized *biphosphate of potash*, or 42.68 grains, was dissolved in 1000 grains of water, with a fall of  $1^{\circ}\cdot12$ , which gives  $2^{\circ}\cdot24$  for the whole equivalent.

Fall from solution of  $2 \text{HO} \cdot \text{KO}, \text{PO}_5$ , . . .  $2^{\circ}\cdot24$

A corresponding proportion of the crystallized *binarsenate of potash*, or 56.38 grains, were dissolved by 1000 grains of water, with a fall in one experiment of  $1^{\circ}\cdot13$ , and in another of  $1^{\circ}\cdot18$ . In a third experiment the solution of a whole equivalent of this salt, or 112.75 grains, was attended by a fall of temperature of  $2^{\circ}\cdot15$ . A greater discrepancy is observable in the results obtained from this than from most other salts, which appeared to arise from the full depression of temperature not occurring at the moment of solution, but a small portion of it being produced in a gradual manner for three or four minutes after the solution. The mean of the three observations gives  $2^{\circ}\cdot26$  for the equivalent quantity of the salt.

Fall from solution of  $2 \text{HO} \cdot \text{KO}, \text{AsO}_5$ , . . .  $2^{\circ}\cdot26$

The thermal properties of these two salts are interesting in relation to the terchromate of potash. The latter salt contains 14 atoms, which is also the number of atoms in both biphosphate and binarsenate of potash, if the equivalents of phosphorus and arsenic be supposed, like that of nitrogen, to represent three atoms.

Potash being common to the terchromate and biphosphate of potash, there remain, on subtracting that constituent from both salts, three equivalents of chromic acid equivalent in some sense to one equivalent of phosphoric acid together with two equivalents of water. This statement respecting phosphoric acid, recalls the view which has lately been proposed by M. Wurtz of the constitution of the hypophosphites, in which the two atoms of water which they all contain are supposed not to be basic, but to form part of the acid; a neutral hypophosphite being represented by  $\text{RO} + \text{PO}, \text{H}_2\text{O}_2$ , or rather by  $\text{RO} + \text{PO}_3\text{H}_2$ . For we are here representing biphosphate of potash as  $\text{KO} + \text{PO}_7\text{H}_2$ , corresponding with the terchromate of potash  $\text{KO} + \text{Cr}_3\text{O}_9$ , in which P is equivalent to  $\text{Cr}_3$ , and  $\text{O}_7 + \text{H}_2$  to  $\text{O}_9$ . The two atoms of water, however, may be replaced by a strong base in a biphosphate, but not in a hypophosphite. The relations of these salts show a progressive and



imperceptible passage of the basic elements of a salt into constituents of its acid, and the existence of intermediate conditions of the elements in question, which we may well conceive although our chemical formulæ fail to enable us to denote them; these formulæ being adapted only for the expression of the extreme conditions.

Of anhydrous *chromic acid* an equivalent, 32.59 grains, was dissolved by 1000 grains of water with a rise of  $0^{\circ}51$ . A second equivalent, dissolved in the previous solution, produced a rise of only  $0^{\circ}38$ . The relations of this acid to water are therefore very different from those of sulphuric acid.

5. *Sulphate of Soda*.—In removing the hygrometric water which the crystals of this salt generally contain in large quantity, by pressure in blotting-paper, the salt is apt to lose a little of its combined water. The crystallized salt contained as determined by analysis, to 100 sulphate of soda, 121.5 water, instead of 126.1 water, which are ten equivalents. The equivalent quantity of the fully hydrated salt is 100.85 grains, but of the salt under examination only 98.79 grains. The last quantity, which contains 54.2 grains of water, was dissolved in 946 grains of water in half a minute, with a fall of  $4^{\circ}43$ . The fall is almost entirely due, as will immediately appear, to the liquefaction of the combined water of the salt, of which the quantity liquefied in the experiment was 54.2 grains instead of 56.2, the ten equivalents. The fall of  $4^{\circ}43$  increased in the proportion of 54.2 to 56.2, becomes  $4^{\circ}59$ .

Fall on solution of  $\text{NaO}, \text{SO}_3 + 10 \text{HO}$ , .  $4^{\circ}59$

The same quantity of the salt was dissolved in the diluted sulphuric acid of the experiments with the previous salts, with a fall of  $5^{\circ}00$ ; which, corrected in the same manner as the last result, gives a fall of  $5^{\circ}19$  for the equivalent of the salt. Hence the fall on the solution of the sulphate of soda in dilute sulphuric acid is  $0^{\circ}60$  greater than in pure water; a circumstance connected probably with the formation of bisulphate of soda.

Sulphate of soda was made anhydrous by a strong heat, without being fused. The solution of the anhydrous salt is difficult, owing to the instantaneous formation of a hard coherent mass when the salt is thrown into the water, which it requires two or three minutes to break up and dissolve. Very little change of temperature occurs. A rise took place in one experiment of  $0^{\circ}10$ . In another experiment, in which the salt was added in a gradual manner with constant stirring, there was less caking, and the solution more rapid, although it still required two minutes. A rise occurred of  $0^{\circ}18$ . The last experiment is most to be depended upon. The results for the sulphate of soda will therefore be,—



Rise on solution of $\text{NaO}, \text{SO}_3$ , . . . .	$0^{\circ}\cdot 18$
Fall on solution of $\text{NaO}, \text{SO}_3 + 10 \text{HO}$ , . .	$4^{\circ}\cdot 59$
Whole heat disengaged by $\text{NaO}, \text{SO}_3$ , . . .	$4^{\circ}\cdot 77$

The last number represents the heat evolved in the formation of a solid hydrate of sulphate of soda containing ten atoms of water; it is remarkable how little it exceeds the heat disengaged in the crystallization of the same salt, or the fall observed on the solution of the crystallized salt. It appears as if water abandoned little more than its heat of fluidity on combining with dry sulphate of soda to form a solid hydrate.

Sulphate of soda, which had been allowed to effloresce in dry air between  $50^{\circ}$  and  $55^{\circ}$  Fahr. for a week, consisted of dry salt 100 and water 0.46. The equivalent quantity of this salt, which is so nearly anhydrous, or 44.81 grains, was dissolved in 1000 grains of water with a very slight change of temperature, namely a rise of  $0^{\circ}\cdot 05$ .

6. *Sulphate of Ammonia*.—Of the hydrated salt crystallized by spontaneous evaporation in air, which contains one atom of water of crystallization, the equivalent quantity, 47.03 grains, was dissolved in 1000 grains of water with a fall of temperature in three experiments of  $0^{\circ}\cdot 65$ ,  $0^{\circ}\cdot 64$ , and  $0^{\circ}\cdot 61$ , of which the mean is  $0^{\circ}\cdot 63$ .

Fall on solution of $\text{NH}_4\text{O}, \text{SO}_3 + \text{HO}$ , . . .	$0^{\circ}\cdot 63$
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The salt was obtained anhydrous by drying at  $248^{\circ}$  Fahr.; it was granular and crystalline, and neutral to test paper. The equivalent quantity, 41.41, produced a fall in three experiments of  $0^{\circ}\cdot 51$ ,  $0^{\circ}\cdot 53$ , and  $0^{\circ}\cdot 49$ ; of which the mean is  $0^{\circ}\cdot 51$ .

Fall on solution of $\text{NH}_4\text{O}, \text{SO}_3$ , . . . .	$0^{\circ}\cdot 51$ .
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A sensible but very small reduction of temperature, not exceeding  $0^{\circ}\cdot 02$ , occurred on mixing the solution of sulphate of ammonia with an equal bulk of water at the same temperature.

Dissolved in the diluted acid, consisting of a mixture of 300 water-grain measures of sulphuric acid of density 1.1 and 700 grains of water, the equivalent, 41.41 grains, of the anhydrous salt produced a fall of temperature in two experiments of  $1^{\circ}\cdot 17$  and  $1^{\circ}\cdot 14$ ; of which the mean is  $1^{\circ}\cdot 16$ . Hence the fall is greater on the solution of the sulphate of ammonia in dilute sulphuric acid than in water, by  $0^{\circ}\cdot 65$ . The fall of sulphate of soda was also greater by nearly the same amount,  $0^{\circ}\cdot 60$ , and of sulphate of potash by  $0^{\circ}\cdot 53$ , when these salts were dissolved in the same dilute acid instead of water.



IV. DOUBLE SULPHATES.

1. *Bisulphate of Potash*.—Of the usual double sulphate of water and potash crystallized in rhombohedral crystals, an equivalent quantity, 85.23 grains, was dissolved in 1000 grains of water, with a fall in two experiments of  $1^{\circ}96$  and  $1^{\circ}95$ . The same salt was fused by heat and pounded; it dissolved afterwards with a fall of  $1^{\circ}94$  and  $1^{\circ}90$  in two experiments. The cold upon solution of this salt appears to be the same before and after fusion. The result is,—

Fall on solution of  $\text{HO}, \text{SO}_3 + \text{KO}, \text{SO}_3$ , . . .  $1^{\circ}95$

I was anxious to compare with this salt the anhydrous bisulphate of potash of M. Jacquelin, which is described as being capable of dissolving in water without decomposition. One equivalent of sulphate of potash was accordingly dissolved in two equivalents of oil of vitriol, with the aid of heat, and an abundant crop was obtained on cooling of a salt in small silky crystals. As these appeared to be the salt in question, an equivalent quantity, or 79.60 grains, was dissolved, and a fall observed of  $1^{\circ}90$ . The result not differing from that of the former salt, the preparation of the anhydrous salt was repeated. The spongy mass of thin prismatic crystals obtained in a second experiment was pressed, dissolved again in water, crystallized and pressed again. The salt was still in minute prisms. The solution of 39.8 grains, half the equivalent quantity, was attended with a fall in two experiments of  $0^{\circ}91$  and  $0^{\circ}95$ ; or, for a whole equivalent,  $1^{\circ}86$ . Of the same salt, before the second solution, half an equivalent produced a fall of temperature of  $0^{\circ}96$ ; or, for the whole equivalent,  $1^{\circ}92$ . These results are identical with those formerly obtained with the hydrated bisulphate, if allowance be made for the smaller quantity of the salt employed, a circumstance which excited a doubt as to the composition of the prismatic salt. The product of the second crystallization was accordingly analysed; 19.30 grains of it gave 32.34 grains of sulphate of barytes, equivalent to 11.12 sulphuric acid, or 57.59 per cent.; 22.53 grains of the crystals lost no weight at  $150^{\circ}$ , but lost 0.24 water, or 1.02 per cent., by cautious fusion. The proportion of acid in the salt is greatly under that of an anhydrous bisulphate, namely 62.98 per cent., while it approaches sufficiently near that of the hydrated bisulphate, 58.74 per cent. The process of M. Jacquelin has not therefore given an anhydrous bisulphate of potash in my hands, and none of my experiments favours the existence of such a salt; the silky prismatic crystals which I obtained being nothing more than an unusual form of the sulphate of water and potash.

2. *Bisulphate of Soda*.—An equivalent quantity, 75.27 grains, of one and the same specimen of this salt, dissolved in three experiments with



a fall of  $0^{\circ}40$ ,  $0^{\circ}28$ , and  $0^{\circ}17$ . It did not dissolve so easily as the bisulphate of potash, possibly from partial decomposition and formation of a portion of neutral sulphate of soda. The same supposition will explain the want of agreement among the results. Taking the mean of the results,—

Fall on solution of  $\text{HO}, \text{SO}_3 + \text{NaO}, \text{SO}_3$ , . . .  $0^{\circ}28$

The fall of temperature observed on dissolving bisulphate of potash in water approaches that observed on dissolving the neutral sulphate of potash in dilute sulphuric acid, the first being  $1^{\circ}95$  and the second  $2^{\circ}04$ . But it is doubtful if the fall in the second case can be ascribed simply to the immediate formation and solution of bisulphate of potash, when the sulphate of potash and dilute sulphuric acid are mixed and dissolved together. In the formation of bisulphate of potash we have both the substitution of sulphate of potash for the second atom of water of the sulphate of water, and the throwing off of all the remaining water combined with the sulphate of water in hydrated sulphuric acid, bisulphate of potash containing no water of crystallization. Now as a great deal of heat was disengaged by this additional water on originally combining with the sulphate of water, we should expect heat again to be assumed by that water on becoming free, or cold to be produced.

3. *Sulphate of Magnesia and Potash*.—An equivalent quantity of the crystallized salt, namely 126.28 grains, containing 33.75 grains of water of crystallization, was dissolved in 976.2 grains of water at  $52^{\circ}$  Fahr., with nearly two minutes' stirring; a fall of temperature was observed of  $2^{\circ}30$  R. The experiment was repeated with the same result. But a slow rise of temperature was afterwards observed to occur in the solution, independent of any external influence, which in the course of four minutes amounted to  $0^{\circ}20$  R. This is not the only salt in which the fall of temperature on solution is immediately followed by a slight but sensible rise.

This salt was made anhydrous by a low red heat to which it was exposed for upwards of two hours, but was not fused. When the salt was thrown into water after this ignition, it gave a liquor which remained white and milky for two or three minutes, but the salt finally dissolved without residue. The rise of temperature on the solution of a whole equivalent of the anhydrous salt, or 92.53 grains, was  $1^{\circ}57$ ; on solution of one-half of an equivalent, or 46.2 grains,  $0^{\circ}80$ ; which gives  $1^{\circ}60$  for the whole equivalent.

Rise on solution of $\text{MgO}, \text{SO}_3 + \text{KO}, \text{SO}_3$ , . . .	$1^{\circ}60$
Fall on solution of $\text{MgO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{HO}$ ,	$2^{\circ}30$
Whole heat disengaged by $\text{MgO}, \text{SO}_3 + \text{KO}, \text{SO}_3$ , .	$3^{\circ}90$



The crystallized sulphate of magnesia and potash, dried by a nitre-bath, was found to retain 18.32 water to 100 anhydrous salt. Now 18.24 water represents 3 HO; the crystallized salt has consequently lost one-half of its water, retaining only three atoms. Of this salt, an equivalent quantity, or 109.4 grains, were dissolved in 1000 grains of water with a fall in three experiments of  $1^{\circ}35$ ,  $1^{\circ}30$ , and  $1^{\circ}35$ , of which the mean is  $1^{\circ}33$ .

Fall on solution of  $\text{MgO}$ ,  $\text{SO}_3 + \text{KO}$ ,  $\text{SO}_3 + 3 \text{HO}$ , . .  $1^{\circ}33$

The fall on the solution of this hydrate is less than on the solution of the former, by the heat disengaged in the combination of the salt with the deficient three atoms of water. The heat disengaged by the union of the salt with the first three atoms of water comes therefore to be  $2^{\circ}93$ , and with the second three atoms of water  $0^{\circ}97$ , making together  $3^{\circ}90$ . Hence as nearly as possible three times as much heat are disengaged by the first three atoms of water as by the last three atoms.

4. *Sulphate of Magnesia and Ammonia*.—The solution of an equivalent quantity, 113.13 grains, of the crystallized salt in 1000 grains of water was attended by a fall of temperature, in two experiments, of  $2^{\circ}20$  and  $2^{\circ}15$ , of which the mean is  $2^{\circ}17$ . If dissolved in 976.2 grains of water, like the potash salt, the fall would have been about  $\frac{1}{30}$ th more, or  $2^{\circ}24$ .

Fall on solution of  $\text{MgO}$ ,  $\text{SO}_3 + \text{NH}_4\text{O}$ ,  $\text{SO}_3 + 6 \text{HO}$ , . .  $2^{\circ}24$

The fall on the solution of the corresponding potash salt was  $2^{\circ}30$ .

5. *Protosulphate of Iron and Ammonia*.—The solution of 122.17 grains, the equivalent quantity of the crystallized salt in 1000 grains of water, was attended with the same fall of  $2^{\circ}20$  in two experiments. But this determination should be increased by  $\frac{1}{30}$ th, like the last; the fall then becomes  $2^{\circ}27$ .

Fall on solution of  $\text{FeO}$ ,  $\text{SO}_3 + \text{KO}$ ,  $\text{SO}_3 + 6 \text{HO}$ , . .  $2^{\circ}27$

6. *Sulphate of Manganese and Ammonia*.—In two experiments 61.20 grains of the crystallized salt, being one-half of the equivalent quantity, were dissolved in 983 grains of water with a fall of  $1^{\circ}11$  and  $1^{\circ}13$ ; or  $2^{\circ}24$  for a whole equivalent.

Fall on solution of  $\text{MnO}$ ,  $\text{SO}_3 + \text{NH}_4\text{O}$ ,  $\text{SO}_3 + 6 \text{HO}$ , . .  $2^{\circ}24$

It thus appears that the heat of liquefaction of the four crystallized double salts, sulphate of magnesia and potash, sulphate of magnesia and ammonia, sulphate of iron and potash, and sulphate of manganese and ammonia, is sensibly the same.

7. *Sulphate of Zinc and Potash*.—The fall on the solution of half an



equivalent, 69.26 grains, of the crystallized salt in 1000 grains of water, was in three experiments  $1^{\circ}33$ ,  $1^{\circ}27$ , and  $1^{\circ}30$ , of which the mean is  $1^{\circ}30$ . The fall for a whole equivalent, 138.52 grains, is therefore  $2^{\circ}60$ .

This salt was made anhydrous by a heat little short of redness, without being fused. Half an equivalent, 52.39 grains, was dissolved in 1000 grains of water with a rise of temperature of  $0^{\circ}83$  and  $0^{\circ}87$  in two experiments, of which the mean is  $0^{\circ}85$ . The rise for a whole equivalent, 104.77 grains of the salt, is therefore  $1^{\circ}70$ .

Rise on solution of $\text{ZnO}, \text{SO}_3 + \text{KO}, \text{SO}_3$ , . . .	$1^{\circ}70$
Fall on solution of $\text{ZnO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{HO}$ , . .	$2^{\circ}60$
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Whole heat disengaged in the hydration of $\text{ZnO}$ , } $\text{SO}_3 + \text{KO}, \text{SO}_3$ , . . . . . }	$4^{\circ}30$

8. *Sulphate of Copper and Ammonia*.—Of the crystallized salt, 62.45 grains, or one half of the equivalent quantity, were dissolved in 983 grains of water with a fall of temperature of  $1^{\circ}33$  and  $1^{\circ}28$  in two experiments; giving  $2^{\circ}63$  for the whole equivalent.

Fall on solution of  $\text{CuO}, \text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3 + 6 \text{HO}$ , . .  $2^{\circ}63$

The fall on the solution of the two immediately preceding salts is therefore sensibly the same.

9. *Protosulphate of Iron and Potash*.—Of this salt in small but well-defined crystals, 67.66 grains, one half of the equivalent quantity, were dissolved in 983 grains of water with a fall, in two experiments, of  $1^{\circ}25$  and  $1^{\circ}22$ ; or for the whole equivalent  $2^{\circ}47$ .

Fall on solution of  $\text{MnO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{HO}$ , . .  $2^{\circ}47$

10. *Sulphate of Zinc and Ammonia*.—Of the crystallized salt half an equivalent, 62.64 grains, was dissolved in 983 grains of water with a fall of  $1^{\circ}37$  and  $1^{\circ}36$ .

Fall on solution of  $\text{ZnO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{HO}$ , . .  $2^{\circ}73$

11. *Sulphate of Copper and Potash*.—The solution of half an equivalent of the crystallized salt, 69.07 grains, in 1000 grains of water, was attended with a fall in two experiments of  $1^{\circ}54$  and  $1^{\circ}50$ ; or for the whole equivalent of the salt, 138.14 grains; the fall is  $3^{\circ}08$  and  $3^{\circ}00$ , of which the mean is  $3^{\circ}04$ .

The crystallized salt was made anhydrous by a heat short of redness, which had the effect of causing it to frit but did not fuse it. The solution of 52.2 grains, half an equivalent, in 1000 grains of water, was attended by a fall in two experiments of  $1^{\circ}01$  and  $0^{\circ}96$ ; or for a whole equivalent,  $2^{\circ}02$  and  $1^{\circ}92$ , of which the mean is  $1^{\circ}97$ .



Rise on solution of $\text{CuO}, \text{SO}_3 + \text{KO}, \text{SO}_3$ , . . . . .	1°·97
Fall on solution of $\text{CuO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6 \text{HO}$ , . . . . .	3°·04
Whole heat disengaged in hydration of $\text{CuO}, \text{SO}_3 + \text{KO}, \text{SO}_3$ , . . . . .	5°·01

The fall on the solution of the preceding crystallized double salt is 3°·04, while the fall on the solution of its constituents dissolved separately is 1°·51 for the sulphate of potash, and 0°·67 for the hydrated sulphate of copper, making together 2°·18, which is less by 0°·86 than the former. The fall on the solution of the crystallized double sulphate of zinc and potash approaches more closely to the united falls of its constituents dissolved separately, the former being 2°·60 and the latter  $1^\circ + 1^\circ\cdot51 = 2^\circ\cdot51$ . The fall on the solution of the crystallized double sulphate of magnesia and potash is 2°·30; the united falls of its constituent salts  $0^\circ\cdot92 + 1^\circ\cdot51 = 2^\circ\cdot43$ . No perceptible change of temperature was observed when the solutions of a pair of these salts are mixed to form the double salt; which is in accordance with the conclusion of Dr. Andrews, that no heat is evolved in the combination of salts.

I have not, however, succeeded in obtaining any direct proof of the formation of the double sulphates on mixture. To a solution of 77·97 grains, or one equivalent, of crystallized sulphate of copper in 1000 grains of water, 41·41 grains, one equivalent, of sulphate of ammonia dried at  $234^\circ$  were added and dissolved. The fall on the solution of the last salt was  $0^\circ\cdot56$ , or the same as when the salt is dissolved in pure water. No change took place in the colour of the solution of the copper salt. The last salt was selected for this experiment, because it appears more disposed to form double salts than even the sulphate of potash.

In certain cases, a double salt is formed on using a bisulphate, while it is not with the neutral sulphate; as in the formation of sulphate of zinc and soda, from sulphate of zinc and bisulphate of soda, but not from sulphate of zinc and neutral sulphate of soda. To a solution of 85·23 grains, or the equivalent, of crystallized bisulphate of potash in 1000 grains of water, 89·59 grains, or the equivalent, of crystallized sulphate of zinc were added and dissolved, with a fall of  $1^\circ\cdot00$ , or the same as in pure water. To a similar solution of bisulphate of potash, 77·35 grains, or one equivalent, of crystallized sulphate of magnesia were added and dissolved, with a fall of  $0^\circ\cdot86$ ; the same fall also as on the solution of the latter salt in pure water. Yet the double salts crystallized out readily from both of these solutions.

I have formerly represented the anhydrous sulphate of magnesia and potash as corresponding with the protohydrated sulphate of magnesia. Now both these salts assume six atoms of water, and the heat then disengaged by the two salts is nearly the same:—



	Heat of hydration.
MgO, SO <sub>3</sub> + KO, SO <sub>3</sub> , . . . . .	3°·90
MgO, SO <sub>3</sub> + HO, . . . . .	3°·95

When the corresponding salts of zinc are compared, the same equality is not observed, but other relations appear.

	Heat of hydration.
ZnO, SO <sub>3</sub> + KO, SO <sub>3</sub> , . . . . .	4°·30
ZnO, SO <sub>3</sub> + HO, . . . . .	3°·45
ZnO, SO <sub>3</sub> , . . . . .	5°·17

These quantities of heat and the quantity disengaged by the anhydrous sulphate of zinc, have a remarkable relation among themselves; if they be all divided by 0°·86, we have

	Ratios of heat of hydration.
ZnO, SO <sub>3</sub> + HO, . . . . .	4·01
ZnO, SO <sub>3</sub> + KO, SO <sub>3</sub> , . . . . .	5
ZnO, SO <sub>3</sub> , . . . . .	6·01

The quantity of heat disengaged by the first atom of water on uniting with sulphate of zinc is 1°·71. If it had been only half that quantity, or 0·86, and had the deficient 0°·86 been evolved by the combination of the six following atoms, in addition to the heat they actually evolve, then the heat disengaged by the six atoms of water which unite with protohydrated sulphate of zinc, and by the double sulphate of zinc and potash, would be the same in both salts, as it is the same in the two corresponding salts of magnesia.

The heat evolved by the corresponding copper salts with their ratios, is as follows :—

	Heat of hydration.	Ratios.
CuO, SO <sub>3</sub> + HO, . . . . .	2°·93	4°
CuO, SO <sub>3</sub> , . . . . .	4°·40	6°
CuO, SO <sub>3</sub> + KO, SO <sub>3</sub> , . . . . .	5°·01	6°·86

It is to be observed, however, that while the protohydrate of sulphate of copper combines with only four atoms of water, the sulphate of copper and potash combines with six atoms; the usual comparison cannot therefore be made between these two salts.

The principal numerical results of the paper are exhibited in the following tables :—

1. Heat absorbed by equivalent quantities of crystallized salts on dissolving in water.

Sulphate of magnesia, . . . . .	7 HO	0°·92
Sulphate of zinc, . . . . .	...	1°·00
Protosulphate of iron, . . . . .	...	1°·06
Sulphate of copper, . . . . .	5 HO	0°·67



Sulphate of manganese, . . .	...	0°·12
Sulphate of magnesia and potash, . . .	6 HO	2°·30
Sulphate of magnesia and ammonia, . . .	...	2°·24
Sulphate of manganese and ammonia, . . .	...	2°·24
Sulphate of iron and ammonia, . . .	...	2°·27
Sulphate of iron and potash, . . .	...	2°·47
Sulphate of zinc and potash, . . .	6 HO	2°·60
Sulphate of copper and ammonia, . . .	...	2°·63
Sulphate of zinc and ammonia, . . .	...	2°·73
Sulphate of copper and potash, . . .	...	3°·04
Sulphate of soda, . . .	10 HO	4°·59
Sulphate of potash, . . .	anhydrous	1°·51
Sulphate of ammonia, . . .	...	0°·51
Chromate of potash, . . .	...	1°·18
Bichromate of potash, . . .	...	3°·96
Nitrate of potash, . . .	...	3°·96
Terchromate of potash, . . .	...	2°·28
Biphosphate of potash, . . .	2 HO	2°·24
Binarsenate of potash, . . .	...	2°·26
Sulphate of water and potash, . . .	anhydrous	1°·95

2. Heat disengaged in the complete hydration of anhydrous salts.

Sulphate of magnesia, . . .	5°·25
Sulphate of zinc, . . .	5°·17
Sulphate of copper, . . .	4°·40
Sulphate of manganese, . . .	3°·34
Sulphate of magnesia and potash, . . .	3°·90
Sulphate of zinc and potash, . . .	4°·30
Sulphate of copper and potash, . . .	5°·01

3. Heat disengaged by the combination of the first atom of water in the magnesian sulphates.

Sulphate of water, . . .	1°·47
Sulphate of copper, . . .	1°·47
Sulphate of manganese, . . .	1°·43
Sulphate of magnesia, . . .	1°·30
Sulphate of zinc, . . .	1°·71

Simple relations are observed between the quantities of heat disengaged by the sulphates of magnesia and zinc, which appear to belong to one class, while the sulphates of water, copper, and manganese belong to another class.



## XI.

EXPERIMENTS ON THE HEAT DISENGAGED IN  
COMBINATIONS.

## PART II.

## NEUTRALIZATION OF VARIOUS ACIDS BY HYDRATE OF POTASH.

THE arrangements adopted for observing the heat evolved on neutralizing acids by potash were similar to those described in the former paper. The same platinum crucible, weighing 1201.9 grains, and hollow cylinder of palladium, weighing 207.6 grains, were employed as the containing vessel and stirrer; but the constant quantity of water employed as a vehicle for the acid and alkali was increased from 1000 grains to 1544 grains, or 100 grammes, while the equivalent quantities of the substances used were the same as before. The solution of the saline body formed in an experiment was consequently one-half more dilute, and the small but sensible effect of further dilution of the solution in producing cold, observable in some of the former experiments, was thus entirely avoided, while the increase of the mass of fluid reduced the influence of external causes on its temperature. A mercurial thermometer of greater delicacy was employed, of which the bulb was a cylinder of 1.25 inch in length and 0.3 inch in diameter; the scale was graduated into degrees Fahrenheit, ranging from 40° to 70°, each degree being 0.42 inch in length (0.74 inch for one degree centigrade), divided into tenths of a degree, each of which could again be subdivided into fifths by the eye, so that the observation was made to one-fiftieth of a degree Fahrenheit. The eye was directed to the scale through a straight cylindrical tube of small diameter, supported in a horizontal position. The mercury in the bulb of the thermometer was equivalent in capacity for heat to 11.5 grains of water, and the containing vessel and stirrer to 49 grains, making together 60.5 grains of water; the capacity of the salt dissolved or formed rarely exceeded that of 12 grains of water.

I. NEUTRALIZATION OF HYDRATE OF POTASH BY NITRIC AND  
HYDROCHLORIC ACIDS.

The equivalent proportion of this acid adopted in these experiments is 33.85 grains, that is one-twentieth of 677, the usual equivalent of nitric acid on the oxygen scale. Nearly one-half the quantity mentioned was used in an experiment, namely 0.455 equivalent, diluted in the crucible with about four-fifths of the water, while the remaining portion of the 1544 grains of water, in a small and thin glass flask, contained



hydrate of potash in quantity sufficient to saturate the acid, and leave a *slight* excess of alkali. The two liquids were afterwards brought to exactly the same temperature, which was observed by two thermometers, the corresponding points of which were accurately determined, and the potash solution then emptied into the nitric acid. The following are the results of three observations of the temperature of the liquids before mixture, and the temperature after mixture:—

Before mixture, . . .	61°·91	62°·13	62°·13
After mixture, . . .	66°·70	66°·91	66°·89
Rise of temperature, .	4°·79	4°·78	4°·76

Increasing 4°·78 the mean of the experiments, in the proportion of 0·455 to 1, we have 10°·50 as the rise of temperature on saturating a whole equivalent of potash by nitric acid.

The heat evolved upon combination is sensibly affected by a considerable difference in the temperatures at which the acid and alkali are mixed; being less at the lower temperature. This appears by the following experiments, in which 0·5 equivalent of nitric acid was neutralized at a temperature twenty-two degrees lower than in the former experiments.

Before mixture, . . .	40°·25	40°·60	
After mixture, . . .	45°·43	45°·80	
Rise of temperature, .	5°·18	5°·20	Mean 5°·19

Hence we have the heat from the neutralization of the nitric acid by hydrate of potash—

10°·50, at 62° F.  
10°·38, at 40° F.

Half an equivalent of hydrochloric acid, 11·38 grains, was neutralized with hydrate of potash in slight excess, exactly as the nitric acid was treated in the preceding experiment.

Before mixture, . . .	60°·20	60°·00	59°·95
After mixture, . . .	65°·30	65°·15	65°·10
Rise of temperature, .	5°·10	5°·15	5°·15

Mean rise 5°·13 for 0·5 equivalent of hydrochloric acid, or 10°·26 for 1 equivalent of that acid. The neutralization of hydrate of potash, therefore, in very dilute solutions with these two different acids produces nearly the same disengagement of heat, the result with nitric acid being 10°·50.

The heat of combination appears also to be sensibly affected in amount by the temperature of the experiment:—



Before mixture, . . .	40°·00	40°·25	
After mixture, . . .	45°·02	45°·30	
Rise of temperature, .	5°·02	5°·05	Mean 5°·03

From which it follows that the heat from the neutralization of hydrochloric acid by hydrate of potash is—

10°·26, at 60° F.

10°·06, at 40° F.

It is remarkable how large a proportion the cold produced on dissolving in water crystallized nitrate of potash and chloride of potassium, the salts produced in these experiments, bears to the heat observed in the formation of the same salts.

One equivalent of crystallized nitrate of potash (63·25 grs.) well dried, pounded and sifted, was dissolved in the usual quantity of water—

Before solution, . .	61°·80	62°·20	61°·88
After solution, . .	56°·10	56°·45	56°·18
Fall of temperature,	5°·70	5°·75	5°·70 Mean 5°·72
Before solution, . .	56°·45	57°·70	55°·45
After solution, . .	50°·80	52°·00	49°·75
Fall of temperature,	5°·65	5°·70	5°·70 Mean 5°·68

The cold on dissolving this salt is not quite constant, but increases sensibly at low temperatures, a law which appears to prevail in a class of salts :—

Before solution, . .	47°·00	46°·40	45°·95
After solution, . .	41°·05	40°·47	40°·00
Fall of temperature,	5°·95	5°·93	5°·95 Mean 5°·94

It appears, on comparing the last set of experiments with that immediately preceding it, that a difference of ten degrees at this part of the scale makes a difference of 0°·26, or  $\frac{1}{2}$ d part, in the fall of temperature consequent upon the solution of an equivalent of nitrate of potash. It is this increased absorption of heat at the low temperature probably which occasions the observed heat of combination of the salt to diminish at the same part of the scale.

On the other hand, the cold, on dissolving several equivalents of nitrate of potash successively at a constant temperature, in the same quantity of water diminishes considerably with the number of equivalents of salt dissolved. The capacity for heat of the crystallized salt is 0·239 (Regnault).



Dissolved in 1544 grains of water,

First equivalent of nitrate of potash :—

	62°·34	63°·68	
	56°·68	57°·90	
Fall,	5°·66	5°·78	Mean 5°·72

Second equivalent of nitrate of potash :—

	63°·47	63°·12	
	58°·17	57°·86	
Fall,	5°·30	5°·26	Mean 5°·28

Third equivalent of nitrate of potash :—

	63°·40	63°·56	
	58°·47	58°·61	
Fall,	4°·93	4°·95	Mean 4°·94

Fourth equivalent of nitrate of potash :—

	63°·57	63°·35	
	58°·95	58°·76	
Fall,	4°·62	4°·59	

Fifth equivalent of nitrate of potash :—

	63°·40	63°·34	
	59°·08	59°·10	
Fall,	4°·32	4°·24	Mean 4°·28

Sixth equivalent of nitrate of potash :—

	63°·45	
	69°·63	
Fall,	3°·82	

In consequence of this diminished absorption of heat in the solution of the latter equivalents of nitrate of potash, the addition of water to the strong solution finally obtained occasions a further absorption of heat; or dilution produces cold.

The last prepared solution, which consisted of 379·5 grains of nitrate of potash dissolved in 1544 grains of water, and is a solution nearly saturated for the temperature, was mixed with another 1544 grains of water in a pint silver crucible with silver spatula, weighing 1650 grains, both liquids being at the same temperature :—



Before mixture,	.	.	.	.	63°·19
After mixture,	.	.	.	.	61°·91
Fall of temperature,	.	.	.	.	<u>1°·28</u>

A second portion of 1544 grains of water being added to the above solution, occasioned a further fall of temperature :—

Before mixture,	.	.	.	.	63°·57
After mixture,	.	.	.	.	63°·19
Fall,	.	.	.	.	<u>0°·38</u>

It appears from these experiments on the solution of successive equivalents of nitrate of potash in the same quantity of water, that much of the cold on dissolving that salt is properly referable to the dilution of the solution, and not to the simple liquefaction or solution of the crystalline salt. But this is more obvious in dissolving a salt of great solubility, such as nitrate of ammonia, of which many more equivalents may be dissolved in succession.

Dissolved in 1544 grains of water,

100·4 grains, or 2 equivalents of nitrate of ammonia :—

66°·25
57°·91
<u>Fall, 8°·34</u>

Third and fourth equivalents :—

66°·43
58°·91
<u>Fall, 7°·52</u>

Fifth and sixth equivalents :—

66°·21
59°·36
<u>Fall, 6°·85</u>

Seventh and eighth equivalents :—

66°·10
59°·82
<u>Fall, 6°·28</u>

Ninth and tenth equivalents :—

66°·26
60°·41
<u>Fall, 5°·85</u>

Eleventh and twelfth equivalents :—

66°·53
61°·06
<u>Fall, 5°·47</u>

Thirteenth and fourteenth equivalents :—

66°·45
61°·29
<u>Fall, 5°·16</u>



Fifteenth and sixteenth equivalents :—

$$\begin{array}{r} 66^{\circ}47 \\ 61^{\circ}55 \\ \hline \text{Fall, } 4^{\circ}92 \end{array}$$

Seventeenth and eighteenth equivalents :—

$$\begin{array}{r} 66^{\circ}61 \\ 61^{\circ}99 \\ \hline \text{Fall, } 4^{\circ}62 \end{array}$$

Nineteenth and twentieth equivalents :—

$$\begin{array}{r} 66^{\circ}26 \\ 61^{\circ}91 \\ \hline \text{Fall, } 4^{\circ}35 \end{array}$$

Twenty-first and twenty-second equivalents :—

$$\begin{array}{r} 66^{\circ}58 \\ 62^{\circ}45 \\ \hline \text{Fall, } 4^{\circ}13 \end{array}$$

Twenty-third and twenty-fourth equivalents :—

$$\begin{array}{r} 66^{\circ}66 \\ 62^{\circ}63 \\ \hline \text{Fall, } 4^{\circ}03 \end{array}$$

Twenty-fifth and twenty-sixth equivalents :—

$$\begin{array}{r} 66^{\circ}83 \\ 63^{\circ}16 \\ \hline \text{Fall, } 3^{\circ}67 \end{array}$$

Twenty-seventh and twenty-eighth equivalents :—

$$\begin{array}{r} 66^{\circ}53 \\ 62^{\circ}97 \\ \hline \text{Fall, } 3^{\circ}56 \end{array}$$

Twenty-ninth and thirtieth equivalents :—

$$\begin{array}{r} 66^{\circ}57 \\ 63^{\circ}24 \\ \hline \text{Fall, } 3^{\circ}33 \end{array}$$

Thirty-first and thirty-second equivalents :—

$$\begin{array}{r} 66^{\circ}80 \\ 63^{\circ}57 \\ \hline \text{Fall, } 3^{\circ}23 \end{array}$$

Thirty-third and thirty-fourth equivalents :—

$$\begin{array}{r} 66^{\circ}37 \\ 63^{\circ}24 \\ \hline \text{Fall, } 3^{\circ}13 \end{array}$$

Thirty-fifth and thirty-sixth equivalents :—

$$\begin{array}{r} 66^{\circ}45 \\ 63^{\circ}50 \\ \hline \text{Fall, } 2^{\circ}95 \end{array}$$

Here we find that while the fall on the solution of the first two equivalents of nitrate of ammonia is  $8^{\circ}34$ , that of the last two dissolved is only  $2^{\circ}95$ , or little more than a third of the former. The liquid, however, finally consisted of 1544 grains of water and 1807.2 grains of salt, and would therefore have a considerably greater capacity for heat than the water alone; but the proper correction for this increase of capacity cannot at present be made, as the specific heat of nitrate of ammonia has not been ascertained.



The last solution of nitrate of ammonia, which was nearly saturated for the temperature, was of density  $1^{\circ}247$ . Three portions of 100 grammes of water were added to it in succession, to discover the cold produced on dilution.

First 100 grammes of water:—

Before mixture,	.	.	66°·83
After mixture,	.	.	60°·27
Fall,	.	.	<u>6°·56</u>

Second 100 grammes of water:—

Before mixture,	.	.	67°·06
After mixture,	.	.	64°·40
Fall,	.	.	<u>2°·66</u>

Third 100 grammes of water:—

Before mixture,	.	.	67°·06
After mixture,	.	.	65°·61
Fall,	.	.	<u>1°·45</u>

The high solubility of the nitrate of soda adapts it for similar experiments. It will be observed that a difference of 13 degrees of temperature does not materially affect the amount of heat absorbed on dissolving a single equivalent of this salt. The capacity for heat of the crystallized salt is 0·278 (Regnault).

One equivalent of nitrate of soda, 53·40 grains, dissolved in 100 grammes of water:—

Before solution,	.	.	65°·07	51°·78	51°·63
After solution,	.	.	61°·56	48°·25	48°·08
Fall,	.	.	<u>3°·51</u>	<u>3°·53</u>	<u>3°·55</u>

Ten equivalents of this salt being dissolved successively in the same 100 grammes of water, the following changes of temperature were observed:—

	I.	II.	III.	IV.	V.
	65°·07	65°·01	64°·63	64°·80	64°·84
	61°·56	61°·70	61°·65	63°·14	62°·29
Fall,	<u>3°·51</u>	<u>3°·31</u>	<u>2°·98</u>	<u>2°·66</u>	<u>2°·55</u>
	VI.	VII.	VIII.	IX.	X.
	64°·77	64°·63	64°·89	64°·77	64°·64
	62°·38	62°·34	62°·74	62°·79	62°·76
Fall,	<u>2°·39</u>	<u>2°·29</u>	<u>2°·15</u>	<u>1°·98</u>	<u>1°·88</u>



The solution of the tenth equivalent of this salt produces therefore only one-half the cold due to the first equivalent.

The solution of chloride of potassium in water is attended with a fall of temperature, which is considerable, although not so great as with nitrate of potash.

One equivalent of chloride of potassium (46·62 grains) dissolved in 100 grammes of water:—

Before solution, . .	62°·05	61°·80	61°·70
After solution, . .	59°·10	58°·88	58°·75
Fall of temperature,	2°·95	2°·92	2°·95 Mean 2°·94

At a lower temperature:—

Before solution, . .	45°·55	45°·04	45°·53
After solution, . .	42°·55	42°·02	42°·50
Fall of temperature,	3°·00	3°·02	3°·03 Mean 3°·02

## II. NEUTRALIZATION OF HYDRATE OF POTASH BY SULPHURIC ACID.

Half an equivalent of sulphuric acid, 12·53 grains, was saturated with a slight excess of hydrate of potash, the united liquids containing 100 grammes of water, as in the preceding experiments with nitric and hydrochloric acids:—

Before mixture, . .	61°·31	61°·45	61°·53
After mixture, . .	67°·01	67°·13	67°·21
Rise, . . . . .	5°·70	5°·68	5°·68 Mean 5°·69

The rise of temperature on saturating a whole equivalent of hydrate of potash with sulphuric acid will therefore be 11°·38.

The saturation of sulphate of water, already in combination with sulphate of potash in the bisulphate of that base, is attended with the disengagement of a still greater quantity of heat. Half an equivalent of fused bisulphate of potash, dissolved in water like the acid of the former experiments, was neutralized by potash, with the usual conditions:—

Before mixture, . .	62°·74	62°·92	63°·05
After mixture, . .	68°·95	69°·12	69°·22
Rise, . . . . .	6°·21	6°·20	6°·17 Mean 6°·19

The saturation of the whole equivalent of sulphate of water in a



solution of the bisulphate of potash therefore occasions the disengagement of  $12^{\circ}38$ ; free sulphate of water only  $11^{\circ}38$ ; the excess in the former case being  $1^{\circ}00$ .

Now, in saturating two equivalents of sulphuric acid, the heat evolved is twice  $11^{\circ}38$ , or  $22^{\circ}76$ ; but as  $12^{\circ}38$  is evolved in saturating the second equivalent of sulphuric acid, it follows that  $10^{\circ}38$  only are evolved in saturating the first equivalent of acid. Hence we have—

Heat disengaged in the formation of bisulphate of potash,	$10^{\circ}38$
“ “ saturating acid of “ “	$12^{\circ}38$
	<hr/> 22°76

The cold, on dissolving an equivalent of crystallized sulphate of potash, 54.55 grains, in 100 grammes of water, was also observed:—

Before solution, . . .	$66^{\circ}69$	$66^{\circ}01$	$66^{\circ}27$
After solution, . . .	$64^{\circ}38$	$63^{\circ}75$	$63^{\circ}96$
Fall, . . . . .	<hr/> 2°31	<hr/> 2°26	<hr/> 2°31
			Mean 2°29

On mixing solutions of sulphate of potash and sulphate of water (dilute sulphuric acid), to form bisulphate of potash, cold is produced, as was formerly observed; and from this cause sulphate of potash, when dissolved in water acidulated with sulphuric acid, produces more cold than in pure water, by about one-third of the quantity from the latter. This excess of heat absorbed I was disposed to connect with the combination of sulphate of water with sulphate of potash, and formation of a double salt. But it is remarkable that the magnesian sulphates, which we do not certainly know to combine with hydrated acids, as sulphate of potash does, likewise produce greater cold on dissolving in acidulated than in pure water.

Thus an equivalent of crystallized sulphate of magnesia, which dissolves in 1000 grains of water with a fall of 0.88 R. (*Chemical Memoirs*, vol. i. p. 111), dissolved in the same quantity of water already containing an equivalent of sulphuric acid with a fall of  $1^{\circ}12$ ,  $1^{\circ}17$ ,  $1^{\circ}18$  R. in three experiments; of which the mean is  $1^{\circ}16$ , being  $0^{\circ}28$  more than in pure water. A second equivalent of crystallized sulphate of magnesia, when dissolved in the same liquor, produced a fall, in three experiments, of  $0^{\circ}96$ ,  $0^{\circ}92$ ,  $0^{\circ}95$  R., of which the mean is  $0^{\circ}94$ , or only  $0^{\circ}06$  more than in pure water.

In an equivalent of nitric or of hydrochloric acid, the fall from the solution of an equivalent of crystallized sulphate of magnesia was nearly double what it is in pure water.

The fall in water containing 1 equivalent of nitric acid was  $1^{\circ}70$ ,  $1^{\circ}68$ ,  $1^{\circ}64$ , of which the mean is  $1^{\circ}67$ .



The fall in water containing 1 equivalent of hydrochloric acid was  $1^{\circ}70$ ,  $1^{\circ}70$ ,  $1^{\circ}68$ ; mean  $1^{\circ}69$  R.

The fall on the solution of 1 equivalent of sulphate of magnesia in  $\frac{1}{2}$  equivalent of hydrochloric acid was  $1^{\circ}37$ ,  $1^{\circ}37$ ,  $1^{\circ}38$ ; mean  $1^{\circ}37$  R. The excess of cold produced by the half equivalent of this acid, over water alone, was therefore  $0^{\circ}50$ ; the excess by the whole equivalent of acid  $0^{\circ}82$ ; so that fully more than one-half of the effect is produced by the first half equivalent of acid.

An excess above 1 equivalent of acid to 1 equivalent of a salt of this class increases the depression of temperature still further, but in a less degree than the direct proportion of its quantity. Thus the cold on dissolving 1 equivalent of sulphate of zinc in water being  $1^{\circ}02$  R.,—

In  $1\frac{1}{2}$  equivalent of sulphuric acid,  $1^{\circ}22$ ,  $1^{\circ}19$ ,  $1^{\circ}25$ ; mean  $1^{\circ}22$ .

In 1 equivalent of nitric acid,  $1^{\circ}56$ ,  $1^{\circ}55$ ,  $1^{\circ}54$ ; mean  $1^{\circ}55$ .

In  $\frac{1}{2}$  equivalent of hydrochloric acid,  $1^{\circ}50$ ,  $1^{\circ}50$ ,  $1^{\circ}47$ ; mean  $1^{\circ}49$ .

In 1 equivalent of hydrochloric acid,  $1^{\circ}82$ ,  $1^{\circ}83$ ,  $1^{\circ}86$ ; mean  $1^{\circ}83$ .

In 2 equivalents of hydrochloric acid,  $2^{\circ}26$ ,  $2^{\circ}26$ ,  $2^{\circ}24$ ; mean  $2^{\circ}25$ .

The solution of an equivalent of crystallized sulphate of iron was attended with a fall of temperature,—

In water of  $1^{\circ}06$  R.

In 1 equivalent of sulphuric acid, of  $1^{\circ}28$ ,  $1^{\circ}20$ ,  $1^{\circ}26$ ,  $1^{\circ}25$ ; mean  $1^{\circ}25$ .

In 1 equivalent of hydrochloric acid, of  $1^{\circ}69$ ,  $1^{\circ}68$ ,  $1^{\circ}73$ ; mean  $1^{\circ}70$ .

The solution of an equivalent of crystallized sulphate of copper was attended with a fall of temperature,—

In water of  $0^{\circ}63$  R.

In 1 equivalent of sulphuric acid, of  $0^{\circ}94$ ,  $0^{\circ}96$ ,  $1^{\circ}02$ ; mean  $0^{\circ}97$  R.

The mixture of an equivalent of *sulphate of water*, 30.68 grains, in 300 grains of water, with another 700 grains of water, occasioned a rise of  $0^{\circ}09$  R.; with 700 grains of water containing 1 equivalent of hydrochloric acid a rise of  $0^{\circ}16$ , and with 700 grains of water containing 1 equivalent of nitric acid,  $0^{\circ}00$ .

The magnesian sulphates generally resemble sulphate of water in producing heat and not cold on dilution of their strong solutions. The solutions of the three following salts were saturated in the cold:—

Sulphate of zinc (density 1.395), with equal bulk of water,  $+0^{\circ}60$ .

Sulphate of magnesia (density 1.294), with equal bulk of water,  $+0^{\circ}60$ .

Protosulphate of iron (density 1.227), with equal bulk of water,  $+0^{\circ}04$ .

The experiments on the solution of salts in acids leave it doubtful, whether the additional depression of temperature is due in every case and entirely to a combination of the salt with the acid, as it may be supposed to be when sulphate of potash is dissolved in dilute sulphuric



acid, bisulphate of potash being then formed, or whether it is a consequence of a partial decomposition of the salt by the free acid to which it is exposed. The small portion of acid, generally a single equivalent, which produces the greatest proportional effect, seems to indicate that combination or decomposition is the cause, rather than any alteration in the solvent power of the liquid. The action of hydrochloric acid and of nitric acid is often the same, and is greater than that of sulphuric acid. This appears even in the solution of a magnesian chloride in water and in these acids.

Thus 42.29 grains, 1 equivalent, of the fused anhydrous chloride of zinc were dissolved in 1000 grains of water with a rise in two experiments of  $3^{\circ}42$ ,  $3^{\circ}45$  R., of which the mean is  $3^{\circ}44$  R. In 1000 grains of water containing 1 equivalent of sulphuric acid, with a rise of  $3^{\circ}43$ ,  $3^{\circ}42$ ,  $3^{\circ}42$  R., in three experiments; which is nearly the same result as in pure water. In the same quantity of water containing 1 equivalent of hydrochloric acid, with a rise of  $2^{\circ}86$ ,  $2^{\circ}88$ ,  $2^{\circ}86$ ; of which the mean is  $2^{\circ}87$  R., being  $0^{\circ}57$  less heat than in water alone. The presence of the hydrochloric acid has therefore occasioned a fall of  $0^{\circ}57$  in the solution of chloride of zinc, while the action of sulphuric acid is insensible.

An alkaline chloride was little affected by the presence of an equivalent of these acids in the water in which it was dissolved. Thus *chloride of sodium* was dissolved with a fall—

In 1000 grs. water,	of $0^{\circ}57$ , $0^{\circ}60$ ,	Mean $0^{\circ}59$ R.
„ „ + HCl,	of $0^{\circ}60$ , $0^{\circ}60$ , $0^{\circ}60$ ,	„ $0^{\circ}60$ R.
„ „ + NO <sub>5</sub> ,	of $0^{\circ}50$ , $0^{\circ}50$ , $0^{\circ}52$ ,	„ $0^{\circ}51$ R.
„ „ + SO <sub>3</sub> ,	of $0^{\circ}50$ , $0^{\circ}50$ , $0^{\circ}43$ ,	„ $0^{\circ}48$ R.

To obtain light upon this influence of acids on the thermal phenomena of the solution of salts, experiments were made upon two other salts. *Sulphate of ammonia* without any water of crystallization (1 equivalent, or 41.41 grains) was observed to dissolve in 1000 grains of water with a fall of  $0^{\circ}51$  R. In water containing  $\frac{1}{2}$  HCl, with a fall of  $1^{\circ}12$ ,  $1^{\circ}10$ , and  $1^{\circ}12$  R.; mean  $1^{\circ}11$ . In water containing HCl, with a fall of  $1^{\circ}30$ ,  $1^{\circ}22$ ,  $1^{\circ}28$ ; mean  $1^{\circ}27$  R. In water containing NO<sub>5</sub>, with a fall of  $1^{\circ}28$ ,  $1^{\circ}30$ ,  $1^{\circ}30$ ; mean  $1^{\circ}29$  R. In water containing SO<sub>3</sub>, with a fall of  $0^{\circ}92$ ,  $0^{\circ}92$ ,  $0^{\circ}90$ ; mean  $0^{\circ}92$  R. The addition of a second equivalent of highly diluted sulphuric acid to the last solution produced a change of temperature in three experiments of  $0^{\circ}02$ ,  $0^{\circ}00$ ,  $0^{\circ}00$ . The addition of a second equivalent of sulphate of ammonia to the preceding solutions of the bisulphate of ammonia, occasioned a fall of  $0^{\circ}58$ ,  $0^{\circ}55$ ,  $0^{\circ}60$  R.; mean  $0^{\circ}58$ , or very little more than in pure water ( $0^{\circ}51$ ). In 1544 grains of water containing 1 equivalent of acetic acid (32.15 grains), with a fall of  $0^{\circ}84$ ,  $0^{\circ}78$ ,  $0^{\circ}81$  F.,



of which the mean is  $0^{\circ}81$  F., the experiment being made at  $67^{\circ}$  F. In 1 equivalent of oxalic acid (22.64 grains), with a fall of  $1^{\circ}20$ ,  $1^{\circ}21$ , and  $1^{\circ}22$  F., the experiment being made at  $65^{\circ}$  F. To render the last two experiments comparable with the former, they must be reduced in the proportion of 19 to 13, that is, the effect of the acetic acid to  $0^{\circ}55$  R., of the oxalic acid to  $0^{\circ}83$  R.; so that the influence of the acetic acid is almost nothing, of the oxalic acid much less than that of the mineral acids.

While 1 equivalent of *nitrate of potash* was dissolved in 1000 grains of water at  $63^{\circ}$  F., with a fall of  $3^{\circ}76$ ,  $3^{\circ}72$  and  $3^{\circ}80$  R., of which the mean is  $3^{\circ}76$ ; it was dissolved in the same quantity of water containing 1 equivalent of nitric acid at  $67^{\circ}$  F., with a fall of  $3^{\circ}64$ ,  $3^{\circ}54$ ,  $3^{\circ}64$  R., of which the mean is  $3^{\circ}57$ ; in the same quantity of water containing 1 equivalent of sulphuric acid at  $58^{\circ}$  F., with a fall of  $3^{\circ}53$ ,  $3^{\circ}50$ ,  $3^{\circ}50$  R., of which the mean is  $3^{\circ}51$ .

The mere mixing of solutions of such neutral salts as are understood to combine together and form a double salt, is not attended with such changes of temperature. No sensible change of temperature was perceived on mixing dilute solutions of a magnesian and potash sulphate; and one of these salts was dissolved in a solution of the other with the same fall of temperature as in pure water. Although I think it all but certain that these salts combine at once on mixing, I could not discover a single circumstance which was decisive of the fact. The density of such a mixture of salts was not altered by boiling it alone or with spongy platinum, and was exactly the same as that of the liquid formed on dissolving in water a corresponding quantity of the crystallized double sulphate. The addition of an equivalent of sulphuric acid already highly diluted to each of the solutions thus compared, produced exactly the same fall of temperature. On the other hand, this fall of temperature was as nearly as possible the same as that obtained on dividing the acid into two equal portions, and mixing separately a solution of each of the constituent salts with each portion. The solution of a double salt appears therefore to be as nearly as possible equivalent to the constituent salts dissolved apart. Even in the formation of *alum* no certain change of temperature was observable; one-fourth of an equivalent of sulphate of potash (13.63 grains), when dissolved in 1000 grains of water, producing a fall of  $0^{\circ}32$  R., while when dissolved in 1000 grains of water containing one-fourth of  $\text{Al}_2\text{O}_3 + 3\text{SO}_3$ , the fall was  $0^{\circ}35$ ,  $0^{\circ}32$ ,  $0^{\circ}35$  R., of which the mean is  $0^{\circ}34$ ; the experiments being made at  $57^{\circ}$  F.

But these double sulphates being all less soluble than their constituent sulphates, it was desirable to make the experiment upon the formation of a double salt, which is more soluble than its constituents; such as the double chloride of mercury and ammonium. One-half of



an equivalent of chloride of mercury, 42.70 grains, was dissolved in 1544 grains of water at 64° F., with a fall of 0°29, 0°30, 0°30 F., of which the mean is 0°30 F. The same quantity of chloride of mercury was dissolved in 1544 grains of water, containing half an equivalent, 16.74 grains, of chloride of ammonium, at 63° F., with a fall of 0°13, 0°12, 0°12 F., of which the mean is 0°12 F. Doubling these results, we have the fall from a whole equivalent of chloride of mercury in water equal to 0°60; from chloride of mercury in chloride of ammonium 0°24; the difference, or 0°36, being due to heat evolved in the formation of the double salt. The latter, however, or sal-alembroth, assumes an atom of water of crystallization in its formation, which may perhaps occasion some change of temperature.

When 1 equivalent of chloride of mercury was dissolved in half an equivalent of chloride of ammonium at 63°, the fall was 0°45, 0°45, 0°47 F., of which the mean is 0°46 F. The disengagement of heat in the formation of this second double salt is therefore  $0^{\circ}60 - 0^{\circ}46 = 0^{\circ}14$  F. It is doubtful whether the heat here can be ascribed to hydration; as the resulting double salt has been crystallized at the usual temperature by Dr. Kane, both anhydrous and with one atom of water. The circumstance however of the chloride of mercury being dissolved by a solution of sal-ammoniac in much larger quantity than by pure water, affords a proof of the immediate formation of a double salt on the solution of its constituents together, which cannot be obtained in the magnesian or aluminous double sulphates.

I may be allowed to place under the present head of sulphuric acid, the results of experiments on the solution in water of two double sulphates, namely, sulphate of zinc and soda, and sulphate of manganese and soda, no experiment on a double salt of the soda division of this class being recorded in the former paper. The *sulphate of zinc and soda*, formed by Mr. Arrott, was in excellent crystals, containing four atoms of water; of which the composition is expressed by the formula  $\text{ZnO}, \text{SO}_3 + \text{NaO}, \text{SO}_3 + 4 \text{HO}$ . One-half of an equivalent, 58.61 grains of the salt, containing 11.25 grains of water of crystallization, was dissolved in 988.8 grains of water at 62° F., with a fall in three experiments of 0°02 R., 0°04, 0°02; mean 0°03 R.

Of the same salt made anhydrous by heat and fused, half an equivalent, or 47.41 grains, was dissolved in 1000 grains of water at 62° F., with a rise in three experiments of 1°86, 1°87, 1°84; mean 1°86 R. Doubling the results of the experiments in both cases, to obtain the changes for a whole equivalent, we find—

Cold on solution of  $\text{ZnO}, \text{SO}_3 + \text{NaO}, \text{SO}_3 + 4 \text{HO}$  0°06 R.

Heat on solution of  $\text{ZnO}, \text{SO}_3 + \text{NaO}, \text{SO}_3$  3°72 R.

As the two sulphates, in all the double sulphates of this class contain—



ing sulphate of soda, crystallize apart when the salt is dissolved in water at  $62^{\circ}$ , the double salt is probably decomposed in these experiments; and the circumstances of its solution may therefore be very different from those of a magnesian double sulphate containing sulphate of potash.

The *sulphate of manganese and soda*, for which I am also indebted to Mr. Arrott, was in good crystals containing two atoms of water; the formula of this salt being  $\text{MnO}, \text{SO}_3 + \text{NaO}, \text{SO}_3 + 2 \text{HO}$ . 1 equivalent of the crystallized salt, 103.2 grains, containing 11.25 grains of water of crystallization, was dissolved in 988.8 grains of water, with a rise of temperature in three experiments of  $0^{\circ}.77$ ,  $0^{\circ}.70$ , and  $0^{\circ}.70$ ; of which the mean is  $0^{\circ}.72$  R.

Of the same salt, fused by heat and anhydrous, 1 equivalent, 91.95 grains, was dissolved in 1000 grains of water, with a rise in two experiments of  $3^{\circ}.02$  and  $2^{\circ}.99$ ; of which the mean is  $3^{\circ}.00$  R. The results therefore, for this double salt, are—

Heat on solution of $\text{MnO}, \text{SO}_3 + 2 \text{HO}$ ,	.	$0^{\circ}.72$
„ „ $\text{MnO}, \text{SO}_3$ ,	.	$3^{\circ}.00$

### III. NEUTRALIZATION OF BICHROMATE OF POTASH BY HYDRATE OF POTASH.

Half an equivalent of bichromate of potash, 47.34 grains, and a little more than half an equivalent of hydrate of potash contained separately in different portions of the usual quantity 1544 grains or 100 grammes of water, were brought to the same temperatures exactly, and mixed in two experiments:—

Before mixture, . . .	$63^{\circ}.23$	$63^{\circ}.50$
After mixture, . . .	$67^{\circ}.71$	$67^{\circ}.97$
Rise of temperature, . . .	$4^{\circ}.48$	$4^{\circ}.47$

Doubling  $4^{\circ}.48$ , the mean result, we have  $8^{\circ}.96$  F. as the heat evolved on neutralizing the second equivalent of chromic acid in bichromate of potash.

Of the neutral or yellow chromate of potash, which is the product of this neutralization, 1 equivalent, 62.08 grains, was dissolved by 1544 grains of water at  $65^{\circ}$  F., with a fall in three experiments of  $1^{\circ}.82$ ,  $1^{\circ}.81$  and  $1^{\circ}.87$ , of which the mean is  $1^{\circ}.83$ .

### IV. NEUTRALIZATION OF ACETIC ACID BY HYDRATE OF POTASH.

Half an equivalent of acetic acid, 16.08 grains, was neutralized by potash in very slight excess, as in the other experiments:—



Before mixture, . .	63°·52	63°·81	63°·94
After mixture, . .	68°·68	68°·98	69°·12
Rise of temperature,	5°·16	5°·17	5°·18

The mean result of these experiments 5°·17 being doubled, we have 10°·34 F. as the heat evolved on the saturation of acetic acid by hydrate of potash.

Of acetate of potash fused without becoming black, 1 equivalent, 61·65 grains, was dissolved in 1544 grains of water at 65° F., with a rise of temperature in three experiments of 2°·45, 2°·47, 2°·44; of which the mean is 2°·45 F.

#### V. NEUTRALIZATION OF OXALIC ACID BY HYDRATE OF POTASH.

Half an equivalent of oxalic acid was neutralized by potash under the usual circumstances:—

Before mixture, . .	64°·60	64°·66	64°·69
After mixture, . .	69°·84	69°·89	69°·95
Rise of temperature,	5°·24	5°·23	5°·26

Doubling 5°·24, the mean result, we have 10°·48 F. as the heat evolved on the saturation of a whole equivalent of oxalic acid by hydrate of potash.

One equivalent of *crystallized oxalic acid*, 39·50 grains, containing 12·5 grains of water of crystallization, was dissolved in 1533 grains of water at 67° F., with a fall of 3°·04, 3°·06, 3°·04; of which the mean is 3°·05.

One equivalent of *oxalate of water* deprived of its water of crystallization, 28·26 grains, was dissolved in 1544 grains of water at 67° F., with a fall of 0°·99, 0°·99, 1°·01; of which 1°·00 is the mean. The difference between the falls on solution of the hydrated and anhydrous oxalate, is occasioned by the hydration of the latter on solution. The heat disengaged when oxalate of water combines with its two atoms of constitutional water is therefore  $3°·05 - 1°·00 = 2°·05$  F.

Neutral *oxalate of potash* crystallizes with a single atom of water, which requires a heat of 212° to expel it. 1 equivalent of the crystallized salt, 57·76 grains, containing 6·25 grains of water, was dissolved in 1538 grains of water at 67° F., with a fall of 2°·65, 2°·66 and 2°·67; of which the mean is 2°·66 F.

Of the same salt made anhydrous by heat, one-half of an equivalent, 25·75 grains, was dissolved in 1544 grains of water, with a fall of 0°·76,



$0^{\circ}71$ ,  $0^{\circ}74$ ; of which the mean is  $0^{\circ}74$ . A whole equivalent of the salt would therefore have dissolved with a fall of  $1^{\circ}58$ , which is  $1^{\circ}08$  less than the fall from the hydrated salt. The last quantity represents the heat of combination of oxalate of potash with one atom of water of crystallization. It approaches nearly to one-half of the heat disengaged by oxalate of water, in combining with two atoms of water, one-half of  $2^{\circ}05$  being  $1^{\circ}025$ ; the difference is within the errors of observation.

When hydrated oxalate of potash is dissolved in water containing oxalic acid, the change of temperature is very much the same as in pure water, although in the former case a superoxalate will be formed. One-fourth of an equivalent of oxalate of potash,  $14^{\circ}44$  grains, was dissolved in 1544 grains of water containing in solution one-fourth of an equivalent of hydrated oxalic acid, at  $67^{\circ}$  F., with a fall of  $0^{\circ}70$ ,  $0^{\circ}68$ ,  $0^{\circ}68$ ; mean  $0^{\circ}68$  F. If it were therefore possible to dissolve a whole equivalent of the salt in a whole equivalent of the acid contained in the quantity of water to which we are restricted, the fall would be four times greater, or  $2^{\circ}72$  F., which is nearly the same as the cold on dissolving crystallized oxalate of potash in water, namely,  $2^{\circ}66$ . Here again little or no heat is observed in forming a double salt, for the binoxalate of potash must be regarded as such.

*Binoxalate of Potash.*  $\text{KO}, \text{C}_2\text{O}_3 + \text{HO}, \text{C}_2\text{O}_3, 2\text{HO}$ .—As with bisulphate of potash, the saturation of the excess of acid in this salt causes the disengagement of more heat than the saturation of the same quantity of free acid. One-fourth of an equivalent of the crystallized binoxalate, 22.91 grains, was neutralized by hydrate of potash at  $67^{\circ}$ :—

Before mixture, . . .	$66^{\circ}80$	$66^{\circ}85$	$66^{\circ}96$
After mixture, . . .	$69^{\circ}91$	$69^{\circ}96$	$70^{\circ}04$
Rise of temperature,	$3^{\circ}11$	$3^{\circ}11$	$3^{\circ}08$ Mean $3^{\circ}10$

The mean quantity, multiplied by four, gives  $12^{\circ}40$  F., as the heat evolved on neutralizing by potash the second equivalent of oxalic acid in binoxalate of potash. Now distributing the heat from the saturation of two equivalents of oxalic acid,  $20^{\circ}68 (= 10^{\circ}34 \times 2)$ , as was done in sulphuric acid, we have—

Heat disengaged in the formation of binoxalate of pot.	$8^{\circ}28$
„ „ in saturating acid of binoxalate of pot.	$12^{\circ}40$
	<hr/> $20^{\circ}68$

One-fourth of an equivalent of binoxalate of potash, 22.91 grains, containing 6.25 grains of water of crystallization, was dissolved in 1538 grains of water at  $64^{\circ}$  F., with a fall of  $1^{\circ}65$ ,  $1^{\circ}66$ ,  $1^{\circ}65$ ; mean  $1^{\circ}65$  F. The mean result multiplied by four, gives  $6^{\circ}60$  F. as the fall



on dissolving a whole equivalent of binoxalate of potash in water. This is  $0^{\circ}89$  more than the sum of the falls on dissolving the constituent salts separately,  $2^{\circ}66 + 3^{\circ}05$  being equal to  $5^{\circ}71$  only.

*Quadroxalate of Potash.*  $\text{KO}, \text{C}_2 \text{O}_3 + \text{HO}, \text{C}_2 \text{O}_3 + 2 (\text{HO}, \text{C}_2 \text{O}_3 + 2 \text{HO})$ .—Four-sixths of an equivalent of hydrated oxalic acid, 26.22 grains, were mixed with one-sixth of an equivalent of potash exactly to form this salt:—

Before mixture, . . .	64°25	64°23	64°25
After mixture, . . .	66°01	66°01	65°99
Rise of temperature, . .	1°76	1°78	1°74

The mean result  $1^{\circ}76$  multiplied by six, gives  $10^{\circ}56$ , as the heat evolved in the formation of quadroxalate of potash; that is, in the saturation of 1 equivalent of potash by 1 of oxalic acid, and the further combination of that oxalate of potash with 3 equivalents of oxalate of water. This rise of temperature is nearly the same as that in the formation of neutral oxalate of potash, namely  $10^{\circ}48$ .

To observe the heat disengaged on neutralizing quadroxalate of potash by hydrate of potash, one-sixth of an equivalent of that acid salt in solution was mixed with three-sixths of an equivalent, or rather more, of the alkali, so as to form neutral oxalate:—

Before mixture, . . .	64°19	64°20	64°51
After mixture, . . .	69°38	69°42	69°71
Rise of temperature, . .	5°19	5°22	5°20

Doubling  $5^{\circ}20$ , the mean result, we have  $10^{\circ}40$  F. as the heat disengaged on saturating 1 equivalent of potash by each of the 3 atoms of oxalate of water in the quadroxalate of potash.

0.192 equivalent (30.70 grains) of quadroxalate of potash was dissolved in 1540 grains of water at  $63^{\circ}$ , with a fall of  $2^{\circ}02$ ,  $2^{\circ}13$ ,  $2^{\circ}14$ ; of which the mean is  $2^{\circ}10$  F. This gives by calculation a fall of  $10^{\circ}93$  for the solution of a whole equivalent of quadroxalate of potash, which is  $0^{\circ}88$  less than the fall of its constituent salts dissolved separately,  $2^{\circ}66$  with three times  $3^{\circ}05$  amounting to  $11^{\circ}81$ .

The different oxalates enumerated appear to absorb quantities of heat, on dissolving, which have a simple relation to each other. Thus, dividing the different falls of temperature by  $0^{\circ}88$ , a number which has more than once presented itself in the discussion of these experiments, we obtain a set of ratios given in the second column; and which, being multiplied by two in the third column, approach nearly to round numbers:—



	I. Cold on solution.	II. Ratios.	III. Ratios.	
Cr. oxalate of potash, .	2°·66	3·02	6·04	6.
Cr. oxalic acid, .	3°·05	3·47	6·94	7.
Cr. binoxalate of potash, .	6°·60	7·50	15·00	15.
Cr. quadroxalate of potash,	10°·93	12·42	24·84	25.

# VI. NEUTRALIZATION OF BICARBONATE OF POTASH WITH HYDRATE OF POTASH.

Half an equivalent of the crystallized salt, 31·38 grains, dissolved in water, was neutralized with hydrate of potash :—

Before mixture, .	67°·28	67°·93	67°·68
After mixture, .	70°·66	71°·24	71°·03
Rise of temperature, .	3°·38	3°·31	3°·35

Doubling 3°·35, the mean result, there is obtained 6°·70 as the heat disengaged on saturating the second proportion of carbonic acid in the bicarbonate of potash.

One equivalent, 62·76 grains, of the crystallized bicarbonate was dissolved in 100 grammes of water at 67°, with a fall in three experiments of 3°·68, 3°·69 and 3°·74 ; mean 3°·70.

One equivalent of anhydrous carbonate of potash was dissolved in 100 grammes of water at 67°, with a rise in three experiments of 2°·48, 2°·43 and 2°·47 ; mean 2°·46. The heat evolved on dissolving anhydrous acetate of potash is nearly the same, being 2°·45.

# VII. NEUTRALIZATION OF ARSENIC AND PHOSPHORIC ACIDS BY HYDRATE OF POTASH.

Half an equivalent of arsenic acid, 36°·00 grains, in solution as usual, was mixed with exactly half an equivalent of hydrate of potash, to form the binarsenate of potash ( $2\text{HO}, \text{KO}, \text{AsO}_5$ ) :—

Before mixture, .	63°·04	63°·19	63°·29
After mixture, .	68°·14	68°·30	68°·38
Rise of temperature, .	5°·10	5°·11	5°·09

Doubling 5°·10, the mean result, we obtain 10°·20 F. as the heat disengaged by neutralizing 1 equivalent of potash in the formation of binarsenate of potash.



One-fourth of an equivalent of arsenic acid, 18.00 grains, was mixed with exactly half an equivalent of potash, to form arseniate of potash ( $\text{HO}, 2\text{KO}, \text{AsO}_5$ ):—

Before mixture, . .	63°·27	63°·33	63°·42
After mixture, . .	67°·87	67°·94	68°·05
Rise of temperature,	4°·60	4°·61	4°·63 Mean 4°·61

Twice 4°·61, or 9°·22 F., is therefore the heat disengaged on neutralizing 1 equivalent of hydrate of potash in the formation of the neutral arseniate of potash.

The same salt was formed by mixing together solutions of half an equivalent of binarsenate of potash, 56.37 grains, and exactly half an equivalent of potash:—

Before mixture, . . .	64°·28	64°·27	64°·20
After mixture, . . .	68°·31	68°·33	68°·26
Rise of temperature, .	4°·03	4°·06	4°·06

Taking 4°·05 as the mean, we have twice that quantity, or 8°·10 F., as the heat disengaged on neutralizing 1 equivalent of potash with the acid in binarsenate of potash.

On forming the subarsenate of potash ( $3\text{KO}, \text{AsO}_5$ ), by mixing together solutions of one-sixth of an equivalent of arsenic acid and exactly half an equivalent of potash:—

Before mixture, . . .	63°·41	63°·50	63°·50
After mixture, . . .	67°·40	67°·52	67°·49
Rise of temperature, .	4°·09	4°·02	3°·99

Doubling 4°·03, the mean result, we have 8°·06 F. as the heat disengaged in the formation of one-third of an equivalent of subarsenate of potash, or in the neutralization of each of 3 equivalents of potash by a single equivalent of arsenic acid.

Hence the successive addition of 3 equivalents of potash to 1 of arsenic occasions the following disengagements of heat:—

By first	KO	10°·20; formation of binarsenate of potash.
„ second	KO	8°·10; formation of arseniate of potash.
„ third	KO	5°·88; formation of subarsenate of potash.
<hr/>		
24°·18 = 8°·06 × 3.		

Of hydrated phosphoric acid, which had been boiled in water for a considerable time to render it fully tribasic, half an equivalent was



mixed with half an equivalent of potash, to form biphosphate of potash ( $2\text{HO}, \text{KO}, \text{PO}_5$ ):—

Before mixture, . . .	64°00	64°00	64°03
After mixture, . . .	69°01	68°99	69°02
Rise of temperature, .	5°01	4°99	4°99

Taking 5°00 as the mean, we have 10°00 F. as the heat disengaged on saturating 1 equivalent of potash with 1 equivalent of phosphoric acid in the formation of biphosphate of potash, containing  $\text{KO} + 2\text{HO}$  as bases.

By mixing one-fourth of an equivalent of phosphoric acid with half an equivalent of potash, phosphate of potash ( $\text{HO}, 2\text{KO}, \text{PO}_5$ ):—

Before mixture, . . .	64°00	63°61	63°63
After mixture, . . .	68°49	68°08	68°18
Rise of temperature, .	4°49	4°47	4°55

Doubling the mean result, 4°50, we have 9°00 F. as the heat disengaged in forming half an equivalent of neutral phosphate of potash, or in saturating each of 2 equivalents of potash by 1 equivalent of phosphoric acid, in the formation of phosphate of potash.

The same phosphate of potash was formed by mixing solutions of half an equivalent of biphosphate of potash with half an equivalent of potash:—

Before mixture, . . .	64°06	64°14	64°15
After mixture, . . .	68°09	68°15	68°16
Rise of temperature, .	4°03	4°01	4°01

Doubling 4°02, the mean result, we have 8°04 F. as the heat disengaged on saturating an equivalent of potash with the acid of biphosphate of potash.

To form the subphosphate of potash ( $3\text{KO}, \text{PO}_5$ ), one-sixth of an equivalent of phosphoric acid, 7·43 grains, was mixed with half an equivalent of potash:—

Before mixture, . . .	63°61	63°67	63°69
After mixture, . . .	67°87	67°93	67°99
Rise of temperature, .	4°26	4°26	4°30

Twice the mean result, 4°27, is 8°54 F., which is the heat disengaged on neutralizing each of three equivalents of potash by a single equivalent of phosphoric acid.

The heat therefore disengaged in the gradual saturation of phosphoric acid by 3 equivalents of potash may be thus distributed:—



By first	equivalent of potash,	. .	10°00
„ second	„	„ . .	8°08
„ third	„	„ . .	7°54
			<hr/>
			25°62 = 8·54 × 3.

## XII.

ON THE DIFFUSION OF LIQUIDS.<sup>1</sup>

## THE BAKERIAN LECTURE.

From *Phil. Trans.* 1850, pp. 1-46, 805-836; 1851, pp. 483-494. [*Annal. de Chimie* xxix. 1850, pp. 197-229; *Brit. Assoc. Rep.* 1851 (Pt. 2), p. 47; *Chem. Soc. Journ.* iii. 1851, pp. 60-67; *Jour. de Pharm.* xix. 1851, pp. 394-401; Liebig, *Annal.* lxxvii. 1851, pp. 56-89, 129-160; *Phil. Mag.* xxxvii. 1850, pp. 181-198, 254-281, 341-349.]

ANY saline or other soluble substance, once liquefied and in a state of solution, is evidently spread or diffused uniformly through the mass of the solvent by a spontaneous process.

It has often been asked whether this process is of the nature of the diffusion of gases, but no satisfactory answer to the question appears to be obtained, owing, I believe, to the subject having been studied chiefly in the operations of endosmose, where the action of diffusion is complicated and obscured by the imbibing power of the membrane, which is peculiar for each soluble substance, but no way connected with the diffusibility of the substance in water. Hence also it was not the diffusion of the salt, but rather the diffusion of the solution, which was generally regarded. A diffusibility like that of gases, if it exists in liquids, should afford means for the separation and decomposition even of unequally diffusible substances, and being of a purely physical character, the necessary consequence and index of *density*, should present a scale of densities for substances in the state of solution, analogous to vapour densities, which would be new to molecular theory.

M. Gay-Lussac proceeds upon the assumed analogy of liquid to gaseous diffusion in the remarkable explanation which he suggests of the cold produced on diluting certain saline solutions, namely, that the molecules of the salt expand into the water like a compressed gas admitted into additional space.

<sup>1</sup> Received November 16,—Read December 20, 1849.



The phenomena of solubility are at the same time considered by that acute philosopher as radically different from those of chemical affinity, and as the result of an attraction which is of a physical or mechanical kind. The characters indeed of these two attractions are strongly contrasted. Chemical combination is uniformly attended with the evolution of heat, while solution is marked with equal constancy by the production of cold. The substances which combine chemically are the dissimilar, while the soluble substance and its solvent are the like or analogous in composition and properties.

In the consideration of solubility, attention is generally engrossed entirely by the quantity of salt dissolved. But it is necessary to apprehend clearly another character of solution, namely, the degree of force with which the salt is held in solution, or the intensity of the solvent attraction, quite irrespective of quantity dissolved. In the two solid crystalline hydrates, pyrophosphate of soda and sulphate of soda, we see the same ten equivalents of water associated with both salts, but obviously united with unequal degrees of force, the one hydrate being persistent in dry air and the other highly efflorescent. So also in the solutions of two salts which are equally soluble in point of quantity, the intensity of the attraction between the salt and the water may be very different, as exemplified in the large but feeble solubility in water of such bodies as the iodide of starch or the sulphindylate of potash, compared with the solubility of hydrochloric acid or of the acetate of potash, which last two substances are capable of precipitating the two former, by displacing them in solution. Witness also the unequal action of animal charcoal in withdrawing different salts from solution, although the salts are equally soluble; and the unequal effect upon the boiling-point of water produced by dissolving in it the same weight of various salts. Besides being said to be small or great, the solubility of a substance has also therefore to be described as weak or strong.

The gradations of intensity observed in the solvent force are particularly referred to, because the inquiry may arise how far these gradations are dependent upon unequal diffusibility; whether indeed rapidity of diffusion is not a measure of the force in question.

I have only further to premise, that two views may be taken of the physical agency by which gaseous diffusion itself is effected, which are equally tenable, being both entirely sufficient to explain the phenomena.

On one theory, that of Dr. Dalton, the diffusibility of a gas is referred immediately to its elasticity. The same spring or self-repulsion of its particles which sends a gas into a vacuum, is supposed to propel it through and among the particles of a different gas.

The existence of an attraction of the particles of one gas for the



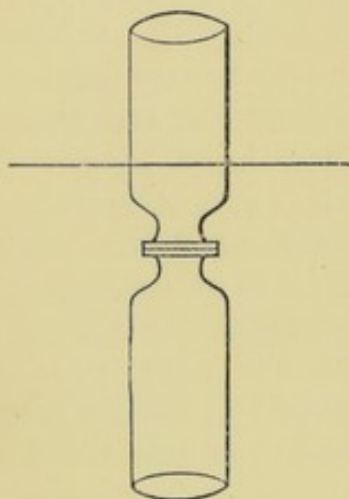
particles of all other gases is assumed in the other theory. This attraction does not occasion any diminution of volume of gases on mixing, because it is an attraction residing on the surfaces only of the gaseous molecules. It is of the same intensity for all gases, hence its effect in bringing about intermixture is dependent upon the weight of the molecules of the gases to be moved by it; and the velocity of diffusion of a gas comes to have the same relation to its density on this hypothesis as upon the other.<sup>1</sup>

The surface attraction of molecules assumed will recall the surface attraction of liquids, which is found necessary to account for the elevation of liquids in tubes and other phenomena of capillary attraction.

(1.) An early preliminary experiment was made upon the liquid diffusion of a body, with whose diffusion as a gas we are already well acquainted, namely, carbonic acid dissolved in water.

Two half-pound stoppered glass bottles were selected, of which the mouths were 1.2 inch in diameter, and the lips were ground flat so as to close tight when applied together (fig. 1.)

FIG. 1.



One of them, placed firmly in an upright position, was filled to the base of the neck with carbonic acid water. Over this distilled water was poured, care being taken to disturb the liquid below as little as possible, in filling up the neck. The second bottle, filled with distilled water and inverted upon a glass plate, was slipped over the first at the water-trough. The solution of carbonic acid in the lower bottle was thus placed in free communication by an aperture of 1.2 inch, with an equal volume of pure water in the upper bottle. It was expected that the carbonic acid would be found, in time, equally diffused through both bottles.

After forty-eight hours, the upper inverted bottle was again slipped off from the lower one, upon a glass plate, and the ratio of the gas found in the upper to that in the lower bottle determined by the weight of carbonate of baryta which the liquids of the two bottles afforded respectively. It was as 1.18 to 12.80 (about 1 to 11), instead of the ratio of equality, which would undoubtedly be the ultimate result of diffusion, were sufficient time allowed.

<sup>1</sup> Both of the molecular theories of the diffusion of gases were first publicly explained, and at the same time ably discussed, with the reference to the law of diffusion which had been drawn from observation, by my late friend Mr. T. S. Thomson of Clitheroe. A decided preference was given by Mr. Thomson, and also by the late Mr. Ivory, to the last, or the attraction theory of diffusion, over that of gases being *vacua* to each other. See *Phil. Mag.*, 3d series, vol. xxv. pp. 51, 282.



After five days, in a second experiment with a weaker solution of carbonic acid, the gas was found to be distributed—

In upper bottle,	.	.	.	1.63
In lower bottle,	.	.	.	8.44

or in the proportion of 1 to 5 nearly.

In other experiments where the liquid in the upper bottle was a solution in water of nitrous oxide gas, instead of pure water, the carbonic acid of the lower bottle was also observed to diffuse into the liquid above it, as freely as it did into pure water in a comparative experiment; the ultimate ratios being 1 to 0.12 in the nitrous oxide liquid, and 1 to 0.10 in the water experiment.

With the necks of the pair of bottles occupied by sponge charged with distilled water, the diffusion of the carbonic acid of the lower bottle proceeded with little change in its rapidity, or in the result when nitrous oxide was placed above it. The carbonic acid found in the upper bottle, and which had diffused into it from the lower, was 0.231 when the upper bottle contained water alone, and 0.229 when it was water charged with three-fourths of its volume of nitrous oxide gas,—to 1 carbonic acid remaining undiffused in the lower bottle in both cases.

It appeared, then, that the liquid diffusion of carbonic acid was a slow process compared with its gaseous diffusion, quite as much as days are to minutes.

That this diffusion of the liquid carbonic acid takes places with undiminished vigour into water already saturated with nitrous oxide, the substance of all others most resembling carbonic acid in solubility and the whole range of its physical qualities. The diffusion of the liquid carbonic acid appears no more repressed by the liquid nitrous oxide, than the diffusion of gaseous carbonic acid is by gaseous nitrous oxide.

But the chief interest of these observations was the practical solution which they give to the question, whether, in conducting experiments on liquid diffusion, accidental causes of disturbance and intermixture of two liquids, communicating freely with each other, can be avoided. It was made evident that little is to be feared from accidental dispersion when ordinary precautions are taken.

An excess of density in the lower liquid of not more than  $\frac{1}{1000}$  part is found adequate to prevent any considerable change of place of the latter,—from expansion by heat, accidental tremors and such disturbing causes, which must exist,—for days together.

(2.) Another early inquiry was, how far is the diffusion of various salts governed or modified by the density of their solutions.

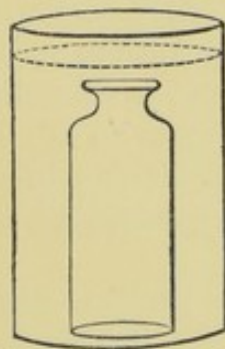
Solutions of eight hydrated acids and salts were prepared, having



the common density of 1.200, and were set to diffuse into water in the following manner :—

Eighteen or twenty six-ounce phials were made use of to contain the solutions, and to form what I shall call the Solution phials or cells. They were of the same make and selected from a large stock, of the common aperture of 1.175 inch. Both the mouths and bottoms of these phials were ground flat. The mode of making an experiment was first to fill the phial to the base of the neck, or rather to a constant distance of 0.6 inch below the ground surface of the lip. A little disc of cork, provided with a slight upright peg of wood, was then floated upon the solution in the neck, after having been first dipt in water. The neck itself was now filled up with pure water by means of a pointed sponge, the drop suspended from the sponge being made to touch the peg of the float, and water caused to flow in the gentlest manner, by slightly pressing the sponge. The only other part of the apparatus, the Water-jar, was a plain cylindrical glass jar, of which the inner surface of the bottom was flat or slightly concave, to give a firm support to the phial. The phial, with its solution only, was first placed in this jar partly filled with distilled water, and the neck of the former was then filled up with distilled water in this position, as before described, to avoid any subsequent movement. The phial was ultimately entirely covered to the depth of an inch with water, which required about 30 ounces of

FIG. 2.



the latter, fig. 2. The saline solution in the diffusion cell or phial thus communicated freely with about 5 times its volume of pure water, the liquid atmosphere which invites diffusion. Another modification of this procedure was the substitution of phials cast in a mould, of the capacity of 4 ounces, or more nearly 2080 grs., which were ground down to a uniform height of 3.8 inches. The neck was 1.25 inch in diameter and 0.5 inch in depth; and the phial was filled up with the solution to be diffused

to that point. The solution cell or phial and the water-jar form together a Diffusion cell.

The diffusion was stopped, after twenty-seven days in the present experiments, by closing the mouth of the phial with a plate of glass, and then raising it out of the water-jar. The quantity of salt or of acid which had found its way into the water-jar,—the diffusion product as it may be called,—was then determined by evaporating to dryness for the salts, and by neutralizing the same liquid with a normal alkaline solution for the acids. The quantities of the acids diffused are estimated at present as protohydrates for the sake of comparison with the salts.



TABLE I.—Diffusion of Solutions of Density 1·200. Temp. 66° Fahr.

	Placed in solution cell.		Found in water-jar.	
	Proportion of anhydrous salt, or of acid protohydrate, to 100 of water.	Boiling-point.	Diffusion product.	
			In grains.	Ratio.
Chloride of sodium.....	34·21	225·5	269·80	100
Nitric acid .....	37·93	227	581·20	215·42
Sulphuric acid.....	29·03	223	455·10	168·68
Chloride of potassium (density 1·178)	34·86	221	320·30	118·71
Bisulphate of potash.....	31·85	216	319·00	118·23
Nitrate of soda.....	32·42	220	260·20	96·44
Sulphate of magnesia.....	22·38	214	95·87	35·53
Sulphate of copper.....	21·56	213½	77·47	28·71

It appears that the diffusion from solutions of the same density is not equal but highly variable, ranging from 1 to 0·1333.

The results also favour the existence of a relation between large or rapid diffusibility and a high boiling-point. The latter property may be taken to indicate of itself a high degree of attraction between the salt and water.

## I. CHARACTERS OF LIQUID DIFFUSION.

### 1. *Diffusion of Chloride of Sodium.*

The characters of liquid diffusion were first examined in detail in the case of this salt.

(1.) Do different proportions of chloride of sodium in solution give corresponding amounts of diffusion?

Solutions were prepared of chloride of sodium in the proportion of 100 water with 1, 2, 3, and 4 parts of the salt.

The diffusion of all the solutions was continued for the same time, eight days, at the mean temperature of 52°·5 Fahr.

Proportion of salt to 100 water.	Diffusion product.	
	In grains.	Ratio.
1	2·78	1·
2	5·54	1·99
3	8·37	3·01
4	11·11	4·00



The quantities diffused appear therefore to be closely in proportion (for this salt) to the quantity of salt in the diffusing solution. The density of the solutions containing 1, 2, 3, and 4 parts of chloride of sodium, was at  $60^{\circ}$ , 1.0067, 1.0142, 1.0213, 1.0285. The increase of density corresponds very nearly with the proportion of chloride of sodium in solution. A close approach to this direct relation is indeed observable in most salts, when dissolved in proportions not exceeding 4 or 5 per cent.

The relation which appears in these results is also favourable to the accuracy of the method of experimenting pursued. The variation from the speculative result does not in any observation exceed 1 per cent.

(2.) Is the quantity of salt diffused affected by temperature?

The diffusion of similar solutions of chloride of sodium was repeated at two new temperatures,  $39^{\circ}6$  and  $67^{\circ}$ , the one being above and the other below the preceding temperature. It was necessary to use artificial means to obtain the low temperature owing to the period of the season. A close box of double walls, namely, the ice-safe of the Wenhams Ice Company, was employed, masses of ice being laid on the floor of the box, and the water-jars supported on a shelf above. The water and solution were first cooled separately for twenty-four hours in the ice-box, before the diffusion was commenced. It was found that the temperature could be maintained within a range of  $2^{\circ}$  or  $3^{\circ}$  for eight days. It was doubtful however whether the temperature was constantly the same to a degree or two in all the jars; and the results obtained at an artificial temperature were always less concordant and sensibly inferior in precision to observations made at the atmospheric temperature.

#### Diffusion of Chloride of Sodium.

Proportion of salt to 100 water.		Diffusion product.	
		In grains.	Ratio.
1	At $39^{\circ}6$	2.63	1.
2	At $39^{\circ}6$	5.27	2.00
3	At $39^{\circ}6$	7.69	2.92
4	At $39^{\circ}6$	10.00	3.80
1	At $67^{\circ}$	3.50	1.
2	At $67^{\circ}$	6.89	1.97
3	At $67^{\circ}$	9.90	2.83
4	At $67^{\circ}$	13.60	3.89

The proportionality in the diffusion is still well preserved at the different temperatures. The deviations are indeed little, if at all, greater



than might be occasioned by errors of observation. The ratio of diffusion, for instance, from the solutions containing 4 parts of salt, is 3.80 and 3.89 for the two temperatures, which numbers fall little short of 4.

The diffusion manifestly increases with the temperature, and as far as can be determined by three observations, in direct proportion to the temperature. The diffusion-product from the 4 per cent. solution increases from 10 grs. to 13.60, with a rise of temperature of  $27^{\circ}4$ , or rather more than one-third. Supposing the same progression continued, the diffusibility of chloride of sodium would be doubled by a rise of 84 or 85 degrees.

(3.) The progress of the diffusion of chloride of sodium in such experiments as have been narrated was further studied by intercepting the operation after it had proceeded for different periods of 2, 4, 6, and 8 days. The solution employed was that containing 4 parts of salt to 100 water. Two of the six-ounce phials were diffused at the same time for each period. The temperature given is the mean of the temperatures of a water-jar observed each each day of the period. The daily fluctuation was not more than two or three-tenths of a degree Fahr.

In 2 days, temperature  $63^{\circ}7$ ; the salt diffused was 4.04 and 3.86 grs.; mean 3.95 grs.

In 4 days, temperature  $63^{\circ}7$ ; the salt diffused was 6.78 and 7.12 grs.; mean 6.95 grs.

In 6 days, temperature  $63^{\circ}8$ ; the salt diffused was 10.02 and 9.70 grs.; mean 9.86 grs.

In 8 days, temperature  $64^{\circ}$ ; the salt diffused was 13.00 and 13.25 grs.; mean 13.12 grs.

The proportion diffused in the first period of two days is given directly in the first experiments. The proper diffusion for each of the three latter periods of two days is obtained by deducting from the result of each period the result of the period which precedes it:—

Diffused in 1st two days,	.	.	3.95 grs.
Diffused in 2d two days,	.	.	3.00 grs.
Diffused in 3d two days,	.	.	2.91 grs.
Diffused in 4th two days,	.	.	3.26 grs.

The diffusion appears to proceed pretty uniformly, if the amount diffused in the first period of two days be excepted. Each of the phials contained at first about 108 grs. of salt, of which the maximum quantity diffused is 13.12 grs. in eight days, or  $\frac{1}{8.24}$  of the whole salt. Still the diffusion must necessarily follow a diminishing progression, which would be brought out by continuing the process for longer time, and appear at the earliest period in the salt of most rapid diffusion.

All the experiments which follow being made like the preceding on



comparatively large volumes of solution in the phial, and for equally short periods of seven or eight days, may be looked upon as exhibiting pretty accurately the initial diffusion of such solutions, the influence of the diminishing progression being still small. The volume of water in the water-jar is also relatively so large, that the experiment approaches to the condition of diffusion into an Unlimited Atmosphere.

*2. Diffusion of various Salts and other Substances.*

With these notions regarding the influence of temperature and proportion of salt on the amount of diffusion, an examination was next undertaken of the relative diffusibility of a variety of salts and other substances. The results of this first survey I shall state as shortly as possible, as I consider these, as well as the experiments which preceded, as of a preliminary character. The experiments were all made by means of the diffusion phials already described, namely, the six-ounce phials, and with similar manipulations.

In the following experiments, the diffusion took place at a temperature ranging from  $62^{\circ}$  to  $59^{\circ}$ , mean  $60^{\circ}5$ , and was continued for a period of eight days; the proportion of salt in solution to be diffused being always 20 salt to 100 water, or 1 to 5. I add as usual the density of the solutions.

TABLE II.—Diffusion of solutions of 20 salt to 100 water, at  $60^{\circ}5$ , for eight days.

Name of Salt.	Density of solution at $60^{\circ}$ .	Anhydrous salt diffused.	
		In grains.	Means.
Chloride of sodium .....	1.1265	58.5	
Chloride of sodium .....	1.1265	58.87	58.68
Sulphate of magnesia .....	1.185	27.42	27.42
Nitrate of soda .....	1.120	52.1	
Nitrate of soda .....	1.120	51.02	51.56
Sulphate of water .....	1.108	68.79	
Sulphate of water .....	1.108	69.86	69.32
Crystallized cane-sugar .....	1.070	26.74	26.74
Fused cane-sugar .....	1.066	26.21	26.21
Starch-sugar (glucose).....	1.061	26.94	26.94
Treacle of cane-sugar .....	1.069	32.55	32.55
Gum-arabic .....	1.060	13.24	13.24
Albumen .....	1.053	3.08	3.08

The following additional ratios of diffusion were obtained from similar solutions at a somewhat lower temperature, namely  $48^{\circ}$ ;—chloride of sodium 100, hydrate of potash 151.93 (ammonia from a 10



per cent. solution, saturated with chloride of sodium to increase its density, 70), alcohol saturated with chloride of sodium 75·74, chloride of calcium 71·23, acetate of lead 45·46.

Where two experiments upon the same salt are recorded in the table they are seen to correspond to within 1 part in 40, which may be considered as the limit of error in the present observations. It will be remarked that the diffusion of cane- and starch-sugar is sensibly equal, and double that of gum-arabic. On the other hand, the sugars have less than half the diffusibility of chloride of sodium. It is remarkable that the specifically lightest and densest solutions, those of the sugars and of sulphate of magnesia, approach each other closely in diffusibility. On comparing together, however, two substances of similar constitution, such as the two salts, chloride of sodium and sulphate of magnesia, that salt appears to be least diffusive of which the solution is densest.

But the most remarkable result is the diffusion of albumen, which is low out of all proportion when compared with saline bodies. The solution employed was the albumen of the egg, without dilution, but strained through calico and deprived of all vesicular matter. As this liquid, with a density of 1·041, contained only 14·69 parts of dry matter to 100 of water, the proportion diffused is increased in the table to that for 20 parts, to correspond with the other substances. In its natural alkaline state the albumen is least diffusive, but when neutralized by acetic acid, a slight precipitation takes place and the liquid filters more easily. The albumen is now sensibly more diffusive than before. Chloride of sodium appears 20 times more diffusible than albumen in the table, but the disparity is really greater; for nearly one-half of the matter which is diffused consisted of inorganic salts. Indeed, the experiment appears to promise a delicate method of proximate analysis peculiarly adapted for animal fluids. The value of this low diffusibility in retaining the serous fluids within the blood-vessels at once suggests itself.

Similar results were obtained with egg albumen diluted and well beaten with 1 and 2 volumes of water. The solution diluted with an equal bulk of water, and made slightly acid with acetic acid, contained  $7\frac{1}{2}$  dry matter to 100 water. Diffused from two four-ounce bottles of 1·25 inch aperture, for seven days, at a mean temperature of 43°·5 Fahr., it gave products of 1·73 and 1·48 gr., from the evaporation of two water-jars, in which cubic crystals of common salt were abundant. The whole matter thus diffused in two cells was found to consist of—

Coagulable albumen,	.	.	0·94 gr.
Soluble salts,	.	.	2·27 grs.
			<hr/>
			3·21 grs.

The diffusion product of the same solution of albumen left alkaline,



or without the addition of acetic acid, in the same circumstances, was 1.41 and 1.20 grs. in two cells, and consisted of—

Coagulable albumen, . . . .	0.63 gr.
Soluble salts, . . . .	1.98 gr.
	<hr/>
	2.61 grs.

The diffusion product of a solution of  $7\frac{1}{2}$  parts of chloride of sodium to 100 water, from similar cells and for the same time and temperature, would amount to about 30 grs. of salt. It is to be remarked also that 5.53 grs. of the ignited salt diffused from albumen contained 1.32 gr. of potash or 23.9 per cent., which is a high proportion, and indicates that salts of potash diffuse out more freely from albumen than salts of soda.

Nor does albumen impair the diffusion of salts dissolved together with it in the same solution, although the liquid retains its viscosity. Three other substances, added separately in the proportion 5 parts to 100 of the undiluted solution of egg albumen, were found to diffuse out quite as freely from that liquid as they did from an equal volume of pure water: these were chloride of sodium, urea, and sugar. Urea proved to be a highly diffusible substance. It nearly coincided in rate with chloride of sodium.

A second series of salts were diffused containing 1 part of salt to 10 of water; a smaller proportion of salt which admits of the comparison of a greater variety of salts. The temperature during the period of eight days was remarkably uniform,  $60^{\circ}$ — $59^{\circ}$ .

TABLE III.—Diffusion of solutions of 10 salt to 100 water at  $59^{\circ}5$ .

Name of Salt.	Density of solution at $60^{\circ}$ .	Anhydrous salt diffused.	
		In grains.	Means.
Chloride of sodium .....	1.0668	32.3	
Chloride of sodium .....	1.0668	32.2	32.25
Nitrate of soda .....	1.0622	30.7	30.7
Chloride of potassium .....	1.0596	40.15	40.15
Chloride of ammonium .....	1.0280	40.20	40.20
Nitrate of potash .....	1.0589	35.1	
Nitrate of potash .....	1.0589	36.0	35.55
Nitrate of ammonia .....	1.0382	35.3	35.3
Iodide of potassium .....	1.0673	37.0	37.0
Chloride of barium.....	1.0858	27.0	27.0
Sulphate of water .....	1.0576	37.18	
Sulphate of water .....	1.0576	36.53	36.85
Sulphate of magnesia.....	1.0965	15.3	
Sulphate of magnesia.....	1.0965	15.6	15.45
Sulphate of zinc.....	1.0984	15.6	
Sulphate of zinc.....	1.0984	16.0	15.80



Before adverting to the relations in diffusibility which appear to exist between certain salts in the preceding table, I may state the results of the diffusion of the same solutions at a lower temperature.

TABLE IV.—Diffusion of solutions of 10 salt to 100 water at 37°·5.

Name of Salt.	Anhydrous salt diffused.	
	In grains.	Means.
Chloride of sodium .....	22·21	
Chloride of sodium .....	22·74	22·47
Nitrate of soda.....	22·53	
Nitrate of soda.....	23·05	22·79
Chloride of ammonium .....	31·14	31·14
Nitrate of potash.....	28·84	
Nitrate of potash.....	28·56	28·70
Nitrate of ammonia.....	29·19	29·19
Iodide of potassium.....	28·10	28·10
Chloride of barium .....	21·42	21·42
Sulphate of water .....	31·11	
Sulphate of water .....	28·60	29·85
Sulphate of magnesia .....	13·03	
Sulphate of magnesia .....	13·11	13·07
Sulphate of zinc .....	11·87	
Sulphate of zinc .....	13·33	12·60

The near equality of the quantities diffused of certain isomorphous salts is striking at both temperatures. Chloride of potassium and chloride of ammonium give 40·15 and 40·20 grs. respectively in the first table. Nitrate of potash and nitrate of ammonia 35·55 (mean) and 35·3 grs. respectively in the first table, and 28·70 and 29·19 grs. in the second table. Sulphate of magnesia and sulphate of zinc 15·45 and 15·8 grs. (means) in the first table, with 13·07 and 12·60 grs. in the second. The relation observed is the more remarkable, that it is that of equal weights of the salts diffused, and not of atomically equivalent weights. In the salts of ammonia and potash, this equality of diffusion is exhibited also, notwithstanding considerable differences in density between their solutions; the density of the solution of chloride of ammonium, for instance, being 1·0280 and that of chloride of potassium 1·0596. It may have some relation however, but not a simple one, to the density of the solutions; sulphate of magnesia, of which the solution is most dense, being most slowly diffusive; and salts of soda being slower, as they are denser in solution, than the corresponding salts of potash. Nor does it depend upon equal solubility, for in none of the pairs is there any approach to equality in that respect.

A comparison was now made of the diffusibility of several acids.



They were diffused from the same six-ounce phials, and for eight days. Solutions were prepared in the proportion of 4 parts of the anhydrous acid to 100 parts of water. The quantity of acid which diffused into the water-jar was estimated by the proportion of carbonate of soda which it neutralized.

TABLE V.—Diffusion of acid solutions (4 acid to 100 water) at 59°·3.

Name of Acid.	Density of solution at 60°.	Anhydrous acid diffused.	
		In grains.	Means.
Nitric acid.....	1·0243	29·21 28·19	28·7
Hydrochloric acid .....	1·0225	34·22 33·99	34·1
Sulphuric acid .....	1·0317	18·71 18·26	18·48
Acetic acid .....	1·0094	19·13 17·19	18·16
Oxalic acid .....	1·0235	12·38 12·38	12·38
Arsenic acid .....	1·0320	12·16 12·16	12·16
Tartaric acid.....	1·0194	9·90 9·69	9·79
Phosphoric acid .....	1·0284	9·09 9·09	9·09
Chloride of sodium .....	1·0285	12·32	12·32

Considerable latitude thus appears to exist in the diffusibility of the different acids. [To make the result for nitric acid fairly comparable with that for hydrochloric acid, the former should be increased in the proportion of 54 to 63, that is estimated as nitrate of water. This calculation gives 33·5 grs. of nitrate of water diffused, which approaches closely to 34·1 grs., the quantity for chloride of hydrogen or hydrochloric acid.] The quantity of soda neutralized by the sulphuric and hydrochloric acids diffused was as 14·32 to 28·97, or nearly as 1 to 2. Sulphuric and acetic acids, on the other hand, appear to be equally diffusible. Phosphoric acid is the least diffusible acid in the series, presenting only about half the diffusion product of the two last-mentioned acids. The solution of phosphoric acid had been boiled for half an hour before diffusion, and was therefore in the tribasic state. The same precaution was not thought of for arsenic acid, although it is possibly required by this acid also. These two acids do not exhibit the equality of diffusion anticipated from their recognised isomorphism, but it is to be stated that the acidimetric method of analysis followed is not so properly applicable to these two acids as it is to all the others.



3. *Diffusion of Ammoniated Salts of Copper.*

It was interesting to compare together such related salts as sulphate of copper, the ammoniated sulphate of copper or soluble compound of sulphate of copper with 2 equivalents of ammonia and the sulphate of ammonia. It is well known that metallic oxides, or subsalts of metallic oxides, when dissolved in ammonia and the fixed alkalies, are easily taken down by animal charcoal. This does not happen with the ordinary neutral salts of the same acids, which are held in solution by a strong attraction. Supposing the existence of a scale of the solvent attraction of water, the preponderance of the charcoal attraction will mark a term in that scale. And if the solvent force is nothing more than the diffusive tendency, it will follow that salts which can be taken down by charcoal must be less diffusible than those which cannot.

Of sulphate of ammonia and sulphate of copper, solutions were prepared, consisting of 4 anhydrous salt to 100 water, the sulphate of ammonia being of course taken as  $\text{NH}_4\text{O} \cdot \text{SO}_3$ . The solution of the copper salt was divided into two portions, one of which had caustic ammonia added to it in slight excess, so as to produce the azure blue solution of ammonio-sulphate of copper.

The solutions were diffused for eight days, at a mean temperature of  $64^\circ.9$  for the sulphates and nitrates, and  $67^\circ.7$  for the chlorides.

TABLE VI.—Diffusion of solutions, 4 salt to 100 water.

Name of Salt.	Density of solution at temperature of experiment.	Anhydrous salt diffused in grains.
Sulphate of ammonia.....	1.0235	12.13
Sulphate of ammonia.....	1.0235	11.96
Sulphate of copper .....	1.0369	6.19
Sulphate of copper .....	1.0369	6.51
Ammonio-sulphate of copper .....	1.0308	1.45
Ammonio-sulphate of copper .....	1.0308	1.43
Nitrate of ammonia .....	1.0136	16.15
Nitrate of ammonia .....	1.0136	15.44
Nitrate of copper .....	1.0323	9.77
Nitrate of copper .....	1.0323	9.77
Ammonio-nitrate of copper .....	1.0228	1.77
Ammonio-nitrate of copper .....	1.0228	1.36
Chloride of ammonium.....	1.0100	16.18
Chloride of ammonium.....	1.0100	17.00
Chloride of copper.....	1.0328	10.83
Chloride of copper.....	1.0328	10.48
Ammonio-chloride of copper.....	1.0209	4.54
Ammonio-chloride of copper.....	1.0209	3.94



It is to be observed, that in preparing the ammoniated salts, the solutions of the neutral salts of copper were slightly diluted by the water of the solution of ammonia added to them, so that the proportion of salt of copper which they possessed was sensibly reduced below 4 per cent. On the other hand, the copper salt which diffused out is estimated, not as ammoniated, but as neutral salt. It will be observed that the quantity of sulphate of copper diffused out in the experiments falls from 6.35 in the neutral salt to 1.44 gr. in the ammoniated salt; of nitrate of copper from 9.77 to 1.56, and of chloride of copper from 10.65 to 4.24. These numbers are to be taken only as approximations; they are sufficient however to prove a much reduced diffusibility in the ammoniated salts of copper.

It will be remarked that the nitrate of ammonia and chloride of ammonium approximate, 15.80 and 16.59 grs.; as do also the nitrate and chloride of copper, 9.77 and 10.65 grs.; the chlorides, which were diffused at the higher temperature by 2°.8, exceeding the nitrates in both cases.

#### 4. *Diffusion of Mixed Salts.*

When two salts can be mixed without combining, it is to be expected that they will diffuse separately and independently of each other, each salt following its special rate of diffusion.

(1.) Anhydrous sulphate of magnesia and sulphate of water (oil of vitriol), one part of each, were dissolved together in 10 parts of water, and the solution allowed to diffuse for four days at 61°.5.

The water-jar was found to have acquired—

Sulphate of magnesia, . . .	5.60 grs.
Sulphate of water, . . .	21.92 grs.
	<hr/>
	27.52 grs.

The experiment with the same diffusion cell and liquid being continued for a second period, this time of eight days, there was found to be simultaneously diffused, of—

Sulphate of magnesia, . . .	9.46 grs.
Sulphate of water, . . .	29.32 grs.
	<hr/>
	38.78 grs.

It is obvious that the inequality should be greatest in the first period of diffusion, or with the initial diffusion, as it actually appears above, and become less and less sensible as the proportion of the low diffusive salt comes to be increased in the solution phial.

In former experiments upon the solution of sulphate of magnesia



alone in water, as 1 salt to 10 water, compared with sulphate of water, also as 1 to 10, the disparity in the diffusion of these two salts was less considerable, being only as 1 to 2·385, instead of 1 to 3 or 4.

(2.) A solution was also diffused of 1 part of anhydrous sulphate of soda and 1 part of chloride of sodium in 10 parts of water, for four days at 61°·5. The salt which diffused out in that time consisted of—

Sulphate of soda,	.	.	9·48	grs.
Chloride of sodium,	.	.	17·80	grs.
			<hr/>	
			27·28	grs.

The sulphate of soda in the last experiment had begun to crystallize in the solution phial, from a slight fall of temperature, before the diffusion was interrupted, a circumstance which may have contributed to increase the inequality of the proportions diffused of these two salts.

(3.) A solution of equal weights of anhydrous carbonate of soda and chloride of sodium, namely, of 4 parts of the one salt and 4 parts of the other, to 100 water, was diffused from 3 four-ounce phials of 1·25 inch aperture, at a mean temperature of 57°·9 and for seven days. The diffusion product amounted to 17·10, 17·58, and 18·13 grs. of mixed salt in the three experiments. The analysis of the last product of 18·13 grs. gave—

Carbonate of soda,	.	5·68	31·33
Chloride of sodium,	.	12·45	68·67
		<hr/>	<hr/>
		18·13	100·00

Here the carbonate of soda presents a diffusion less than one-half of that of chloride of sodium. The difference is again greater than the peculiar diffusibilities of the same salts as they appear when the salts are separately diffused. For in experiments made in the same phials with solutions of 4 parts of each salt singly to 100 water, but with a lower temperature by 3°·6, namely, at 54°·3, the diffusion product of the carbonate of soda was 7·17 and 7·34 grs. in two experiments, of which the mean is 7·25 grs.; while the diffusion product of the chloride of sodium was 11·18 and 10·73 grs. in two experiments, of which the mean is 10·95 grs. The quantity of chloride of sodium diffused being taken at 100 in both sets of experiments, we have diffused—

Of carbonate of soda 66·18, when diffused singly.

Of carbonate of soda 45·64, when diffused with chloride of sodium.

The least soluble of the two salts appears in all cases to have its diffusibility lessened in the mixed state. The tendency to crystallization of the least soluble salt must evidently be increased by the admixture. Now it is this tendency, or perhaps more generally the increased



attraction of the particles of a salt for each other, when approximated by concentration, which most resists the diffusion of a salt, and appears to weaken the diffusive force in mixtures, as it is also found to do so in a strong solution of a single salt.

(4.) Equal weights of nitrates of potash and ammonia dissolved, as in certain preceding experiments, in five times the weight of the mixed salts of water, and diffused for eight days, gave in two experiments—

	At 59° 4.	At 52° 6.
Nitrate of potash, .	28.39	25.88
Nitrate of ammonia, .	36.16	30.36
	<hr/> 64.55	<hr/> 56.24

The inequality in the diffusion of these two nitrates is singular, considering that in solutions of 1 salt to 10 water, they appeared before to be equally diffusive. But on now comparing the diffusion of solutions of 1 salt to 5 water, at 52° 6, the salts no longer diffused in equal proportions :—

Nitrate of potash gave .	57.93 grs.
Nitrate of ammonia gave .	82.08 grs.

The solution of nitrate of potash last diffused was nearly a saturated one, while that of nitrate of ammonia is far from being so. The first has its diffusibility, in consequence, impaired, and falls considerably below the second.

The relatively diminished diffusibility of sulphate of magnesia, when associated with sulphate of water, is probably connected with a similar circumstance ; sulphate of magnesia being less soluble in dilute sulphuric acid than in pure water.

(5.) The salt which diffused from a strong solution of sulphates of zinc and magnesia, consisting of 1 part of each of these salts in the anhydrous state and 6 parts of water, did not consist of the two salts in exactly equal proportions. The mixture of salts, diffused for eight days, as in the late experiments, gave the following results :—

	Exp. I.	II.	III.
Sulphate of zinc, .	8.12	7.49	8.12
Sulphate of magnesia, .	8.68	8.60	8.75
	<hr/> 16.80	<hr/> 16.09	<hr/> 16.87

There is therefore always a slight but decided preponderance of sulphate of magnesia, the more soluble salt, in the diffusion product. These last experiments were made at an early period with another object in view, namely, to ascertain whether in closely related salts, such as the present sulphates of magnesia and zinc, the two salts might



be elastic to each other, like the particles of one and the same salt, so that one salt might possibly suppress the diffusion of the other, and diffuse alone for both. The experiments lend no support to such an idea.

It appears from all the preceding experiments, that the inequality of diffusion which existed is not diminished but exaggerated in mixtures,—a curious circumstance, which has also been observed of mixed gases.

#### 5. *Separation of Salts of different Bases by Diffusion.*

It was now evident that inequality of diffusion supplies a method for the separation, to a certain extent, of some salts from each other, analogous in principle to the separation of unequally volatile substances by the process of distillation. The potash salts appearing to be always more diffusive than the corresponding soda salts, it follows, that if a mixed solution of two such salts be placed in the solution phial, the potash salt should escape into the water atmosphere in largest proportion, and the soda salt be relatively concentrated in the phial. This anticipation was fully verified.

(1.) A solution was prepared of equal parts of the anhydrous carbonates of potash and soda in 5 times the weight of the mixture of water. Diffused from a small thousand-grain phial of 1·1 inch aperture into 6 ounces of water, for nineteen days, at a temperature above 60°, it gave a liquid of density 1·0350, containing a considerable quantity of the salts. Of these mixed salts, converted into chlorides by the addition of hydrochloric acid, 9·39 grs., being treated with bichloride of platinum in the usual manner, gave 19·39 grs. of the double chloride of platinum and potassium, equivalent to 5·91 grs. of chloride of potassium; and left in solution 3·44 grs. of chloride of sodium: loss 0·04 gr. These chlorides represent 5·46 grs. of carbonate of potash and 3·12 grs. of carbonate of soda. The salts actually diffused out were therefore in the proportion of—

Carbonate of soda, . . .	36·37
Carbonate of potash, . . .	63·63
	<hr/>
	100·00

(2.) In another similar experiment from a six-ounce phial into 8½ ounces of water, the liquid of the water-jar, after twenty-five days' diffusion, contained the two carbonates in nearly the same proportions as before, namely—

Carbonate of soda, . . .	35·2
Carbonate of potash, . . .	64·8
	<hr/>
	100·0



(3.) A partial separation of the salts of sea-water was effected in a similar manner.

The sea-water (from Brighton) was of density 1.0265. One thousand grs. of the liquid yielded 35.50 grs. of dry salts, of which 2.165 grs. were magnesia. The dry salts contain therefore 6.10 per cent. of that earth.

Six thousand-grain phials, of 1.1 inch aperture, were properly filled with the sea-water and placed in six tumblers, each of the last containing 6 ounces of water. Temperature about 50°. The diffusion was interrupted after eight days. The salts of the sea-water were now found to be divided as follows:—

Diffused into the tumblers, .	92.9 grs., or	36.57 per cent.
Remaining in the phials, .	161.1 grs., or	63.43 per cent.
	<hr/> 254.0	<hr/> 100.00

Rather more than one-third of the salts has therefore been transferred from the solution phials to the water-jars by diffusion.

Of the diffused salts in the tumblers, 46.5 grs. were found to contain 1.90 gr. magnesia, or 4.09 per cent. Hence we have the following result—

Magnesia originally in salts of sea-water, .	6.01 per cent.
Magnesia in salts diffused from sea-water, .	4.09 per cent.

The magnesia, also, must in consequence be relatively concentrated in the liquid remaining behind in the diffusion cells.

A probable explanation may be drawn from the last results of the remarkable discordance in the analysis of the waters of the Dead Sea, made by different chemists of eminence. I refer to the relative proportion of the salts, and not their absolute quantity, the last necessarily varying with the state of dilution of the saline water when taken up. The lake in question falls in level 10 or 12 feet every year by evaporation. A sheet of fresh water of that depth is thrown over the lake in the wet season, which water may be supposed to flow over a fluid nearly 1.2 in density, without greatly disturbing it. The salts rise from below into the superior stratum by the diffusive process, which will bring up salts of the alkalies with more rapidity than salts of the earth, and chlorides, of either class, more rapidly than sulphates. The composition of water near the surface must therefore vary greatly, as this process is more or less advanced.

(4.) I may be allowed to add another experiment which is curious for the protracted immobility of a column of water which it exhibits, as well as for the separation occurring, which last may be interesting in a geological point of view. A plain glass cylinder with a foot, 11 inches



in height, and of which the capacity was 64 cubic inches, had 8 cubic inches poured into it of a saturated solution of carbonate of lime in carbonic acid water, containing also 200 grs. of chloride of sodium dissolved. Distilled water was then carefully poured over the saline solution, so as to fill up the jar, a float being used and the liquid disturbed as little as possible in the operation. The mouth of the jar was lastly closed by a ground glass plate, and it was left undisturbed upon the mantelpiece of a room without a fire, from March 20 to September 24 of the present year, or for six months and four days. Afterwards, on removing the cover, the fluid was observed not to have evaporated sensibly, and it exhibited no visible deposit. This I was not surprised at, as no deposit appeared in a similar experiment with the jar uncovered, after the lapse of six weeks. The liquid in the former jar was now carefully drawn off by a small siphon with the extremity of both its limbs recurved so as to open upwards, in four equal portions, which may be numbered from above downwards. Equal quantities of the four strata of liquids gave the following proportions of chloride of sodium and carbonate of lime :—

	Chloride of sodium.	Carbonate of lime.
No. 1.	21·91	0·10
No. 2.	23·41	0·22
No. 3.	23·55	0·38
No. 4.	23·99	0·42

The diffusion of the chloride of sodium has therefore not yet reached complete uniformity, although approaching it, the proportion of that salt obtained from the top and bottom strata being as 11 to 12. But the diffusion of the carbonate of lime appears much less advanced, the proportion of that substance being as 1 to 4 at the top and bottom of the liquid column. The slight difference in density of the strata, it may be further remarked, must have been sufficient to preserve such a column of liquid entirely quiescent, as shown by the distribution of the carbonate of lime, during the considerable changes of temperature of the season.

Chemical analysis, which gives with accuracy the proportions of acids and bases in a solution, furnishes no means of deciding how these acids and bases are combined, or what salts exist in solution. But it is possible that light may be thrown on the constitution of mixed salts, at least when they are of unequal diffusibility, by means of a diffusion experiment. With reference to sea-water, for instance, it has been a question in what form the magnesia exists, as chloride or as sulphate ; or how much exists in the one form and how much in the other. Knowing, however, the different rates of diffusibility of these two salts, which is nearly chloride 3 and sulphate 2, and their relation to the



diffusibility of chloride of sodium, we should be able to judge from the proportion in which the magnesia travels in company with chloride of sodium, whether it is travelling in the large proportion of chloride of magnesium, in the small proportion of sulphate of magnesia, or in the intermediate proportion of a certain mixture of chloride and sulphate of magnesia. But here we are met by a difficulty. Do the chloride of magnesium and sulphate of magnesia necessarily pre-exist in sea-water in the proportions in which they are found to diffuse? May not the more easy diffusion of chlorides determine their formation in the diffusive act, just as evaporation determines the formation of a volatile salt—producing carbonate of ammonia, for instance, from hydrochlorate of ammonia with carbonate of lime in the same solution? We shall see immediately that liquid diffusion, as well as gaseous evaporation, can produce chemical decompositions.

#### 6. *Decomposition of Salts by Diffusion.*

(1.) At an early period of the inquiry, a solution was diffused of bisulphate of potash, saturated at  $68^{\circ}$  and of density 1.280, from the six-ounce phial of 1.175 inch aperture, into 20 ounces of water. The period of diffusion extended to fifty days. About the middle of that period, a few small crystals of sulphate of potash, amounting probably to 3 or 4 hundredths of a grain, appeared in the diffusion cell and never afterwards dissolved away. When terminated, the liquid remaining in the solution cell was found of density 1.154; that in the water-jar 1.0326. A portion of the latter liquid, containing the salts diffused, gave by analysis—

Sulphate of potash,	.	.	20.37	} Bisulphate of potash.
Sulphate of water,	.	.	11.47	
Sulphate of water,	.	.	12.77	
			<hr/> 44.61	

It thus appears that the bisulphate of potash undergoes decomposition in diffusing, and that the acid diffuses away to about double the extent, in equivalents, of the sulphate of potash. This greater escape of the acid will also account for the deposition of crystals of the neutral sulphate in the solution cell.

(2.) A similar experiment was made with another double sulphate of greater stability, common potash-alum. The solution of 4 anhydrous alum in 100 water, was diffused from the six-ounce phial into 24 ounces of water, at  $64^{\circ}2$ , for eight days. The quantity of salt diffused in that time amounted only to 7.48 grs. It contained 1.06 gr. alumina, which is equivalent to 5.33 grs. of alum. The diffused salt gave off no acid



vapours at  $600^{\circ}$ . We may therefore suppose the excess of salt which is diffused to be sulphate of potash. The diffusion product of alum, at  $64^{\circ}$ , appears therefore to be—

Alum, . . . . .	5.33	71.26
Sulphate of potash, . . . . .	2.15	28.74
	<hr/> 7.48	<hr/> 100.00

In a second experiment, the diffusion product amounted to 6.39 grs., of which 0.95 gr. was alumina; and it is represented by 4.77 alum and 1.52 sulphate of potash.

In connexion with the low diffusibility of the sulphate of alumina of alum, it was found that the addition of caustic potash to the alum solution, so as to convert it into an aluminate of potash, increased the diffusibility of the alumina. The diffusion product from the 4 per cent. solution of alum so treated contained 1.62 gr. of alumina in one experiment and 1.54 in another, or one-half more than from alum itself.

As alum is a salt of great stability, it presents a severe test of the influence in question. The decomposition of this double salt by diffusion was further confirmed therefore in experiments made by means of the four-ounce diffusion phials of 1.25 inch aperture, and the alteration which the salt undergoes in the process more exactly ascertained. The experiments were made at a mean temperature of  $57^{\circ}.9$ , and lasted seven days; the solution employed being of 4 anhydrous alum to 100 water, as before.

In three experiments, the salt diffused out amounted to 5.73, 5.80, and 5.65 grs.; of which the mean is 5.73 grs. The latter quantity gave 0.82 alumina and 3.22 sulphuric acid, which correspond to 4.11 anhydrous alum and 1.62 neutral sulphate of potash. Or, we have as the diffusion product of alum, in 100 parts—

Alum, . . . . .	71.73
Sulphate of potash, . . . . .	28.27
	<hr/> 100.00

This analysis corresponds closely with the diffusion product of the former experiments, which gave 71.26 per cent. of alum, and 28.74 sulphate of potash. The solution of alum which remains behind in the solution phials must of course acquire an excess of sulphate of alumina.

The salt, sulphate of alumina, did not appear to be decomposed when diffused alone. A four per cent. solution of the hydrated sulphate of alumina, which is manufactured at Newcastle, when diffused in the same circumstances as the preceding solutions of alum, gave 3.40 grs. of anhydrous sulphate of alumina, in which the acid was to the alumina as 2.95



equivalents of the former to 1 equivalent of the latter, or as nearly as possible in the proportion of 3 equivalents of acid to 1 of base. As the Newcastle salt contained almost exactly half its weight of water, the 3.40 grs. of anhydrous salt diffused out are equivalent to 6.80 grs. of hydrated sulphate of alumina. The sulphate of alumina appears thus to be more diffusive than the double sulphate of alumina and potash, in the proportion of 6.80 to 5.73.

(3.) It was interesting to observe what really diffuses from the ammoniated sulphate of copper ( $\text{CuO}, \text{SO}_3, 2\text{NH}_3 + \text{HO}$ ), and to find if the low diffusibility of that salt is attended with decomposition. The diffusion of the ammoniated sulphate of copper was therefore repeated from a 4 per cent. solution in the six-ounce solution phial, for eight days, at  $64^\circ.2$ . In evaporating the water of the jar afterwards, the ammoniated sulphate of copper present was necessarily decomposed, by the escape of ammonia, and a subsulphate of copper precipitated. The copper found, however, was estimated as neutral sulphate of copper. The diffusion product of two experiments may be represented as follows, in grains:—

	I.	II.
Sulphate of copper, . . .	0.81	0.97
Sulphate of ammonia, . . .	5.46	5.53
	<hr/> 6.27	<hr/> 6.50

The abundant formation and separation of sulphate of ammonia in these experiments prove that the ammoniated sulphate of copper is largely decomposed in diffusion.

(4.) Perhaps the most interesting result of this kind is a method which diffusion suggests for the decomposition of the alkaline sulphates by means of lime.

Solutions were prepared, in lime-water, of  $\frac{1}{2}$  per cent. of sulphate of potash and of chlorides of potassium and sodium. Two solution phials were filled with each of these solutions, and placed for diffusion in water-jars filled with lime-water, at  $49^\circ$ , for seven days.

In the sulphate no deposition of crystallized sulphate of lime took place within the solution phial, while the water-jar acquired an alkaline reaction, which remained after precipitating the lime entirely by carbonic acid gas and evaporating twice to dryness. Hydrate of potash, it will afterwards appear, is an eminently diffusive salt, having double the diffusibility of sulphate of potash. The tendency of the former to diffuse enables the affinity of the lime for sulphuric acid to prevail, and the alkali is liberated and diffused away into the external atmosphere of lime-water. By the latter, hydrate of lime is returned to the solution cell and the decomposition continued. The salt diffused in the two cells amounted to 2.60 grs., of which 0.62 gr., or 23.85 per cent., was



hydrate of potash. The chlorides of potassium and sodium, on the contrary, were not sensibly decomposed.

It is known that a precipitation of sulphate of lime may occur, with a larger proportion of sulphate of potash in lime-water, in a close phial without external diffusion. As the decomposition of the sulphate of potash, in the latter case, has been referred to the insolubility of the sulphate of lime, so the decomposition in the former circumstances may be referred, in a similar sense, to the high diffusibility of hydrate of potash.

### 7. *Diffusion of Double Salts.*

How is the diffusion of two salts affected by their condition of combination as a double salt? A solution of the double sulphate of magnesia and potash, in the proportion of 100 water to 4 anhydrous salt, was operated upon in the four-ounce diffusion phials of 1.25 inch aperture, with a period of diffusion of seven days, at 57°·9 Fahr. The diffusion product of the double salt was 8.09 and 7.81 grs. in two experiments: mean 7.95 grs.

The constituent salts, sulphate of magnesia and sulphate of potash, were now dissolved separately, in the proportions in which they existed in the double salt, namely, 1.65 gr. anhydrous sulphate of magnesia in 100 water, and 2.35 grs. sulphate of potash in 100 water, making up together 4 parts of salts. The two solutions thus contain equivalent quantities of the different sulphates.

The separate diffusion of the sulphate of magnesia was 2.09, 2.11, and 2.40 grs. in three cells; and of the sulphate of potash, 5.83, 5.97, and 5.54 grs. in three cells; the circumstances of the experiments being the same as those of the double salt. The means of the two salts are 2.20 and 5.78 grs.; and the sum of the two means 7.98 grs. The result is, that the separate diffusion of the constituent salts is almost identical with their diffusion when combined as a double salt:—

Diffusion of the double sulphate of magnesia and potash,	7.95 grs.
Diffusion of equivalents of sulphate of magnesia and	} 7.98 grs.
sulphate of potash in separate cells,	

It would thus appear that the diffusibility of this double salt is the sum of the separate diffusions of its constituent salts.

It has been a question whether a double salt is formed at once when its constituent salts are dissolved together, or not till the act of crystallization of the compound salt. Equivalents of the same two sulphates, making up 4 parts, were dissolved together without heat in 100 water. Now the diffusion from this mixture, which has the composition of the preceding solution of the double salt, exhibited notwithstanding a sen-



sibly different result of diffusion, giving 7.28, 7.37, and 7.26 grs. in three cells: mean, 7.30 grs. The diffusion of the double salt was greater, namely, 7.95 grs. Hence a strong presumption that the mixed salts last diffused were not combined, and that the double sulphate of magnesia and potash is not necessarily formed immediately upon dissolving together its constituent salts.

In early experiments of a similar nature made upon the double salt, sulphate of copper and potash, and upon a mixture of the two sulphates newly dissolved together, a similar result was obtained. While the diffusion of the mixed salts was 25.6 grs., that of the same weight of the combined salts (the double sulphate) was 30 grs. The double salt appears more diffusible, in both cases, than its mixed constituents.

These double salts appear to dissolve in water without decomposition, although the single salts may meet in solution without combining. Hence in a mixture of salts we may have more than one state of equilibrium possible. And when a salt, like alum, happens to be dissolved in such a way as to decompose it, the constituents are not necessarily reunited by subsequent mixing. Many practices in the chemical arts, which seem empirical, have their foundation possibly in facts of this kind.<sup>1</sup>

#### 8. *Diffusion of one Salt into the Solution of another Salt.*

It was curious and peculiarly important, in reference to the relation of liquid to gaseous diffusion, to find whether one salt A would diffuse into water already charged with an equal or greater quantity of another salt B, as a gas *a* freely diffuses into the space already occupied by another gas *b*; the gas *b* in return diffusing at the same time into the space occupied by *a*. Or whether, on the contrary, the diffusion of the salt A is resisted by B. The latter result would indicate a neutralization of the water's attraction, and a kind of equivalency or equality of power and exchangeability of different salts, in respect of that effect, which would divide entirely the phenomena of liquid from those of gaseous diffusion.

(1.) A solution of 4 parts of carbonate of soda to 100 water, of density 1.0406, was placed in the six-ounce diffusion phial of 1.175 inch aperture, and allowed to communicate with 24 ounces of water.

Two similar diffusion phials, equally charged, were immersed in 24 ounces of a solution of chloride of sodium in the proportion of 4 parts of the latter to 100 water, having the density 1.0282. The diffusion proceeded for eight days, in all cases, at 64°. The proportion of carbonate of soda found without in the water-jar afterwards, was ascertained

<sup>1</sup> The circulation in crystallizing tartaric acid necessary from the low diffusibility of the acid?



by an alkalimetical process, the neutralization being effected at the boiling-point. The following are the results :—

Experiment I. Diffusion product into water, . . . . .	} 9.06 grs. of carbonate of soda.
Experiment II. Diffusion product into solution of chloride of sodium, . .	} 8.82 grs. of carbonate of soda.
Experiment III. Diffusion product into solution of chloride of sodium, . .	} 9.10 grs. of carbonate of soda.

It hence appears that 4 per cent. of chloride of sodium present in the water atmosphere of the jar has no sensible effect in retarding the diffusion into it, from the solution cell, of carbonate of soda from a solution containing also 4 per cent. of the latter.

(2.) The experiment was varied by allowing the solution of carbonate of soda to diffuse into a solution of sulphate of soda, a salt more similar to the former in composition and solubility. The solution of the latter, containing 4 per cent., was of density 1.0352. The temperature and period of diffusion were the same as before :—

Experiment IV. Diffusion product into solution of sulphate of soda, . .	} 7.84 grs. of carbonate of soda.
Experiment V. Diffusion product into solution of sulphate of soda, . .	} 7.82 grs. of carbonate of soda.

Here we find a small reduction in the quantity of carbonate of soda diffused, amounting to one-eighth of the whole. The sulphate of soda has therefore exercised a positive interference in checking the diffusion of the carbonate to that extent. So small and disproportionate an effect however is scarcely sufficient to establish the existence of a mutual elasticity and resistance between these two salts.

Still it might be said, may not the diffusion of one salt be resisted by another salt which is strictly isomorphous with the first?

(3.) A solution of 4 parts of nitrate of potash to 100 of water, of density 1.0241, placed in the solution phial, was allowed to communicate with water containing 4 per cent. of nitrate of ammonia in the water-jar, which last solution was of density 1.0136; with all other circumstances as before. With one solution phial having the usual aperture, 1.175 inch, the diffusion product was 15.32 grs. of nitrate of potash. With a second phial, having a larger aperture of 1.190 inch, the diffusion product was 18.03 grs. of nitrate of potash. No comparative experiment, on the diffusion of nitrate of potash into water, was made at the same time. But nitrate of ammonia, which appeared before to coincide in diffusibility with nitrate of potash, gave on a former occasion, in similar



circumstances, and at  $64^{\circ}9$ , nearly the same temperature, a diffusion product of 15.80 grs. The quantity of nitrate of potash (15.32 grs.) which diffused into the solution of nitrate of ammonia approaches so closely to the number quoted, that we may safely conclude that the diffusion of nitrate of potash is not sensibly resisted by nitrate of ammonia, although these two salts are closely isomorphous. They are still therefore inelastic to each other, like two different gases.

These experiments have been made upon dilute solutions, and it is not at all impossible that the result may be greatly modified in concentrated solutions of the same salts, or when the solutions approach to saturation. But there is reason to apprehend that the phenomena of liquid diffusion are exhibited in the simplest form by dilute solutions, and that concentration of the dissolved salt, like compression of a gas, is attended often with a departure from the normal character.

On approaching the degree of pressure which occasions the liquefaction of a gas, an attraction appears to be brought into play, which impairs the elasticity of the gas; so on approaching the point of saturation of a salt, an attraction of the salt molecules for each other, tending to produce crystallization, comes into action, which will interfere with and diminish that elasticity or dispersive tendency of the dissolved salt which occasions its diffusion.

We are perhaps justified in extending the analogy a step further between the characters of a gas near its point of liquefaction and the conditions which we may assign to solutions. The theoretical density of a liquefiable gas may be completely disguised under great pressure. Thus, under a reduction by pressure of 20 volumes into 1, while the elasticity of air is 19.72 atmospheres, that of carbonic acid is only 16.70 atmospheres, and the deviation from their normal densities is in the inverse proportion. Of salts in solution the densities may be affected by similar causes, so that although different salts in solution really admit of certain normal relations in density, these relations may be concealed and not directly observable.

The analogy of liquid diffusion to gaseous diffusion and vaporization is borne out in every character of the former which has been examined. Mixed salts appear to diffuse independently of each other, like mixed gases, and into a water atmosphere already charged with another salt as into pure water. Salts also are unequally diffusible, like the gases, and separations, both mechanical and chemical (decompositions), are produced by liquid as well as by gaseous diffusion. But it still remains to be found whether the diffusibilities of different salts are in any fixed proportion to each other, as simple numerical relations are known to prevail in the diffusion velocities of the gases, from which their densities are deducible.



## II. DIFFUSION OF SALTS OF POTASH AND AMMONIA.

It was desirable to make numerous simultaneous observations on the salts compared, in order to secure uniformity of conditions, particularly of temperature. The means of greatly multiplying the experiments were obtained by having the solution phial cast in a mould, so that any number of solution cells could be procured of the same form and dimensions. The phials were of the form represented (fig. 3), holding about 4 ounces, or more nearly 2080 grs. of water to the base of the neck, and the mouths of all were ground down, so as to give the phial a uniform height of 3.8 inches. The mouth or neck was also ground to fit a gauge-stopper of wood, which was 0.5 inch deep and slightly conical, being 1.24 inch in diameter on the upper, and 1.20 inch on the lower surface. These are therefore the dimensions of the diffusion aperture of the new solution cells. A little contrivance to be used in filling the phials to a constant distance of half an inch from the surface of the lip, proved useful. It was a narrow slip of brass plate, having a descending pin of exactly half an inch in length fixed on one side of it (fig. 4). This being laid across the mouth of the phial with the pin downwards in the neck, the solution was poured into the phial till it reached the point of the pin. The brass plate and pin being removed, the neck was then filled up with distilled water, with the aid of the little float as before described. The water-jar, in which the solution phial stood, was filled up with water also as formerly, so as to cover the phial entirely to the depth of 1 inch. This water atmosphere amounted to 8750 grs., or about 20 ounces. A glass plate was placed upon the mouth of the water-jar itself to prevent evaporation. Sometimes 80 or 100 diffusion cells were put in action at the same time. The period of diffusion chosen was now always exactly seven days, unless otherwise mentioned.

Solutions were prepared of the various salts, in a pure state, in certain fixed proportions, namely, 2, 4,  $6\frac{2}{3}$ , and 10 parts of salt to 100 parts of water by weight. The density of these solutions was observed by the weighing-bottle, at  $60^{\circ}$ . The solutions were frequently diffused at two different temperatures; one, the temperature of the atmosphere, which was fortunately remarkably constant during most of the experiments to be recorded at present, and the other, a lower temperature, obtained in a close box of large dimensions, containing masses of ice.

FIG. 3.

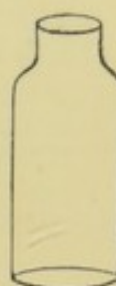
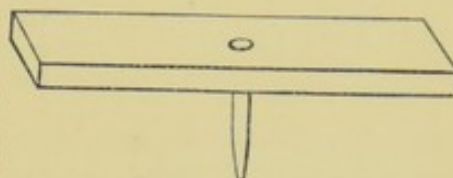


FIG. 4.





The results at the artificial temperature were obviously less accurate than those of the natural temperature, but have still considerable value. Three experiments were generally made upon the diffusion of each solution at the higher, with two experiments at the lower temperature.

(1.) The carbonate and sulphate of potash and sulphate of ammonia were first diffused during a period of seven days, of which the temperatures observed by a thermometer placed near the water-jars were  $64^{\circ}5$ ,  $65^{\circ}$ ,  $63^{\circ}5$ ,  $63^{\circ}$ ,  $63^{\circ}5$ ,  $65^{\circ}$ , and  $66^{\circ}$ ; mean temperature  $64^{\circ}2$ .

TABLE VII.—Diffusion of Carbonate of Potash, Sulphate of Potash, and Sulphate of Ammonia.

Parts of anhydrous salt to 100 water.	Density of solution at $60^{\circ}$ .	At $64^{\circ}2$ .		At $37^{\circ}6$ .	
		Experiments.	Mean.	Experiments.	Mean.
Carbonate of potash.					
2	1.0178	5.36		3.80	
		5.55	5.45	3.91	3.85
4	1.0347	10.39		6.99	
		10.11	10.25	7.19	7.09
$6\frac{2}{3}$	1.0572	16.50		11.42	
		16.46		11.08	11.25
		17.05	16.67		
10	1.0824	24.42			
		24.94			
		24.70	24.69		
Sulphate of potash.					
2	1.0155	5.62		3.93	
		5.42	5.52	3.98	3.95
4	1.0318	10.49		7.50	
		10.65	10.57	7.31	7.40
$6\frac{2}{3}$	1.0512	17.07		11.62	
		16.89		11.71	11.66
		17.54	17.17		
10	1.0742	23.40			
		23.59			
		23.88	23.62		
Sulphate of ammonia, $\text{NH}_4\text{O}.\text{SO}_3$ .					
2	1.0117	5.71		3.73	
		5.45	5.58	3.79	3.76
4	1.0229	10.72		7.54	
		10.30	10.51	7.86	7.70
$6\frac{2}{3}$	1.0369	17.28		10.94	
		16.28		10.98	10.96
		16.80	16.79		
10	1.0529	21.86			
		22.49			
		22.25	22.20		



The diffusion product was obtained by evaporating the water of each jar separately as before, and the result is expressed in grains.

It will be observed at once, on comparing the means of the experiments, that the three salts under consideration are remarkably similar in their diffusion, particularly with the smaller proportions of salt. Thus the mean diffusion of the 2, 4, 6 $\frac{3}{4}$ , and 10 parts of the salts is as follows:—

Diffusion at 64°·2.

	2.	4.	6 $\frac{3}{4}$ .	10.
Carbonate of potash .....	5·45	10·25	16·67	24·69
Sulphate of potash .....	5·52	10·57	17·17	23·62
Sulphate of ammonia .....	5·58	10·51	16·79	22·20

Diffusion at 37°·6.

	2.	4.	6 $\frac{3}{4}$ .
Carbonate of potash .....	3·85	7·09	11·25
Sulphate of potash .....	3·95	7·40	11·66
Sulphate of ammonia .....	3·76	7·70	10·96

The proportions diffused are sensibly equal, of the different salts, at the higher temperature, with the exception of the largest proportion of salt, 10 per cent., when a certain divergence occurs. This last fact is consistent with our expectations, that the diffusion of salts would prove most highly normal in dilute solutions. Some of the irregularities at the lower temperature are evidently of an accidental kind.

(2.) The neutral chromate and acetate of potash were diffused at a temperature ranging from 63° to 65°, or at a mean temperature of 64°·1, which almost coincides with the higher temperature of the last experiments.



TABLE VIII.—Diffusion of Chromate of Potash and Acetate of Potash, at 64°·1.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	Experiments.	Mean.
Chromate of potash.			
2	1·0158	5·79 5·66 5·86	5·77
4	1·0313	11·10 11·35 11·13	11·19
6½	1·0512	17·76 17·72 17·32	17·60
10	1·0750	24·49 24·92 24·85	24·75
Acetate of potash.			
2	1·0095	5·93 5·75 5·88	5·85
4	1·0184	10·55 10·56 10·98	10·70
6½	1·0306	16·53 16·06 16·84	16·48
10	1·0447	24·27 24·82 25·46	24·85

We have the same close correspondence in the diffusion products of these two salts as in the preceding group, and here the correspondence extends to the 10 per cent. solution.

## Diffusion at 64°·1.

	2.	4.	6½.	10.
Chromate of potash .....	5·77	11·19	17·60	24·75
Acetate of potash.....	5·85	10·70	16·48	24·85

The 10 per cent. solution of these two salts also agrees with the same solution of carbonate of potash, which was 24·69 grs. Nor do the lower proportions diverge greatly from the preceding group of salts.



(3.) Another pair of salts were simultaneously diffused, but with an accidental difference of  $0^{\circ}4$  of temperature.

TABLE IX.—Diffusion of Bicarbonate of Potash,  $\text{KO} \cdot \text{CO}_2 + \text{HO} \cdot \text{CO}_2$ , at  $64^{\circ}1$ , and Bichromate of Potash,  $\text{KO} \cdot 2\text{CrO}_3$ , at  $64^{\circ}5$ .

Parts of anhydrous salt to 100 water.	Density of solution at $60^{\circ}$ .	At $64^{\circ}1$ and $64^{\circ}5$ .	
		Experiments.	Mean.
Bicarbonate of potash. 2	1.0129	5.74 5.77 5.91	5.81
4	1.0252	10.75 11.16 11.13	
Bichromate of potash. 2	1.0139	5.64 5.73 5.59	5.65
4	1.0273	11.55 11.54 11.39	

Here again the two salts approach closely in diffusion, and also correspond well with the two preceding series.

Mean Diffusion at  $64^{\circ}1$  and  $64^{\circ}5$ .

	2.	4.
Bicarbonate of potash.....	5.81	11.01
Bichromate of potash.....	5.65	11.49

It is singular to find that salts differing so much in constitution and atomic weight as the chromate and bichromate of potash, may be confounded in diffusibility. The diffusion products of these two salts are, for the 2 per cent. solutions, 5.77 and 5.65 grs., and for the 4 per cent. solution, 11.19 and 11.49 grs. The bicarbonate of potash also exhibits a considerable analogy to the carbonate, but resembles still more closely the acetate. It is thus obvious that equality, or similarity, of diffusion is not confined to the isomorphous groups of salts.



(4.) The nitrates of potash and ammonia have already appeared to be equi-diffusive at two different temperatures. They were diffused again in the same proportions as the last salts, at a temperature varying from  $63^{\circ}$  to  $67^{\circ}5$ .

TABLE X.—Diffusion of Nitrate of Potash and Nitrate of Ammonia at  $65^{\circ}9$ .

Parts of anhydrous salt to 100 water.	Density of solution at $60^{\circ}$ .	Experiments.	Mean.
Nitrate of potash.			
2	1.0123	7.34 7.58 7.49	7.47
4	1.0243	13.66 14.24 14.02	13.97
$6\frac{2}{3}$	1.0393	22.11 22.94 22.05	22.37
10	1.0581	32.06 32.90 32.50	32.49
Nitrate of ammonia, $\text{NH}_4\text{O}, \text{NO}_3$ .			
2	1.0080	7.85 7.71 7.64	7.73
4	1.0154	14.20 14.79 14.45	14.48
$6\frac{2}{3}$	1.0256	23.66 23.35 22.22	22.74
10	1.0375	34.94 33.49 34.23	34.22

The solution of nitrate of ammonia of the water-jars was evaporated carefully at a temperature not exceeding  $120^{\circ}$  Fahr., to prevent loss of the salt by sublimation or decomposition.

Diffusion at  $65^{\circ}9$ .

	2.	4.	$6\frac{2}{3}$ .	10.
Nitrate of potash .....	7.47	13.97	22.37	32.49
Nitrate of ammonia .....	7.73	14.48	22.74	34.22

Although these salts correspond closely, it is probable that neither the diffusion of these nor the diffusion of any others is absolutely iden-



tical. The nitrate of ammonia appears to possess a slight superiority in diffusion over the nitrate of potash, which increases with the large proportion of salt in solution. They are both considerably more diffusible than the seven preceding salts.

(5.) A second pair of isomorphous salts was compared, the chlorides of potassium and ammonium.

TABLE XI.—Diffusion of Chloride of Potassium and Chloride of Ammonium.

Parts of anhydrous salt to 100 water.	Density of solu- tion at 60°.	At 66°·2.		At 64°·7.	
		Experiments.	Mean.	Experiments.	Mean.
Chloride of potassium.					
2	1·0127	7·83 7·72 7·55	7·70	8·03 7·89	7·96
4	1·0248	15·22 15·59 15·07		15·21 14·82	
6 $\frac{2}{3}$	1·0401	24·88 24·64 25·09		24·83 24·62	
10	1·0592	36·23 37·63	24·87 36·93		24·72
Chloride of ammonium.					
2	1·0061	7·10 8·52	7·81	7·10 7·24	7·17
4	1·0118	14·55 14·64		13·91 14·91	
6 $\frac{2}{3}$	1·0190	24·30		24·12 24·13	
10	1·0272	36·53	36·53		24·12

These two salts agree well in diffusibility, and are also evidently related to the preceding nitrates. The quantity of chloride of ammonium diffused was determined by evaporation, which is troublesome and may lead to small errors, from the volatility and efflorescent tendency of this salt. It would be easier and more accurate to determine this and other chlorides by the use of a normal solution of nitrate of silver, and so avoid evaporation.

Diffusion at 66°·2.

	2.	4.	6 $\frac{2}{3}$ .	10.
Chloride of potassium .....	7·70	15·29	24·87	36·93
Chloride of ammonium .....	7·81	14·60	24·30	36·53



The quantities diffused of these two chlorides are more closely in proportion to the strength of the original solution, than with any of the preceding salts of potash. Thus the quantities diffused from the 2 and 10 per cent. solutions of chloride of potassium are 7.70 and 36.93 grs., which are as 2 to 9.6, which is nearly as 2 to 10. Chloride of sodium was observed before to be nearly uniform in this respect; but other salts appear to lose considerably in diffusibility with the higher proportions of salt. It is possibly a consequence of the crystallizing attraction, to which reference was lately made, coming into action in strong solutions and resisting diffusion.

(6.) The diffusion of chlorate of potash was observed at a temperature ranging from  $63^{\circ}$  to  $65^{\circ}$ , of which the mean was  $64^{\circ}1$ .

TABLE XII.—Diffusion of Chlorate of Potash.

Parts of salt to 100 water.	Density of solution at $60^{\circ}$ .	At $64^{\circ}1$ .	
		Experiments.	Mean.
2	1.0129	6.97	7.22
		7.54	
		7.16	
4	1.0246	13.03	13.31
		13.64	
		13.27	
6.5 (saturated solution).	1.0395	21.30	20.78
		20.29	
		20.76	

The solutions of chlorate of potash must be evaporated and the residuary salt dried at a temperature not exceeding  $212^{\circ}$ , otherwise a very sensible quantity of chloride of potassium may be formed. The chloride appears to be sensibly inferior in diffusibility to the nitrate of potash. From the four per cent. solution of the chlorate we have a diffusion product of 13.27 grs., and from the corresponding solution of the nitrate 13.97 grs.; but the latter was obtained at a temperature  $1^{\circ}8$  higher than the former. It remains a question whether chlorate of potash does not really belong to the nitre group of salts, but has its diffusion interfered with by some secondary agency, such as its sparing solubility and consequent nearer approach to the saturating proportion.

It is certainly true that the uniformity of diffusion generally increases with the dilution of the solutions. This appears on comparing the diffusion of the 4 per cent. solution of what may be called the sulphate of potash group, with the diffusions of the 2 per cent. solutions of the same salts.



*Diffusion of Salts of the Sulphate of Potash Class.*

	4.	2.
Carbonate of potash .....	10·27	5·45
Sulphate of potash .....	10·57	5·52
Sulphate of ammonia .....	10·51	5·58
Acetate of potash.....	10·70	5·85
Bicarbonate of potash.....	11·01	5·81
Chromate of potash.....	11·19	5·77
Bichromate of potash .....	11·49	5·65

Thus while the 4 per cent. solutions range from 10·27 to 11·49 grs., or from 100 to 111·8, the 2 per cent. solutions range from 5·45 grs. to 5·85 grs., or from 100 to 107·3.

As it appeared to be in dilute solutions that the greatest uniformity of diffusion is to be expected, a series of experiments was instituted upon the preceding salts, with the addition of acetate of potash, which appeared to belong to the same class, the solution employed being that of 1 salt to 100 water. The experiments were made in a vault, of which the temperature was nearly uniform, falling in a gradual manner from 59° to 58°, with a mean of 58°·5 during the period of seven days which the diffusion lasted. Eight phials of each salt were diffused, and the liquids of four water-jars evaporated together.

Carbonate of potash gave 10·42 and 10·59 grs. of salt diffused: mean 10·51 grs., or 2·63 grs. for one cell.

Sulphate of potash gave 10·72 and 10·78 grs. of salt diffused: mean 10·75 grs., or 2·69 grs. for one cell.

Acetate of potash, its diffusion product being treated with an excess of hydrochloric acid, gave 8·30 and 8·04 grs. of chloride of potassium, equivalent to 10·91 and 10·57 grs. of acetate of potash: mean 10·74 grs. of acetate of potash, or 2·68 grs. for one cell. The diffusion of these three salts is therefore remarkably similar:—

*Diffusion of 1 per cent. solutions at 58°·5.*

Carbonate of potash, . . .	2·63 grs.
Sulphate of potash, . . .	2·69 grs.
Acetate of potash, . . .	2·68 grs.

The 1 per cent. solution of neutral or yellow chromate of potash in good crystals gave 11·28 and 11·35 grs.; mean 11·31 grs., or 2·83 grs. for each cell. It was remarked of the diffused chromate in this experiment, that it contained a sensible quantity of green oxide of chromium. The



diffusion of a salt appears indeed to try its tendencies to decomposition very severely. (*The Author's copy has a ? here on the margin.*)

The bicarbonate of potash gave 8.83 and 8.35 grs. of chloride of potassium, the diffusion product being neutralized with hydrochloric acid; equivalent to 11.25 and 11.21 grs. of bicarbonate of potash; mean 11.23 grs., or 2.81 grs. for one cell.

The bichromate of potash gave 11.54 and 11.49 grs. of salt diffused; mean 11.51 grs., or 2.88 grs. for one cell. These last three salts give all a larger diffusion product than the preceding three, while they agree well together. It is doubtful whether this excess in their diffusion is occasioned by a partial decomposition in the act of diffusion, which might be of such a kind as to increase the real or apparent diffusion in every one of them, or whether it is a peculiar character of this little subdivision, to which the ferricyanide of potassium, it will be afterwards seen, falls to be added, while the ferrocyanide appears to belong to the other group:—

*Diffusion of 1 per cent. solutions at 58°·5.*

Chromate of potash, . . . .	2.83 grs.
Bicarbonate of potash, . . . .	2.81 grs.
Bichromate of potash, . . . .	2.88 grs.

The divergence from each other of two salts so closely isomorphous as sulphate and chromate of potash, in the proportion of 100 to 105.2, is certainly remarkable, unless due to a slight decomposition of the latter.

*(7.) Ferrocyanide and Ferricyanide of Potassium.*

Of these two salts the 1 per cent. solution only was diffused. The time of diffusion was seven days, as usual; the mean temperature 54°·5. In evaporating the liquid of the water-jars, both salts were partially decomposed, so that it became necessary to estimate the diffusion product by a determination of the potash. Eight cells were employed for one salt and six for the other, and the liquids of the water-jars evaporated two together.

The diffusion product of ferrocyanide of potassium (anhydrous) was 5.02, 5.22, 5.02, and 5.20 grs.; mean 5.12 grs., or for one cell 2.56 grs.

The diffusion product of ferricyanide of potassium was 5.54, 5.64, and 5.36 grs.; mean 5.51 grs., or for one cell 2.75 grs.

Three cells of a similar solution of sulphate of potash which were diffused for seven days at a mean temperature 1° lower, or of 53°·5, gave 2.56, 2.53, and 2.62 grs.; mean for one cell 2.57 grs., a number which



almost coincides with that of the ferrocyanide of potassium (2.56 grs.). The ferricyanide of potassium, on the other hand, is sensibly more diffusive, as 107.6 to 100, and appears to rank with the bicarbonate and bichromate of potash. The ferrocyanide of potassium, again, is a salt which probably undergoes a slight decomposition in diffusion like those salts mentioned:—

*Diffusion of 1 per cent. solutions.*

Sulphate of potash, . . . . .	2.57 grs. at 53°.5.
Ferrocyanide of potassium, . . . . .	2.56 grs. at 54°.5.
Ferricyanide of potassium, . . . . .	2.75 grs. at 54°.5.

The salts of the nitre class may also be compared in the same manner, and I shall now add a third series of results obtained from the diffusion of 1 per cent. solutions of the same salts. The temperature of diffusion of this new series was 64°.5. Six phials of each salt were diffused, and they were evaporated afterwards two and two. This double diffusion product, however, is divided by 2 in the table.

*Diffusion of Salts of the Nitre Class.*

	4.	2.	1.
Nitrate of potash .....	13.97	7.47	3.72
Nitrate of ammonia .....	14.48	7.73	3.75
Chloride of potassium .....	15.01	7.70	3.88
Chloride of ammonium.....	14.41	7.81	3.89
Chlorate of potash .....	13.31	7.22	3.66
Mean .....	14.23	7.58	3.78

It is interesting to observe how the chlorate of potash rises in the lower proportions and approaches to the normal rate of its class. The diffusion products of all the salts are obviously more similar for the two than for the 4 per cent. solutions, and again more similar for the 1 than for the 2 per cent. solutions. The extremes in the 1 per cent. solutions are 3.66 grs. chlorate of potash, and 3.89 grs. chloride of ammonium, which are as 1 to 1.0628. We have here an approach to equality in diffusion, which appears to be as close as the experimental determinations are of the specific heat of different bodies belonging to one class. The numbers for the specific heat of equivalents of the metallic elements are known to vary as 38 to 42.

The salts of potash thus appear to fall into two groups of very similar if not equal diffusibility. What is the relation between these groups?



The diffusion of 4 per cent. solutions of carbonate and nitrate of potash was repeated at a temperature rising gradually from  $63^{\circ}$  to  $65^{\circ}$  during the seven days of the experiment, with a mean of  $64^{\circ}1$ . The diffusion products of the carbonate were 10.31, 10.05, and 10.44 grs. in three different cells; mean 10.27 grs. Of the nitrate, 13.98, 13.86, and 13.60 grs.; mean 13.81 grs. We have thus a diffusion in equal times of—

Carbonate of potash,	.	10.27	1
Nitrate of potash,	.	13.81	1.3447

These experiments are almost identical with the former results, 10.25 carbonate of potash, and 13.97 nitrate of potash, which are as 1 to 1.363.

But the numbers thus obtained cannot be fairly compared, owing to the diminishing progression in which the diffusion of a salt takes place. Thus when the diffusion of nitrate of potash was interrupted every two days, as in a former experiment with chloride of sodium, the progress of the diffusion for eight days was found to be as follows in a 4 per cent. solution, with a mean temperature of  $66^{\circ}$ .

*Nitrate of Potash.*

Diffused in first two days,	.	4.54 grs.
Diffused in second two days,	.	4.13 grs.
Diffused in third two days,	.	4.06 grs.
Diffused in fourth two days,	.	3.18 grs.
		15.91

The absence of uniformity in this progression is no doubt chiefly due to the want of geometrical regularity in the form of the neck and shoulder of the solution phial. A plain cylinder, as the solution cell, might give a more uniform progression, but would increase greatly the difficulties of manipulation.

The diffusion of carbonate of potash will no doubt follow a diminishing progression also; but there is this difference, that the latter salt will not advance so far in its progression, owing to its smaller diffusibility, in the seven days of the experiment, as the more diffusible nitrate does. The diffusion of the carbonate will thus be given in excess, and as it is the smaller diffusion, the difference of the diffusion of the two salts will not be fully brought out.

The only way in which the comparison of the two salts can be made with perfect fairness, is to allow the diffusion of the slower salt to proceed for a longer time, till in fact the quantity diffused is the same for this as for the other salt, and the same point in the progression has therefore been attained in both; and to note the time required. The



problem takes the form of determining the times of equal diffusion of the two salts. This procedure is the more necessary from the inapplicability of calculation to the diffusion progression.

Further, allowing the Times of Equal Diffusion to be found, it is not to be expected that they will present a simple numerical relation. Recurring to the analogy of gaseous diffusion, the times in which equal volumes or equal weights of two gases diffuse are as the square roots of the densities of the gases. The times, for instance, in which equal quantities of oxygen and hydrogen escape out of a vessel into the air, in similar circumstances, are as 4 to 1; the densities of these two gases as 16 to 1. Or, the times of equal diffusion of oxygen and protocarburetted hydrogen are as 1.4142 to 1, that is as the square root of 2 to the square root of 1; the densities of these gases being 16 and 8, which are as 2 to 1. The densities are the squares of the equal diffusion times. It is not therefore the times themselves of equal diffusion of two salts, but the squares of those times which are likely to exhibit a simple numerical relation.

(1.) While the 4 per cent. solution of nitrate of potash was diffused as usual for seven days, the corresponding solution of carbonate of potash was now allowed to diffuse for 9.90 days; times which are as 1 to 1.4142, or as 1 to the square root of 2.

The results were as follows: diffused of—

Nitrate of potash at $64^{\circ}1$ , in seven days, 13.81 grs.,	. 100
Carbonate of potash at $64^{\circ}3$ , in 9.9 days, 13.92 grs.,	. 100.8

The three experiments on the nitrate of potash, of which 13.81 grs. is the mean, were 13.98, 13.86 and 13.60 grs., as already detailed. The three experiments on the carbonate were 14.00, 13.97 and 13.78 grs. The difference in the means of the two salts is only 0.11 gr. The results appear to be as near to equality as could be reasonably expected from the method of experimenting. 7 and 9.90 may therefore be considered as the times of equal diffusion indicated for nitrate and carbonate of potash. The times of equal diffusion, or the diffusibilities of nitrate and carbonate of potash, would appear therefore to be in the proportion of the square root of 1 to the square root of 2.

The explanation of such a relation suggested by gaseous diffusion has been anticipated. It is that the two salts have different densities in solution, that of nitrate of potash being 1, and that of carbonate of potash 2. We are thus led to ascribe, what may be called Solution Densities, to the salts. The two salts in question are related exactly like protocarburetted hydrogen gas, of density 1, to oxygen gas of density 2. The parallel would be completed by supposing that the single volume of oxygen to be diffused was previously mixed with 100 volumes



of air (or any other diluting gas), while the two volumes of protocarburetted hydrogen were also diluted with 100 volumes of air; the diluting air here representing the water in which the salts to be diffused are dissolved in the solution cell. The time in which a certain quantity of protocarburetted hydrogen would come out from a vessel containing 1 per cent. of that gas being 1 (the square root of density 1), the time in which an equal quantity of oxygen would diffuse out from a similar vessel, containing also 1 per cent., would be 1.4142 (the square root of density 2).

(2.) A solution of 4 parts of sulphate of potash in 100 water was diffused simultaneously with the last solution of carbonate of potash, and therefore in similar circumstances. The diffusion products of three experiments were 14.46, 14.21, and 14.53 grs.; mean 14.40 grs. This is in the proportion of 104.27 sulphate of potash to 100 nitrate of potash; so that the approximation to equality of diffusion with nitrate of potash, in the selected times, is not so close for the sulphate as for the carbonate of potash.

(3.) The diffusion was repeated of 2 per cent. solutions of the nitrate and carbonate of potash at a lower temperature by about  $10^{\circ}$ . The temperature of the solutions was rather unsteady; ranging from  $56^{\circ}$  to  $52^{\circ}25$  for the first period of seven days, from  $56^{\circ}$  to  $50^{\circ}5$  for the period of 9.90 days, and from  $55^{\circ}$  to  $50^{\circ}5$  for a second period of seven days; the external atmospheric temperature having fallen during the same period more than 20 degrees. Six phials of each solution were diffused and evaporated two together; so that the results are all double quantities.

At a mean temperature of  $54^{\circ}3$ , the nitrate of potash gave in seven days 12.60 and 12.13 grs.; mean 12.36 grs.

Again, at a mean temperature of  $52^{\circ}4$ , the nitrate of potash gave in seven days 11.85, 12.40, and 11.95 grs.; mean 12.06 grs.

The carbonate of potash gave in 9.90 days, with a mean temperature of  $53^{\circ}4$ , 12.69, 12.40, and 12.12 grs.; mean 12.40 grs.

The general results are—

Nitrate of potash, in seven days, at $54^{\circ}3$ ,	. . .	12.36 grs.
Carbonate of potash, in 9.9 days, at $53^{\circ}4$ ,	. . .	12.40 grs.
Nitrate of potash, in seven days, at $52^{\circ}4$ ,	. . .	12.06 grs.

As the first nitrate is  $0^{\circ}9$  above the carbonate and the second nitrate  $1^{\circ}$  below it, we may take the mean of the two nitrates as corresponding to the temperature of the carbonate. We thus finally obtain, diffused at  $53^{\circ}4$ , of—

Nitrate of potash in seven days, 12.22 grs.,	. . .	100
Carbonate of potash in 9.9 days, 12.40 grs.,	. . .	101.47



The difference in the amount of the diffusion of the two salts in these times is only 0.18 gr., or  $1\frac{1}{2}$  per cent.

These last experiments may be held therefore as tending to the same conclusion as the former series, although the circumstances were more than usually unfavourable to their success. To find whether the same relation existed between the salts through a considerable range of temperature, an opportunity was taken during cold weather to repeat the experiments at a low temperature.

(4.) Solutions of 1 salt in 100 water were diffused from eight solution cells, for each salt. The times were increased, but the same ratio of 1 to 1.4142 was preserved between them. The liquids of the cells were found to retain a temperature ranging slowly between  $41^{\circ}$  and  $38^{\circ}.8$  during the whole period of the observations. Sulphate of potash was substituted for the carbonate, as of these two equi-diffusive salts the former had been found to be least in accordance with nitrate of potash, in the 4 per cent. solutions, and appeared therefore to afford the severest test of the relation.

For nitrate of potash, at a mean temperature of  $39^{\circ}.7$ , during nine days, the diffusion product of two cells together was 6.97, 6.93, 6.77, and 6.64 grs.; mean 6.83 grs. for two cells.

For sulphate of potash, at the same mean temperature of  $39^{\circ}.7$ , during 12.728 days (twelve days, seventeen hours, twenty-eight minutes), the diffusion product of two cells together was 7.05, 6.93, 7.28, and 6.90 grs.; mean 7.04 grs. for two cells.

The general results are—

Nitrate of potash in nine days at $39^{\circ}.7$ ,	6.83 grs.	100
Sulphate of potash in 12.728 days at $39^{\circ}.7$ ,	7.04 grs.	103.07

(5.) Solutions of 2 salt in 100 water were diffused simultaneously with the preceding experiments, and in precisely the same conditions of time and temperature.

The diffusion product of nitrate of potash during nine days, at a mean temperature of  $39.7$ , was 7.03, 6.63, 6.83, and 6.83 grs. for one cell; mean 6.83 grs. for one cell, or the same number as for two cells with the 1 per cent. solution.

The diffusion product of sulphate of potash during 12.728 days was 6.84, and 6.80; mean 6.82 grs. for one cell. These experiments almost coincide with the number for nitrate of potash.

Nitrate of potash, 6.83 grs.,	100
Sulphate of potash, 6.82 grs.,	99.85

(6.) The existence of the relation in question was also severely tested in another manner. Preserving the ratio in the times of diffusion for the two salts, the actual times were varied in duration, in three series of experiments, as 1, 2, and 3. The experiments were made in



the vault, with a uniformity of temperature favourable to accuracy of observation. Eight cells of the 1 per cent. solution of each salt were always diffused at the same time.

(a.) Nitrate of potash diffused for 3·5 days, at  $47^{\circ}2$ , gave for two cells, 3·55, 3·63, 3·33, and 3·51 grs.; mean for two cells, 3·50 grs.

Sulphate of potash diffused for 4·95 days, at  $47^{\circ}3$ , gave for two cells, 3·54, 3·31, 3·51, and 3·63 grs.; mean for two cells, 3·50 grs., or exactly the same as for nitrate of potash above.

(b.) Nitrate of potash diffused for seven days, at  $48^{\circ}6$ , gave 6·1, 6·2, 5·9, and 5·92 grs.; mean for two cells, 6·04 grs.

Sulphate of potash diffused for 9·9 days, at  $49^{\circ}1$ , gave 6·13, 5·92, 6·18, and 6·59 grs.; mean 6·20 grs., or, excluding the last experiment, 6·08 grs.

Chromate of potash diffused also for 9·9 days, at  $49^{\circ}1$ , gave 6·19, 6·18, 6·40, and 6·38 grs.; mean for two cells, 6·29 grs. The diffused chromate presented no appearance of decomposition on this occasion.

(c.) Nitrate of potash diffused for 10·5 days, at  $48^{\circ}$ , gave 8·36, 8·95, 8·82, and 8·84 grs.; mean for two cells, 8·74 grs.

Sulphate of potash diffused for 14·85 days, at  $48^{\circ}6$ , gave 8·99, 8·94, 8·66, and 8·56 grs.; mean for two cells, 8·79 grs.

The mean results for the three different sets of periods of diffusion are as follows:—

3·5 and 4·95 days	{	Nitrate of potash, at $47^{\circ}2$ , 3·50 grs.,	100
		Sulphate of potash, at $47^{\circ}3$ , 3·50 grs.,	100
7 and 9·9 days	{	Nitrate of potash, at $48^{\circ}6$ , 6·04 grs.,	100
		Sulphate of potash, at $49^{\circ}1$ , 6·20 grs.,	102·65
		Chromate of potash, at $49^{\circ}1$ , 6·29 grs.,	104·14
10·5 and 14·85 days	{	Nitrate of potash, at $48^{\circ}$ , 8·74 grs.,	100
		Sulphate of potash, at $48^{\circ}6$ , 8·79 grs.,	100·57

The concurring evidence of these three series of experiments appears to be quite decisive in favour of the assumed relation of 1 to 1·4142, between the times of equal diffusion for the nitrate and sulphate of potash, and consequently of the times for the two classes of potash salts, of which the salts named are types. The same experiments are also valuable as proving the similarity of the progression of diffusion, in two salts of unequal diffusibility. I shall return again to the relation between nitrates and sulphates, under the salts of soda.

#### (8.) *Hydrate of Potash.*

(1.) Eight cells of the 1 per cent. solution of pure fused hydrate of potash were diffused for seven days in the vault, with a temperature ranging only from  $59^{\circ}$  to  $58^{\circ}$ , of which the mean was  $58^{\circ}6$ . The product of four cells evaporated together was 17·57 grs. of hydrate of



potash, and of the other four cells 17.19 grs. ; mean 17.38 grs., or 4.345 grs. for one cell. The hydrate of potash was estimated from the chloride of potassium which it gave when saturated with hydrochloric acid. The diffusion product of sulphate of potash for seven days, at  $58^{\circ}5$ , or almost the same temperature, was 10.75 grs. for the four cells, as already stated, and consequently 2.64 grs. for one cell. It thus appears that the hydrate of potash is greatly more diffusive than the sulphate of potash in the same period of seven days, namely, as 4.345 to 2.64. Such a result indeed is not inconsistent with the times of equal diffusion of these two substances, differing as much as 1 to 2.

(2.) Of pure fused hydrate of potash, a 1 per cent. solution was diffused from four cells for 4.95 days at a mean temperature of  $53^{\circ}7$ , against a 1 per cent. solution of nitrate of potash in six cells, for seven days, at a mean temperature  $0^{\circ}1$  lower, or of  $53^{\circ}6$ . The hydrate of potash which diffused, is calculated as before from the chloride of potassium which it gave, when neutralized by hydrochloric acid. Hydrate of potash diffused from two cells 5.97 and 6.28 grs. ; mean 6.12 grs., or 3.06 grs. for a single cell.

Nitrate of potash diffused from two cells 6.22, 6.54, and 5.93 grs. ; mean 6.23 grs., or 3.11 grs. for a single cell. The diffusion of nitrate of potash being 100, that of the hydrate of potash is 98.2, numbers which are sufficiently in accordance. But the times were as 1 to 1.4142, and their squares as 1 to 2. So far then as this series of experiments on hydrate of potash entitles us to conclude, we appear to have for the salts of potash a close approximation to the following simple series of squares of equal diffusion times :—

*Squares of Times of Equal Diffusion, or Solution Densities.*

Hydrate of potash,	.	.	1
Nitrate of potash, .	.	.	2
Sulphate of potash,	.	.	4

(3.) The hydrate of potash was also diffused at the lower temperature,  $39^{\circ}7$ , in company with the nitrate and sulphate of potash for a period of 6.364 days (six days, eight hours, forty-four minutes).

The 1 per cent. solution of hydrate of potash gave in eight cells, evaporated two together, 6.93, 6.93, 6.93, and 6.89 grs. ; mean 6.92 grs.

The 2 per cent. solution of hydrate of potash gave in three single cells, 6.77, 6.49, and 7.10 grs. ; mean 6.79 grs.

The diffusion of nitrate of potash in nine days at the same temperature, as already detailed, was sensibly the same, or 6.83 grs. for both the 1 and 2 per cent. solutions. The times for the two salts were as 1 to 1.4142.

The diffusion of hydrate of potash, at  $39^{\circ}7$ , may therefore be stated with reference to that of nitrate of potash, for the selected times, as follows :—



Nitrate of potash, 1 and 2 per cent. solutions,	100
Hydrate of potash, 1 per cent. solution,	101.3
Hydrate of potash, 2 per cent. solution,	99.4

These experiments at the low temperature concur, therefore, with those made at the higher temperature, in proving that the times of equal diffusion of the two substances have been properly chosen.

### III. DIFFUSION OF SALTS OF SODA.

(1.) The only salts of soda which I have yet had an opportunity of diffusing in a sufficient variety of circumstances are the carbonate and sulphate. These salts appear to be equi-diffusive, but to diverge notwithstanding more widely in the solutions of the higher proportions of salt than the corresponding potash salts. It is a question whether this increased divergence is not due to the less solubility of the soda salts, and the nearer approach consequently to their points of saturation in the stronger solutions.

TABLE XIII.—Diffusion of Carbonate and Sulphate of Soda.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 64°.		At 37° 7.	
		Experiments.	Mean.	Experiments.	Mean.
Carbonate of soda.					
2	1.0202	4.15 4.08		2.78 2.62	
4	1.0405	4.21 7.96 7.70	4.14	2.73 5.31 4.94	2.71
6 $\frac{2}{3}$	1.0653	7.68 12.16 12.06	7.78	5.35 8.50 8.45	5.20
10	1.0957	12.45 17.13 16.53 17.00	12.22 16.88	8.05	8.33
Sulphate of soda.					
2	1.0179	4.35 4.32		2.96 3.03	
4	1.0352	4.25 8.14 8.10	4.31	3.09 5.63 5.64	3.03
6 $\frac{2}{3}$	1.0578	8.28 13.26 13.63	8.17	5.42 8.77 8.84	5.56
10	1.0847	13.61 18.71 19.73 18.91	13.50 19.14		8.80



The range of the thermometer during the continuance of the experiments at the higher temperature was from  $64^{\circ}5$  up to  $65^{\circ}$  and falling again to  $63^{\circ}$ ; the mean of all the days being  $64^{\circ}$ . The temperature of the other series, or of the ice-box, was  $42^{\circ}$  the first day,  $38^{\circ}$  the second, and  $37^{\circ}$  steadily for the remainder of the period; the mean being  $37^{\circ}7$ .

The mean results at  $64^{\circ}$  are as follows:—

	2.	4.	$6\frac{2}{3}$ .	10.
Carbonate of soda.....	4.14	7.78	12.22	16.88
Sulphate of soda .....	4.31	8.17	13.50	19.14

Another series of experiments was made upon a 1 per cent. solution of the same salts at a mean temperature of  $64^{\circ}9$ . Six phials of each solution were diffused, and the water of two jars afterwards evaporated together, so that the quantities stated are double.

The diffusion product in three experiments with the sulphate of soda was 4.77, 4.75, and 4.80 grs.; mean 4.77 grs. The diffusion product in three experiments with the carbonate of soda was 4.61, 4.68, and 4.67 grs.; mean 4.65 grs. The difference between the carbonate and sulphate is 0.12 gr.; it is less for the present proportion of 1 per cent. of salt, than for 2 per cent., so that the diffusion of the salts may be converging to a perfect equality in very weak solutions. One-half of the preceding quantities, or the mean results for a single diffusion cell, are—

*Diffusion of 1 per cent. solutions at  $64^{\circ}9$ .*

Carbonate of soda, 2.32 grs,	.	.	100
Sulphate of soda, 2.38 grs.,	.	.	102.58

(2.) The diffusion of the carbonate of soda was further compared with the nitrate of the same base, to find whether their times of equal diffusion are related like those of the corresponding potash salts. The mean temperature of the first seven days, which was the period of diffusion for the nitrate of soda, was  $66^{\circ}9$ ; of the last three days,  $65^{\circ}2$ ; and of the whole period of 9.9 days occupied by the carbonate of soda,  $66^{\circ}4$ . The 4 per cent. solutions were employed.

The nitrate of soda gave a diffusion product, in three experiments, of 11.48, 11.58, and 12.13 grs.; mean 11.73 grs.

The carbonate of soda, in three experiments, gave 11.66, 11.53, and 11.52 grs.; mean 11.57 grs. A slight addition should be made to the latter quantity to raise the diffusion product from  $66^{\circ}4$  to  $66^{\circ}9$ . It will appear from a subsequent experiment that the diffusion of the carbonate of soda increases 0.096 gr. for a rise of one degree of tempera-



ture; which will give 0.05 gr. for the half degree in question. Bringing the diffusion of the two salts to the same temperature of 66.9, we have therefore diffused, of—

Nitrate of soda, in seven days, 11.73 grs.,	. 100
Carbonate of soda, in 9.9 days, 11.62 grs.,	. 99.06

The difference in the quantity diffused of the two salts is only 0.11 gr., or 1 per cent., which is quite within the unavoidable errors of observation.

(3.) The diffusion of a 2 per cent. solution of the same salts was repeated at the same inferior temperature of 54.3 as with the salts of potash, and under the same difficulties from fluctuation of atmospheric temperature. Two water-jars were evaporated together, so that the results are double.

Nitrate of soda, diffused for seven days at a mean temperature of 54.3, gave 10.15, 10.24, and 9.92 grs. in three experiments; mean 10.10 grs.

Carbonate of soda, diffused for 9.9 days at a mean temperature of 53.4, gave 9.93, 9.54, and 10.10 grs. in three experiments; mean 9.86 grs. But the latter amount is to be increased by 0.09 gr. to bring it to the diffusion of 54.3. We have then for the diffusion product of the two salts at the same temperature of 54.3—

Nitrate of soda, in 7 days, 10.10 grs.,	. 100
Carbonate of soda, in 9.9 days, 9.95 grs.,	. 98.51

The difference is again small, namely, 0.15 gr., or  $1\frac{1}{2}$  per cent., and within the limits of unavoidable error.

It appears therefore that the times of equal diffusion of the nitrate and carbonate of soda are related like those of the nitrate and carbonate of potash, or as the square root of 1 and 2, that is, as 1 to 1.4142.

#### *Relation of Salts of Potash to Salts of Soda.*

It appeared probable, from many of the experiments already recorded, that if any relation, in the times of equal diffusibility, existed between the corresponding salts of potash and soda, it was that of the square root of 2 to the square root of 3. They were accordingly diffused for times having this ratio; namely, the nitrate of potash for seven days, the nitrate of soda for 8.57325 days; the sulphate and carbonate of potash for 9.9 days, and the sulphate and carbonate of soda for 12.125 days. If these times are rightly chosen, the eventual diffusion products of all the experiments should be equal. The 1 per cent. solution was selected, and the number of experiments simultaneously made on each salt was eight or six. The liquids of two water-jars were evapor-



ated together, so that each of the results in the table below represents the diffusion of two cells. These experiments also afford another opportunity of testing the assumed relation between the nitrates and sulphates of the same base.

TABLE XIV.—Solution: 1 Salt to 100 Water, at  $55^{\circ}4$ — $56^{\circ}1$ .

	Temperature.	Time in days.	Square of times. Sol. density.	Diffusion product of two cells in grs.				
				Exp. I.	Exp. II.	Exp. III.	Exp. IV.	Mean.
Nitrate of potash .....	$56^{\circ}1$	7	2	6.67	6.87	6.90	6.57	6.75
Nitrate of soda .....	$55^{\circ}7$	8.57	3	6.59	6.80	6.94	6.57	6.78
Sulphate of potash ...	$55^{\circ}4$	9.90	4	6.73	6.77	6.96	6.68	6.78
Sulphate of soda .....	$55^{\circ}4$	12.125	6	6.43	6.94	6.80	6.68	6.72
Carbonate of potash ...	$55^{\circ}4$	9.90	4	6.54	6.64	6.40	6.67	6.56
Carbonate of soda.....	$55^{\circ}4$	12.125	6	6.40	6.63	6.60	6.67	6.54

The range of temperature during the period of these experiments rather exceeded 3 degrees, so that they cannot be considered as fortunate in that respect; but still the similarity between the different sets of experiments, and the near equality of their means, is very remarkable. The two nitrates and the two sulphates may be said to coincide, the extreme difference of the means of the four salts not being quite so much as 1 per cent. The two carbonates fall about 3.4 per cent. below the sulphates and nitrates, but agree perfectly with each other, showing a uniformity in their irregularity. This deviation of the carbonates would appear essential, as it has been observed every time they have been compared with the sulphates.

The double relation between salts of potash and salts of soda, and between the nitrate and sulphate class of each of these bases, will, I believe, be allowed to acquire considerable additional support from this new series of observations.

#### IV. DIFFUSION OF SULPHATE OF MAGNESIA.

In a set of preliminary experiments upon sulphate of magnesia in comparison with sulphate of potash, the 4 per cent. solutions of both salts were diffused for seven days at a mean temperature of  $57^{\circ}9$ , with very little fluctuation, the extreme range being from  $58^{\circ}5$  to  $57^{\circ}75$ . The sulphate of magnesia is taken anhydrous in all the following experiments.

The diffusion of sulphate of potash in three cells was 9.16, 9.22, and 9.57 grs.; mean 9.32 grs.



The diffusion of sulphate of magnesia in three cells was 5.21, 4.98, and 5.34 grs.; mean 5.18 grs. The diffusion, in equal times, appears here to be as 100 sulphate of potash to 55.58 sulphate of magnesia. We know, however, that when unequally diffusible salts are diffused for equal times, the diffusion of the slower is exaggerated. Consequently the diffusion of sulphate of magnesia is likely to be represented in excess in these experiments.

In a second preliminary series of experiments the same 4 per cent. solutions were diffused, the sulphate of potash for eight days and the sulphate of magnesia for nineteen days, with the view of discovering their times of equal diffusibility.

During the first period of eight days the temperature fluctuated considerably, beginning at  $54^{\circ}$ , falling gradually in four days to  $50^{\circ}5$ , and rising again in four days to  $53^{\circ}$ ; the average of the whole period was  $52^{\circ}2$ . The diffusion of sulphate of potash from three cells was  $9^{\circ}36$ ,  $9^{\circ}25$ , and  $10^{\circ}52$  grs.; mean  $9^{\circ}71$  grs.

During the second period of nineteen days, which included the first period, the mean temperature was  $54^{\circ}6$ . The diffusion of sulphate of magnesia from three cells was 11.81, 11.61, and 10.90 grs.; mean 11.44 grs. The variation in the amounts diffused of both salts is greater than usual, owing no doubt to the changes of temperature, which were imperfectly controlled.

Dividing the quantity of salt diffused by the number of days, we have of sulphate of potash 1.214 gr. diffused per day, and of sulphate of magnesia 0.602 gr. per day; or the latter salt exhibits sensibly half the diffusibility of the former in equal times. This suggested the trial of times for these two salts in the proportion of 1 to 2, with the view of obtaining equal diffusions.

(1.) A one per cent. solution of sulphate of magnesia (anhydrous) was diffused for the long period of 19.8 days, at a mean temperature of  $54^{\circ}7$ , in 8 cells. The diffusion products of four pairs of cells were 7.07, 6.71, 7.07, and 7.35 grs.; mean 7.05 grs., or for one cell, 3.53 grs.

A similar solution of sulphate of potash diffused for 9.9 days, or half the preceding period, at a mean temperature of  $55^{\circ}4$ , or  $0^{\circ}7$  higher, gave a mean product, for two cells, of 6.79 grs., as before stated, or for one cell, of 3.40 grs. The diffusion of sulphate of potash being 100, that of sulphate of magnesia is therefore 103.7, a fair approximation to equality.

(2.) In a second series of experiments upon 1 per cent. solutions of the same two salts, diffused in the vault for fourteen and seven days respectively, with a mean temperature of  $53^{\circ}8$  for the sulphate of magnesia, and  $54^{\circ}3$  for the sulphate of potash, the temperature was



remarkably uniform, gradually falling from  $55^{\circ}2$  to  $53^{\circ}$  during the longer period, but without any injurious oscillation.

From eight cells, evaporated two together, the sulphate of magnesia obtained was 6.12, 6.12, 6.04, and 6.03 grs.; mean 6.08 grs., or 3.04 grs. for one cell.

The sulphate of potash gave from eight cells, in experiments already detailed, a mean result of 5.84 grs. of salt for two cells, or 2.92 grs. for one cell. The diffusion is in the proportion of 100 sulphate of potash to 104.11 sulphate of magnesia, the times being as 1 to 2 for the two salts respectively.

From these two series of experiments, it appears that, at  $54^{\circ}$ , sulphate of magnesia has nearly, if not exactly, half the diffusibility of sulphate of potash, and consequently one-fourth of that of hydrate of potash. Or, the times of equal diffusion for these three salts appear to be 1, 2, and 4. The squares of these times and the solution densities are 1, 4, and 16. Hydrate of potash may possibly therefore have the same relation to sulphate of magnesia in solution density and diffusibility that hydrogen gas has to oxygen gas.

(3.) A two per cent. solution of sulphate of magnesia, diffused for fourteen days, gave at  $53^{\circ}9$ , for two pairs of cells, 9.57 and 10.00 grs. of salt, of which the mean is 9.79 grs., or 4.85 grs. for one cell.

A similar solution of sulphate of potash diffused for seven days gave a mean result of 4.97 grs. of salt for one cell, at  $54^{\circ}2$ , as already stated. The result is a diffusion of 100 sulphate of potash to 97.59 sulphate of magnesia.

(4.) A four per cent. solution of sulphate of magnesia, diffused for fourteen days, gave at  $53^{\circ}7$ , in two pairs of cells, 18.00 and 18.20 grs. of salt; mean 18.10 grs. for two cells, or 9.05 grs. for a single cell.

A similar solution of sulphate of potash, diffused for seven days at  $54^{\circ}2$ , gave a mean result of 9.30 grs. of salt for a single cell, as already stated. This is a diffusion of 100 sulphate of potash to 97.4 sulphate of magnesia.

The diffusion of the 2 and 4 per cent. solutions of sulphate of magnesia is so nearly equal to the diffusion of the same proportions of sulphate of potash in half the time, that they may be considered as supplying additional support to the assumed relation between the diffusibilities of these salts.

I may add, that a 4 per cent. solution of anhydrous sulphate of zinc was diffused for fourteen days, simultaneously with the similar solution of sulphate of magnesia, and of course at the same temperature of  $53^{\circ}7$ . Two cells, evaporated two together, gave 17.40 and 17.36 grs. of ignited sulphate of zinc; mean 17.38 grs. The salt remained, after ignition, entirely soluble. This is a diffusion of 8.69 grs. for one cell, while the



sulphate of magnesia gave 9.05 grs.; or of 100 sulphate of zinc to 104.14 sulphate of magnesia. This result is interesting, as we here find two salts which are isomorphous, and of which the equi-diffusion is on that account in a high degree probable, differing between themselves so much as 4 per cent.

Another numerous series of experiments was made at a considerably lower temperature, with the view of testing several of the same relations. The temperature in commencing the diffusion was  $41^{\circ}$ , but fell in the course of three days to  $38^{\circ}8$ , and afterwards rose to  $39^{\circ}$ , from which it never varied afterwards more than a degree during the diffusion of the salts of potash and soda. The mean temperature for their periods did not vary above  $0^{\circ}1$  or  $0^{\circ}2$  from  $39^{\circ}7$ , so that it may be supposed the same for all these salts. For the sulphates of magnesia, the mean temperature was  $38^{\circ}9$ , or  $0^{\circ}8$  lower. The times chosen are as the square roots of 2, 3, 6, and 16.

TABLE XV.—Solutions of 1 and 2 Salt to 100 Water, at  $39^{\circ}7$ .

	Time in days.	Square of times. Sol. density.	Diffusion product of two cells in 1 per cent. solutions, and one cell in 2 per cent. solutions.				
			Exp. I.	Exp. II.	Exp. III.	Exp. IV.	Mean.
Chloride of potassium, 2 per cent.	9	2	6.58	6.79	6.82	...	6.73
Nitrate of soda, 2 per cent. ....	11.022	3	6.66	6.98	6.79	...	6.81
Chloride of sodium, 1 per cent. .	11.022	3	6.33	6.63	6.73	7.06	6.69
Chloride of sodium, 2 per cent. .	11.022	3	6.50	6.60	6.64	6.74	6.62
Sulphate of soda, 1 per cent. ....	15.589	6	6.60	6.56	6.56	6.50	6.55
Sulphate of soda, 2 per cent. ...	15.589	6	6.50	5.43	6.33	...	6.42
Sulphate of magnesia, 1 per cent.	25.456	16	6.36	6.20	6.86	6.59	6.50
Sulphate of magnesia, 2 per cent.	25.456	16	6.42	6.78	6.50	6.84	6.63

Several other salts were diffused in the same circumstances as the preceding, of which the diffusion products have been previously given. Of these salts, both the 1 and 2 per cent. solutions of nitrate of potash gave 6.83 in nine days, or in the same time as chloride of potassium in the table. The latter salt maintains a sensible equality of diffusion with the present series at the low, as well as it was found to do at the former high temperature. Chloride of sodium is here introduced for the first time: it appears to be equi-diffusive with nitrate of soda. If the sulphate of magnesia diffused be increased by 0.07, for its lower temperature, this salt will be in close accordance with the salts of potash and soda.

Taking nitrate of potash 6.83, as 100, for a standard, the salt which deviates most considerably is sulphate of soda, which for the 1 per cent.



solution is 6.55, or 95.9. A low temperature, however, must be unfavourable to diffusion experiments, from increasing the tendency of salts to crystallize.

In conclusion, I may sum up the results of most interest which this inquiry respecting liquid diffusion has hitherto furnished.

1. I would place first the method of observing liquid diffusion. This method, although simple, appears to admit of sufficient exactness. It enables us to make a new class of observations which can be expressed in numbers, and of which a vast variety of substances may be the object, in fact everything soluble. Diffusion is also a property of a fundamental character, upon which other properties depend, like the volatility of substances; while the number of substances which are soluble and therefore diffusible, appears to be much greater than the number of volatile bodies.

2. The novel scale of Solution Densities, which are suggested by the different diffusibilities of salts, and to which alone, guided by the analogy of gaseous diffusion, we can refer these diffusibilities. Liquid diffusion thus supplies the densities of a new kind of molecules, but nothing more respecting them.

The fact that the relations in diffusion of different substances refer to equal weights of those substances, and not to their atomic weights or equivalents, is one which reaches to the very basis of molecular chemistry. The relation most frequently possessed is that of equality, the relation of all others most easily observed. In liquid diffusion we appear to deal no longer with chemical equivalents or the Daltonian atoms, but with masses even more simply related to each other in weight. Founding still upon the chemical atoms, we may suppose that they can group together in such numbers as to form new and larger molecules of equal weight for different substances, or if not of equal weight, of weights which appear to have a simple relation to each other. It is this new class of molecules which appear to play a part in solubility and liquid diffusion, and not the atoms of chemical combination.

3. The formation of classes of equi-diffusive substances. These classes are evidently often more comprehensive than the isomorphous groups, although I have reason to imagine that they sometimes divide such groups; that while the diffusion of salts of baryta and strontia, for instance, is similar, the diffusion of salts of lead may be different.

4. The separation of the whole salts (apparently) of potash and of soda into two divisions, the sulphate and nitrate groups, which must have a chemical significancy. The same division of the salts in question



has been made by M. Gerhardt, on the ground that the nitrate class is monobasic and the sulphate class bibasic.

5. The application of liquid diffusion to the separation of mixed salts, in natural and in artificial operations.

6. The application of liquid diffusion to produce chemical decompositions.

7. The assistance which a knowledge of liquid diffusion will afford in the investigation of endosmose. When the diffusibility of the salts in a liquid is known, the compound effect presented in an endosmotic experiment may be analysed, and the true share of the membrane in the result be ascertained.

But on the mere threshold of so wide a subject as liquid diffusion, I must postpone speculation to the determination of new facts and the enlargement of my data, of the present incompleteness of which I am fully sensible.

#### SUPPLEMENTARY OBSERVATIONS ON THE DIFFUSION OF LIQUIDS.<sup>1</sup>

THE experiments of my former paper furnished strong grounds for believing that isomorphous salts possess a similar diffusibility. All the salts of potash and ammonia, which were compared, appeared to be equi-diffusive; so also were the salts of certain magnesian bases. A single preliminary observation on the nitrates of lead and baryta, however, opposed the general conclusion, and demanded further inquiry. It is scarcely necessary to say that any new means of recognising the existence of the isomorphous relation between different substances, must prove highly valuable. Let us inquire therefore how far liquid division is available for that purpose.

The salts were still diffused from weak solutions, that is from solutions containing from 1 to 8 per cent. of salt; but now a measure of the solution, equal to 100 grs. of water, was made to contain 1 grain of the salt, to form what is called the 1 per cent. solution; instead of 1 grain of salt being added to 100 grs. of water, as before, without reference to the condensation which generally occurs. The quantities 1, 2, 4, and 8 per cent. thus indicate the parts of salt present in a constant volume of liquid,—as 10, 20, 40, and 80 grs. of the salt in 1000 water grain-measures of the solution. The same phials for the solution and jars for the external water-atmosphere continued to be used, and the manipulations were

<sup>1</sup> *Phil. Trans.* 1850. Received May 2, —Read June 20, 1850.



similar. It is believed, however, that the temperature of the liquids was maintained more uniform in the new experiments than the old, partly by the better regulation of the temperature of the apartment, and partly by placing the jars close together upon a table with upright ledges, and covering the whole over with sheets of paper during the continuance of an experiment. The mass of fluid in 80 or 100 jars, which were employed at once and placed together, made the small oscillations of temperature, which might still occur, slow and less injurious.

The investigation is also extended to several new substances, such as hydrocyanic acid, acetic acid, sulphurous acid, alcohol, ammonia and salts of organic bases without reference to isomorphous relations. It is very necessary to have data which are minute and accurate respecting the diffusion of a considerable variety of substances. This it is my present object to endeavour to supply, leaving speculative deductions in general respecting the nature and laws of liquid diffusion for a future occasion.

The density of all the solutions was observed at a constant temperature, namely, 60° Fahr.

### 1. *Hydrochloric Acid.*

The period of diffusion arbitrarily chosen for this acid was five days. The diffusate, or quantity of acid diffused, was determined by precipitating the liquid of the external reservoirs with nitrate of silver, and weighing the chloride of silver formed. In the 1 and 2 per cent. solutions, the liquids of two jars were generally mixed and precipitated together.

(1.) Hydrochloric acid, 0.99 per cent.; density 1.0043. Diffused at 53° 5, in six cells, 7.52, 7.52, 7.42; mean 7.49 grs. for 2 cells. Calculated for 1 per cent., 7.56 grs. at 53° 5 for two cells, or 7.41 grs. at 51°, when corrected for that temperature.

(2.) Hydrochloric acid, 1.92 per cent.; density 1.009. Diffused at 51°, in eight cells, 14.71, 14.05, 14.54, 14.47; mean 14.44 grs. for two cells. Calculated for 2 per cent., 15.04 grs. at 51° for two cells.

(3.) Hydrochloric acid, 1.993 per cent.; density 1.0094. Diffused at 62° 8, in six cells, two experiments on one-sixth part of the mixed jars gave 8.203, 8.198; mean 8.20 grs. for one cell, or 16.40 grs. for two cells. Calculated for 2 per cent., 16.46 grs. at 62° 8 for two cells.

(4.) Hydrochloric acid, 3.90 per cent.; density 1.0190. Diffused at 51°, in 8 cells, 29.18, 30.70, 30.70, 29.26; mean 29.96 grs. for two cells. Calculated for 4 per cent., 30.72 grs. at 51° for two cells.



(5.) Hydrochloric acid, 7.90 per cent.; density 1.0380. Diffused at  $51^{\circ}$ , in four cells, 32.71, 33.64, 33.64, 33.74; mean 33.43 grs. for one cell. Calculated for 8 per cent., 33.84 grs. at  $51^{\circ}$  for one cell.

Comparing the diffusibilities of the 2 per cent. solutions (2 and 3) at  $51^{\circ}$  and  $62^{\circ}8$ , an increase is observed from 15.04 to 16.40 grs., or from 100 to 109.1, which gives an increase of 0.77 per cent. for  $1^{\circ}$ . This method of estimating the effect of temperature is not exact, as the times only in which an equal diffusion at the different temperatures takes place are truly comparable. We may deduce from it, however, the effect of the small difference of temperature of  $2^{\circ}5$  of the 1 per cent. solution from the others, as has been done, without sensible error. The diffusates at the same temperature would then be as follows:—

Diffusion of Hydrochloric Acid in five days at  $51^{\circ}$  Fahr.; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . .	7.41	0.97
From 2 per cent. solution, . . .	15.04	2.00
From 4 per cent. solution, . . .	30.72	4.08
From 8 per cent. solution, . . .	67.68	9.00

The increasing diffusibility with the larger proportions of acid here observed is unusual, at least in the degree exhibited by the 8 per cent. solution. Other substances, as will be immediately observed of nitric acid, appear to lose proportionally in diffusibility as their solutions are concentrated.

Hydrochloric acid belongs to the most diffusive class of substances known; it appears to exceed hydrate of potash at  $53^{\circ}5$ , as 7.56 to 6.12, or as 100 to 80.9.<sup>1</sup>

The rapidity with which hydrochloric acid diffuses, and the facility with which that substance may be estimated, induced me to examine the progression with which its diffusion takes place with increasing times in a minute manner. The 2 per cent. solution was diffused for times increasing by six hours, from twelve hours or 0.5 day to 4.75 days, six cells being diffused for every period. Instead of determining the acid diffused separately in each jar or pair of jars, the contents of the six jars of each experiment were mixed together, and a definite proportion of the liquid precipitated by nitrate of silver, so as to obtain at once the mean result. Another observation for 5.75 days is added, although made at a sensibly higher temperature.

<sup>1</sup> *Philosophical Transactions*, 1850, p. 39.



Diffusion of Hydrochloric Acid, 2 per cent. solution; one cell.

Time.	Temperature.	Diffusate in grains.	Differences.
Days.	°		
0·5	53·75	0·909	
0·75	53·75	1·312	·403
1	53·75	1·766	·454
1·25	53·75	2·353	·587
1·5	53·75	2·596	·243
1·75	53·58	3·178	·582
2	53·58	3·410	·232
2·25	53·42	3·967	·557
2·5	53·58	4·339	·372
2·75	53·50	4·618	·279
3	53·50	4·969	·351
3·25	53·50	5·304	·335
3·5	54·85	5·857	·553
3·75	54·85	6·254	·397
4	54·85	6·407	·153
4·25	54·85	6·795	·388
4·5	54·71	7·034	·239
4·75	54·71	7·473	·339
5·75	56·46	8·363	

The differences are evidently affected by accidental errors of observation. The diffusion at 3·5 days is also increased by a rise of temperature of more than 1° in that and the following experiments. The diffusion always increases with the time, but less rapidly, according to a gradually diminishing progression.

## 2. *Hydriodic Acid, Hydrobromic Acid and Bromine.*

*Hydriodic Acid.*—Time of diffusion five days, as for hydrochloric acid. The acid diffused was estimated from the iodide of silver which it gave when precipitated by nitrate of silver.

Hydriodic acid, 1·98 per cent.; density 1·0142. Diffused at 53°·5, in eight cells, 14·90, 15·67, 15·25, 15·27; mean 15·27 grs. for two cells. Calculated for 2 per cent., 15·42 grs. at 53°·5 for two cells, or 15·11 grs. at 51°.

These experiments indicate a similarity of diffusion between the two isomorphous substances, hydrochloric and hydriodic acids.

Diffusion from 2 per cent. solutions at 51° Fahr.

Hydrochloric acid,	.	15·04	100
Hydriodic acid, .	.	15·11	100·46

*Hydrobromic Acid.*—Time of diffusion five days. The diffusate was estimated from the bromide of silver.



(1.) Hydrobromic acid, 1.556 per cent.; density 1.0112. Diffused at  $59^{\circ}7$ , in eight cells. The whole diffusates mixed together gave by analysis a mean of 12.90 grs. of hydrobromic acid in two cells; calculated for 2 per cent., 16.58 grs. in two cells, at  $59^{\circ}7$ .

(2.) The experiment was repeated at  $59^{\circ}8$ , with a solution containing 1.578 per cent. of hydrobromic acid, of density 1.0116, with five diffusion phials not employed above. The mean diffusate for a pair of cells was 13.05 grs. of hydrobromic acid; that is, 16.53 grs. for a 2 per cent. solution, which is as nearly as possible the result of the preceding series of experiments.

(3.) Another solution containing exactly 2 per cent. of hydrochloric acid was diffused for comparison in eight cells, in the same circumstances of time and temperature as (1.); its density was 1.0104.

Diffusate from 2 per cent. solutions at  $59^{\circ}7$  Fahr.

Hydrochloric acid,	.	.	16.55	100
Hydrobromic acid,	.	.	16.58	100.18

Hydrobromic acid appears therefore to coincide in diffusibility with hydrochloric acid at this temperature. It may be remarked that these three acids, hydrochloric, hydrobromic and hydriodic, do not exhibit the same correspondence in another physical property, namely, the densities of their aqueous solutions containing the same proportion of acid. The densities of 2 per cent. solutions of hydrochloric and hydriodic acids appear to be respectively 1.0104 and 1.0143, at  $60^{\circ}$  Fahr., and that of hydrobromic acid will obviously be an intermediate number. The same acids are also known to differ considerably in the boiling-points of solutions containing the same proportion of acid. A considerable diversity of physical properties appears here to be compatible with equal diffusibility in substances which are isomorphous.

*Bromine.*—Pure water readily dissolves more than 1 per cent. of this substance. The solution prepared, however, contained only 0.864 per cent. of bromine, as was ascertained by treating it with sulphurous acid and afterwards precipitating by nitrate of silver. Its density was 1.0070. It was evident, from the slow appearance of the brown colour in the exterior cell, that bromine diffuses less rapidly than hydrobromic acid.

The diffusion-time of bromine was made ten days, or double the time of hydrobromic acid. Two cells contained together a diffusate of 5.80 grs. of bromine; another two cells a diffusate of 5.88 grs.; mean 5.84 grs. at  $60^{\circ}1$  Fahr.; or 6.76 grs. for a 1 per cent. solution. Doubling the last result we have 13.52 grs. for a 2 per cent. solution, which is



still considerably under the diffusate of hydrobromic acid (16.58 grs.) in half the time.

### 3. *Hydrocyanic Acid.*

Time of diffusion five days. The acid diffused was estimated from the cyanide of silver which it gave with nitrate of silver.

Hydrocyanic acid, 1.766 per cent., made up to a density of 1.0142 with sulphate of potash. Diffused at  $64^{\circ}2$ , in six cells, 11.40, 11.86, 11.80; mean 11.68 grs. for two cells. Calculated for 2 per cent., 13.23 grs. at  $64^{\circ}2$  in two cells, or about 13.10 grs. at  $62^{\circ}8$ , assuming this acid to be affected in the same way by temperature as hydrochloric acid.

Hydrocyanic acid here appears less diffusive than hydrochloric acid, at the same temperature  $62^{\circ}8$ , as 13.10 to 16.40, or as 79.6 to 100, and not to belong therefore to the same class of diffusive substances.

### 4. *Nitric Acid.*

Time of diffusion five days. The quantity of this acid diffused was always determined with great exactness by neutralization by means of a normal solution of carbonate of soda.

1. Nitrate of water ( $\text{HO} \cdot \text{NO}_3$ ), 1 per cent.; density 1.0052. Diffused at  $50^{\circ}8$ , in eight cells, 6.77, 6.77, 7.26, 6.97; mean 6.94 grs. of nitrate of water in two cells at  $50^{\circ}8$ , and 6.99 grs. by estimate at  $51^{\circ}2$ .

2. Nitrate of water, 1 per cent.; density 1.0052. Diffused at  $53^{\circ}5$ , in six cells, 7.32, 7.32, 7.20; mean 7.28 grs. in two cells.

3. Nitrate of water, 1.92 per cent.; density 1.0112. Diffused at  $51^{\circ}2$ , in eight cells, 14.34, 14.24, 14.10, 13.96; mean 14.16 grs. in two cells. Calculated for 2 per cent., 14.74 grs. at  $51^{\circ}2$  in two cells.

4. Nitrate of water, 2 per cent.; density 1.0106. Diffused at  $63^{\circ}2$ , in eight cells, 16.97, 16.64, 16.81, 16.64; mean 16.76 grs. in two cells.

5. Nitrate of water, 3.88 per cent.; density 1.0209. Diffused at  $51^{\circ}2$ , in eight cells, 27.76, 28.34, 27.90, 27.62; mean 27.90 grs. in two cells. Calculated for 4 per cent., 28.76 grs. at  $51^{\circ}2$  in two cells.

6. Nitrate of water, 7.96 per cent.; density 1.0432. Diffused at  $51^{\circ}2$ , in four cells, 29.17, 29.17, 29.17, 27.76; mean 28.82 grs. in one cell. Calculated for 8 per cent., 28.96 grs. at  $51^{\circ}2$  in one cell.

For the difference of temperature between  $51^{\circ}2$  and  $63^{\circ}2$ , the diffusion rises, in the 2 per cent. solution, from 14.74 to 16.76 grs., or from 100 to 113.7; which gives an increase of 1.142 per cent. for one degree of temperature.

The diffusion of the different proportions of this acid at one temperature is as follows:—



Diffusion of Nitrate of Water in five days at  $51^{\circ}2$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	6.99	0.95
From 2 per cent. solution, .	14.74	2
From 4 per cent. solution, .	28.76	3.90
From 8 per cent. solution, .	57.92	7.86

The 2 per cent. solution is taken as the standard of comparison for the ratios, instead of the 1 per cent. solution, from the greater accuracy with which the diffusion of the former can be observed.

The usual approach to equality of diffusion, between chlorides and nitrates, is observable in hydrochloric and nitric acids, at least in the 1 and 2 per cent. solutions.

Diffusion from 1 per cent. solution at  $53^{\circ}5$ .

Hydrochloric acid, . . .	7.56	100
Nitrate of water, . . .	7.28	96.3

## Diffusion from 2 per cent. solution.

Hydrochloric acid at $51^{\circ}$ , .	15.04	100
Nitrate of water at $51^{\circ}2$ , .	14.74	98.0

The 2 per cent. solutions of both acids were also diffused at higher temperatures.

## Diffusion from 2 per cent. solution.

Hydrochloric acid at $62^{\circ}8$ , .	16.46	100
Nitrate of water at $63^{\circ}2$ , .	16.76	101.8

Here the diffusibility of the two acids is as nearly as possible equal.

## Diffusion from 4 per cent. solution.

Hydrochloric acid at $51^{\circ}$ , .	30.72	100
Nitrate of water at $51^{\circ}2$ , .	28.76	93.7

## Diffusion from 8 per cent. solution.

Hydrochloric acid at $51^{\circ}$ , .	67.68	100
Nitrate of water at $51^{\circ}2$ , .	57.92	85.3

The wide divergence between these two acids, in the 8 per cent. solution, is produced by the remarkably increased diffusion of hydrochloric acid in that high proportion.



5. *Sulphuric Acid.*

The time of diffusion arbitrarily chosen for this acid was ten days. The diffusate of this acid was determined in the same manner as that of nitric acid.

1. Sulphate of water ( $\text{HO.SO}_3$ ), 0.993 per cent.; density 1.0065. Diffused at  $51^\circ.7$ , in eight cells, 8.87, 8.87, 8.87, 8.69; mean 8.82 grs. of sulphate of water for two cells. Calculated for 1 per cent., 8.91 grs. at  $51^\circ.7$  for two cells, and 8.69 grs. at  $49^\circ.7$ .

2. Sulphate of water, 1.89 per cent.; density 1.0130. Diffused at  $49^\circ.7$ , in eight cells, 16.13, 16.16, 15.58, 16.03; mean 15.98 grs. for two cells. Calculated for 2 per cent., 16.91 grs. at  $49^\circ.7$  for two cells.

3. Sulphate of water, 2 per cent.; density 1.0133. Diffused at  $63^\circ.5$ , in eight cells, 19.80, 20.05, 19.67, 19.41; mean 19.73 grs. for two cells.

4. Sulphate of water 3.87 per cent.; density 1.0261. Diffused at  $49^\circ.7$ , in eight cells, 32.72, 32.72, 33.06, 32.58; mean 32.77 grs. for two cells. Calculated for 4 per cent., 33.89 grs. at  $49^\circ.7$  for two cells.

5. Sulphate of water, 7.90 per cent.; density 1.0513. Diffused at  $49^\circ.7$ , in four cells, 34.08, 34.76, 33.74, 33.63; mean 34.05 grs. for one cell. Calculated for 8 per cent., 34.48 grs. at  $49^\circ.7$  for one cell.

In the 2 per cent. solution the diffusion rises, with the difference of temperature between  $49^\circ.7$  and  $63^\circ.5$ , from 16.91 to 19.73 grs. or from 100 to 116.68. This is an increase of 1.209 per cent. for one degree of temperature.

The diffusion of the different proportions of sulphuric acid is as follows:—

Diffusion of Sulphate of Water in ten days at  $49^\circ.7$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . .	8.69	1.03
From 2 per cent. solution, . . .	16.91	2
From 4 per cent. solution, . . .	33.89	4.01
From 8 per cent. solution, . . .	68.96	8.16

The diffusibility of different strengths of this acid appears to be pretty uniform, but with a slight tendency to increase in the higher proportions, like hydrochloric acid.

Sulphuric acid is greatly inferior in velocity of diffusion to hydrochloric acid, but still appears to possess considerably more than half the diffusibility of the latter.

6. *Chromic Acid.*

Time of diffusion ten days. The diffusates from four cells of the 2 per cent. solution were mixed together, and the quantity of chromic



acid diffused for two cells reduced by means of hydrochloric acid and alcohol, and weighed as oxide of chromium.

1.762 per cent. of anhydrous chromic acid, density 1.01404, diffused at  $67^{\circ}3$ , gave 19.78 grs. of chromic acid in two cells. Calculated for 2 per cent., 22.43 grs. of chromic acid, in two cells, at  $67^{\circ}3$ . The diffusion of sulphuric acid at  $63^{\circ}5$ , was 19.73 grs., which would give about 21 grs. of that acid at  $67^{\circ}3$ .

### 7. *Acetic Acid.*

Time of diffusion ten days. This acid cannot be determined accurately by the acidimetical method, owing to the acetates of potash and soda being essentially alkaline to test-paper, like the carbonates of the same bases, although neutral in composition. The weight of carbonate of baryta dissolved by the acid was had recourse to.

1. Acetate of water ( $\text{HO.C}_4\text{H}_3\text{O}_3$ ), 2 per cent.; density 1.0030. Diffused at  $48^{\circ}8$ , in eight cells, 12.62, 10.94, 11.10, 11.39 grs. of acetate of water; mean 11.51 grs. for two cells.

2. Acetate of water, 4 per cent.; density 1.0060. Diffused at  $48^{\circ}8$ , in eight cells, 22.12, 21.71, 21.59, 22.67; mean 22.02 grs. for two cells.

3. Acetate of water, 8 per cent.; density 1.0117. Diffused at  $48^{\circ}8$ , in four cells, 21.19, 20.13, 21.84, 20.44; mean 20.90 grs. for one cell. The diffusion of the different proportions of acetic acid is as follows:—

Diffusion of Acetate of Water in ten days at  $48^{\circ}8$ ; two cells.

	Grs.	Ratio.
From 2 per cent. solution, . . .	11.31	2
From 4 per cent. solution, . . .	22.02	3.83
From 8 per cent. solution, . . .	41.80	7.26

The diffusibility diminishes with the larger proportions of acid. This acid appears to be considerably less diffusive than sulphuric acid. I was led to over-estimate the diffusion of acetic acid in a preliminary observation of my former paper, by trusting to the acidimetical method of determination. Hydrochloric acid appears to diffuse about two and a half times more rapidly than acetate of water, at the same temperature.

### 8. *Sulphurous Acid.*

The time of diffusion chosen for this acid was ten days, for comparison with sulphuric acid. The usual number of eight cells of the 1 and 2 per cent. solutions were diffused, and four cells of the 4 and 8 per cent. solutions. The whole diffusates of each proportion were then mixed together, and the proportional quantity of liquid representing two



cells in the 1 and 2 per cent. solutions, and one cell in the 4 and 8, was converted into sulphuric acid by a slight excess of bromine, and determined from the sulphate of baryta.

1. 0.982 per cent. of sulphurous acid, density 1.0056, diffused at  $68^{\circ}1$ , gave 7.94 grs. in two cells. Calculated for 1 per cent., 8.09 grs. of sulphurous acid in two cells at  $68^{\circ}1$ .

2. 1.965 per cent. of sulphurous acid, density 1.01055, diffused at  $68^{\circ}1$ , gave 16.66 grs. for two cells. Calculated for two 2 per cent., 16.96 grs. of sulphurous acid in two cells at  $68^{\circ}1$ .

3. 3.93 per cent. of sulphurous acid, density 1.01991, diffused at  $68^{\circ}1$ , gave 16.21 grs. for one cell. Calculated for 4 per cent., 16.50 grs. of sulphurous acid in one cell at  $68^{\circ}1$ .

4. 7.86 per cent. of sulphurous acid, density 1.0384, diffused at  $68^{\circ}1$ , gave 32.60 grs. for one cell. Calculated for 8 per cent., 33.19 grs. of sulphurous acid in one cell at  $68^{\circ}1$ .

#### Diffusion of Sulphurous Acid in ten days at $68^{\circ}1$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	8.09	0.954
From 2 per cent. solution, .	16.96	2
From 4 per cent. solution, .	33.00	3.891
From 8 per cent. solution, .	66.38	7.827

This substance appears to be less diffusive than sulphuric acid at the same temperature; the diffusion of sulphurous acid at  $68^{\circ}1$  considerably resembles that of sulphuric acid at  $49^{\circ}7$  (p. 503).

#### 9. *Ammonia.*

The time of diffusion chosen was 4.041 days, or that of hydrate of potash with chloride of sodium at seven days. The usual number of eight cells of the 1 and 2 per cent. solutions were diffused, and four cells of the 4 and 8 per cent. solutions. The whole diffusates of each proportion were then mixed together, and the quantity of ammonia diffused for two cells determined by an alkalimetical experiment, which was always repeated twice. It was necessary for diffusion to have the ammoniacal solution made denser than water, which was effected by the addition of common salt.

1. 1.005 per cent. of ammonia, density made up to 1.00352 with chloride of sodium, diffused at  $63^{\circ}4$ , gave 4.96 grs. for two cells; calculated for 1 per cent., 4.93 grs. of ammonia in two cells at  $63^{\circ}4$ .

2. 2.01 per cent. of ammonia, density made up to 1.00617 with chloride of sodium, diffused at  $63^{\circ}4$ , gave 9.64 grs. for two cells; calculated for 2 per cent., 9.59 grs. of ammonia in two cells at  $63^{\circ}4$ .



3. 4.02 per cent. of ammonia, density made up to 1.01141 with chloride of sodium, diffused at  $63^{\circ}4$ , gave 9.91 grs. for one cell; calculated for 4 per cent., 9.86 grs. of ammonia, in one cell, at  $63^{\circ}4$ .

4. 8.04 per cent. of ammonia, density made up to 1.0215 with chloride of sodium, diffused at  $63^{\circ}4$ , gave 20.71 grs. for one cell; calculated for 8 per cent., 20.61 grs. of ammonia in one cell at  $63^{\circ}4$ .

Diffusion of Ammonia in 4.04 days at  $63^{\circ}4$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	4.93	1.029
From 2 per cent. solution, .	9.59	2
From 4 per cent. solution, .	19.72	4.117
From 8 per cent. solution, .	41.22	8.605

Ammonia appears to have a diffusibility approaching to that of hydrate of potash. It appears somewhat less diffusive than hydrocyanic acid at the same temperature, in the proportion of 12 to 13 nearly; or to possess about three-fourths of the diffusibility of hydrochloric acid.

10. *Alcohol.*

Time of diffusion ten days. The quantity of alcohol diffused was determined by careful distillation.

1. Alcohol, 2 per cent.; density made up to 1.0237 with chloride of sodium. Diffused at  $40^{\circ}7$ , in eight cells, 17.80, 16.70; mean 17.25 grs. for four cells, or 8.62 grs. for two cells.

2. Alcohol, 4 per cent.; density made up to 1.0203 with chloride of sodium. Diffused at  $48^{\circ}7$ , in eight cells, 34.30, 30.20; mean 32.25 grs. for four cells, or 16.12 grs. for two cells.

3. Alcohol, 8 per cent.; density made up to 1.0154 with chloride of sodium. Diffused at  $48^{\circ}7$ , in four cells, 30.80, 40.2; mean 35.50 grs. for two cells, or 17.75 grs. for one cell.

The results accord less closely with each other than usual, owing, I believe, chiefly to the difficulties of manipulation when the density of the liquid placed in the phials to be diffused approaches so nearly to that of water. This is more particularly true of the 8 per cent. solution.

Diffusion of Alcohol in ten days at  $48^{\circ}7$ ; two cells.

From 2 per cent. solution, .	8.62
From 4 per cent. solution, .	16.12
From 8 per cent. solution, .	35.50

It would be unsafe to draw any conclusion as to the proportionality of the diffusion of alcohol to the strength of the solution from these experiments.



Alcohol does not appear to belong to the same class of diffusive substances as acetic acid, which might be expected from their similarity of composition, but possesses a considerably lower diffusibility.

Diffusion from 2 per cent. solutions in ten days.

Acetate of water at $48^{\circ}8$ ,	.	11.51	100
Alcohol at $48^{\circ}7$ ,	.	8.62	74.9

The diffusion of alcohol approaches to one-half of that of sulphate of water at nearly the same temperature, p. 503.

Alcohol may be substituted for water to dissolve certain salts, and also as an atmosphere into which these salts may diffuse. From experiments which have been commenced on this subject, it appears that the diffusion of hydrate of potash, iodide of potassium, chloride of calcium, and others is about four times slower into alcohol of density 0.840 than into water. The salts likewise often exhibit the same relations in their diffusibility in alcohol, as in water, with some singular exceptions, such as chloride of mercury.

#### 11. Nitrate of Baryta.

Time of diffusion 11.43 days.<sup>1</sup> The salt diffused was precipitated by sulphuric acid, and calculated from the weight of the sulphate of baryta formed.

1. Nitrate of baryta, 1 per cent.; density 1.0083. Diffused at  $51^{\circ}5$ , in eight cells, 6.71, 6.71, 6.84, 6.68; mean 6.73 grs. for two cells.

2. Nitrate of baryta, 0.993 per cent.; density 1.00886. Diffused at  $64^{\circ}1$ , in eight cells, 7.64, 7.70, 7.74, 7.61; mean 7.67 grs. for two cells. Calculated for 1 per cent., 7.72 grs. for two cells.

3. Nitrate of baryta, 2 per cent.; density 1.01686. Diffused at  $64^{\circ}1$ , in eight cells, 15.63, 14.81, 14.41, 15.32; mean 15.04 grs. for two cells.

4. Nitrate of baryta, 4 per cent.; density 1.03319. Diffused at  $64^{\circ}1$ , in four cells, 15.36, 14.78, 14.79, 14.30; mean 14.80 grs. for one cell.

5. Nitrate of baryta, 8 per cent.; density 1.06556. Diffused at  $64^{\circ}1$ , in four cells, 26.46, 26.77, 28.63, 27.13; mean 27.25 grs. for one cell.

The diffusion from the 1 per cent. solution increases by a rise of temperature from  $51^{\circ}5$  to  $64^{\circ}1$ , from 6.73 grs. to 7.72, or from 100 to 114.7, which is an increase of 1.17 per cent. for  $1^{\circ}$ .

<sup>1</sup> This time is to that of sulphate of magnesia (16.166 days) as the square root of 8 is to the square of 16; but does not appear to express the true relation between these salts.



Diffusion of Nitrate of Baryta in 11·43 days at  $64^{\circ}1$  ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . .	7·72	1·026
From 2 per cent. solution, . . .	15·04	2
From 4 per cent. solution, . . .	29·60	3·936
From 8 per cent. solution, . . .	54·50	7·247

### 12. Nitrate of Strontia.

Time of diffusion 11·43 days. Of anhydrous nitrate of strontia 0·82 per cent. ; density 1·0063. Diffused at  $51^{\circ}5$ , in 8 cells, 5·59, 5·62, 5·44, 5·69 ; mean 5·59 grs. for two cells ; calculated for 1 per cent., 6·79 grs. at  $51^{\circ}5$  for two cells.

The diffusion of nitrate of strontia almost coincides with that of the isomorphous nitrate of baryta at the same temperature.

Diffusion from 1 per cent. solutions at  $51^{\circ}5$  in 11·43 days.

Nitrate of baryta, . . . . .	6·73	100
Nitrate of strontia, . . . . .	6·79	100·89

### 13. Nitrate of Lime.

Time of diffusion 11·43 days. The diffusate was evaporated to dryness with an excess of sulphuric acid, and the nitrate of lime, which is always supposed anhydrous, was estimated from the sulphate of lime produced.

1. Nitrate of lime, 1·17 per cent. ; density 1·0088. Diffused at  $51^{\circ}5$ , in eight cells, 7·39, 7·76, 7·69, 7·80 ; mean 7·66 grs. for two cells ; calculated for 1 per cent., 6·54 grs. at  $51^{\circ}5$  for two cells.

2. Nitrate of lime, 0·985 per cent. ; density 1·00802. Diffused at  $64^{\circ}1$ , in eight cells, 7·47, 7·38, 7·63, 7·72 ; mean 7·55 grs. for two cells ; calculated for 1 per cent., 7·66 grs. at  $64^{\circ}1$  for two cells.

3. Nitrate of lime, 1·97 per cent. ; density 1·01508. Diffused at  $64^{\circ}1$ , in eight cells, 15·04, 14·74, 14·55, 14·83 ; mean 14·79 grs. for two cells ; calculated for 2 per cent., 15·01 grs. at  $64^{\circ}1$  for 2 cells.

4. Nitrate of lime, 3·94 per cent. ; density 1·0296. Diffused at  $64^{\circ}1$ , in four cells, 14·30, 15·29, 13·79, 13·93 ; mean 14·33 grs. for one cell ; calculated for 4 per cent., 14·52 grs. at  $64^{\circ}1$  for one cell.

5. Nitrate of lime, 7·88 per cent. ; density 1·0582. Diffused at  $64^{\circ}1$ , in four cells, 27·95, 27·10, 26·80, 26·73 ; mean 27·14 grs. for one cell ; calculated for 8 per cent., 27·55 grs. at  $64^{\circ}1$  for one cell.

By a rise of temperature from  $51^{\circ}5$  to  $64^{\circ}1$ , the diffusion of the 1



per cent. solution increases from 6.54 to 7.66 grs., or from 100 to 117.1; which is an increase of 1.357 per cent. for 1°.

Diffusion of Nitrate of Lime in 11.43 days at 64°1; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	7.66	1.021
From 2 per cent. solution, .	15.01	2
From 4 per cent. solution, .	29.04	3.872
From 8 per cent. solution, .	55.10	7.334

The results throughout for this salt are almost identical with those of nitrate of baryta (p. 508), although these two salts differ greatly in solubility, and in one being a hydrated, and the other an anhydrous salt.

#### 14. *Acetate of Lead.*

Diffused for 16.166 days; the time chosen before for sulphate of magnesia, with seven days for chloride of sodium. The solution contained 0.965 per cent. of anhydrous salt, with the density 1.0080. As this solution of acetate of lead was found to be precipitated by pure water, about 2 per cent. of strong acetic acid was introduced into the solution, and the same acid was added in a less proportion to the water jars. The salt of lead diffused was afterwards determined by means of sulphuric acid. Diffused in eight cells, at 53°1, 7.45, 7.29, 7.46 and 8.07 grs.; mean 7.56; or 7.84 for 1 per cent. in two cells.

#### 15. *Acetate of Baryta.*

Diffused for 16.166 days. The solution contained 0.977 per cent. of anhydrous salt, with the density 1.0073. The same addition of acetic acid was made to it as to the preceding acetate of lead, in order that the circumstances of diffusion might be similar for both salts. The salt diffused was estimated also in the form of sulphate.

Diffused at 53°5, in eight cells, 7.30, 7.38, 7.40, and 7.21 grs. in two cells; mean 7.33; or 7.50 for 1 per cent. in two cells.

Diffusion of 1 per cent. solutions in 16.166 days; two cells.

Acetate of baryta at 53°5, .	7.50	100
Acetate of lead at 53°1, . . .	7.84	104.53

Here, of two isomorphous salts, that of greatest atomic weight sensibly exceeds the other in diffusibility.



16. *Chloride of Barium.*

Time of diffusion 11.43 days. The diffused salt was weighed as sulphate of baryta.

1. Chloride of barium, 0.99 per cent. Diffused at  $50^{\circ}9$ , in eight cells, 7.91, 7.27, 7.42, 7.12; mean 7.43 grs. of chloride of barium for two cells; calculated for 1 per cent., 7.50 grs. at  $50^{\circ}9$  for two cells.

The diffusion of this salt being manifestly more rapid than that of the chloride of calcium, a shorter time was tried, which is to seven days, the time of chloride of sodium, as the square root of 3 to the square root of 4.5. Time of diffusion 8.57 days.

2. Chloride of barium, 1.01 per cent.; density 1.0095. Diffused at  $63^{\circ}$ , in eight cells, 6.46, 6.44, 6.41, 6.27; mean 6.39 grs. for two cells; calculated for 1 per cent., 6.32 grs. at  $63^{\circ}$  for two cells.

3. Chloride of barium, 2.02 per cent.; density 1.0183. Diffused at  $63^{\circ}$ , in eight cells, 11.98, 12.03, 12.75, 12.03; mean 12.20 grs. for two cells; calculated for 2 per cent., 12.07 grs. at  $63^{\circ}$  for two cells.

4. Chloride of barium, 4.04 per cent.; density 1.0359. Diffused at  $63^{\circ}$ , in four cells, 12.43, 12.30, 11.87, 11.86; mean 12.10 grs. for one cell; calculated for 4 per cent., 11.98 grs. at  $63^{\circ}$  for one cell.

5. Chloride of barium, 8.08 per cent.; density 1.0712. Diffused at  $63^{\circ}$ , in four cells, 23.17, 23.05, 22.98, 23.62; mean 23.20 grs. for one cell; calculated for 8 per cent., 22.96 grs. at  $63^{\circ}$  for one cell.

Diffusion of Chloride of Barium in 8.57 days at  $63^{\circ}$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution,	6.32	1.047
From 2 per cent. solution,	12.07	2
From 4 per cent. solution,	23.96	3.970
From 8 per cent. solution,	45.92	7.608

17. *Chloride of Strontium.*

First time of diffusion 11.43 days. The diffused salt was weighed as sulphate of strontia.

1. Chloride of strontium, 0.803 per cent.; density 1.0076. Diffused at  $51^{\circ}$ , in eight cells, 6.36, 6.06, 5.93, 5.73; mean 6.02 grs. of chloride of strontium for two cells; calculated for 1 per cent., 7.52 grs. at  $51^{\circ}$  for two cells.

Second time of diffusion 8.57 days.

2. Chloride of strontium, 1 per cent.; density 1.00936. Diffused at  $63^{\circ}$ , in eight cells, 6.10, 6.17, 6.02, 6.09; mean 6.09 grs. for two cells.

3. Chloride of strontium, 2 per cent.; density 1.01806. Diffused at



63°, in eight cells, 11·62, 11·71, 11·53, 11·79; mean 11·66 grs. for two cells.

4. Chloride of strontium, 4·014 per cent.; density 1·03537. Diffused at 63°, in four cells, 12·09, 11·75, 11·64, 11·79; mean 11·82 grs. for one cell; calculated for 4 per cent., 11·78 grs. at 63° for one cell.

5. Chloride of strontium, 8·028 per cent.; density 1·06959. Diffused at 63°, in four cells, 22·29, 22·34, 22·03, 22·57; mean 22·31 grs. for one cell; calculated for 8 per cent., 22·23 grs. at 63° for two cells.

Diffusion of Chloride of Strontium in 8·57 days at 63°; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	6·09	1·045
From 2 per cent. solution, .	11·66	2
From 4 per cent. solution, .	23·56	4·041
From 8 per cent. solution, .	44·46	7·626

The series of ratios in the preceding table will be found on comparison to correspond closely with the ratios of chloride of barium. It may be useful to compare further the amounts diffused from similar solutions of these two isomorphous compounds.

Diffusion in 8·57 days at 63°; two cells.

Chloride of barium, 1 per cent.,	6·32	100
Chloride of strontium, 1 per cent.,	6·09	96·36
Chloride of barium, 2 per cent.,	12·07	100
Chloride of strontium, 2 per cent.,	11·66	96·90
Chloride of barium, 4 per cent.,	23·96	100
Chloride of strontium, 4 per cent.,	23·56	99·16
Chloride of barium, 8 per cent.,	45·92	100
Chloride of strontium, 8 per cent.,	44·46	96·83

The near coincidence of the 4 per cent. solutions probably arises from an accidental error of observation in the chloride of barium, for the latter departs here from the progression of its ratios. We appear then to have a small but constant difference of about  $3\frac{1}{2}$  per cent. in the diffusion of these two isomorphous salts, the chloride of barium, which possesses the highest atomic weight, having the advantage.

The diffusion of the 1 per cent. solution of the same salts for the longer period of 11·43 days, gives 7·50 for chloride of barium at 50°·9, and 7°·52 for chloride of strontium at 51°, or nearly the same temperature. For the first time we have in the barytic salts a divergence between chlorides and nitrates, for the nitrates of the same bases have a number about 6·8 only at the same temperature. I am led however to



believe that this discrepancy becomes much less at low temperatures by experiments which are at present in progress.

### 18. *Chloride of Calcium.*

Time of diffusion 11·43 days. The salt diffused was weighed as sulphate of lime.

1. Chloride of calcium, 1·065 per cent.; density 1·0091. Diffused at  $50^{\circ}9$ , in eight cells, 6·95, 7·09, 6·78, 6·94; mean 6·94 grs. of chloride of calcium for two cells; calculated for 1 per cent., 6·51 grs. at  $50^{\circ}9$  for two cells.

2. Chloride of calcium, 1·03 per cent.; density 1·0089. Diffused at  $63^{\circ}8$ , in 8 cells, 8·08, 8·13, 8·28, 8·19; mean 8·17 grs. for two cells; calculated for 1 per cent., 7·92 grs. at  $63^{\circ}8$  for two cells.

3. Chloride of calcium, 2·06 per cent.; density 1·0171. Diffused at  $63^{\circ}8$ , in eight cells, 15·70, 15·33, 16·48, 15·82; mean 15·83 grs. for two cells; calculated for 2 per cent., 15·35 grs. at  $63^{\circ}8$  for two cells.

4. Chloride of calcium, 4·12 per cent.; density 1·0334. Diffused at  $63^{\circ}8$ , in four cells, 15·24, 16·20, 15·89, 16·20; mean 15·88 grs. for one cell; calculated for four per cent., 15·39 grs. at  $63^{\circ}8$  for one cell.

5. Chloride of calcium, 8·23 per cent.; density 1·0652. Diffused at  $63^{\circ}8$ , in four cells, 32·97, 31·17, 30·64, 31·90; mean 31·67 grs. for one cell; calculated for 8 per cent., 30·78 grs. at  $62^{\circ}8$  for one cell.

The diffusion of the 1 per cent. solution of chloride of calcium is increased by a rise of temperature from  $50^{\circ}9$  to  $63^{\circ}8$ , from 6·51 to 7·92, or from 100 to 121·6, which is an increase of 1·674 per cent. for  $1^{\circ}$ .

Diffusion of Chloride of Calcium in 11·43 days at  $63^{\circ}8$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	7·92	1·032
From 2 per cent. solution, .	15·35	2
From 4 per cent. solution, .	30·78	4·010
From 8 per cent. solution, .	61·56	8·021

We may now observe how far the diffusion of the chloride of calcium is analogous to that of nitrate of lime. At the inferior temperatures, the results for the 1 per cent. solution of these two salts were as follows:—

Chloride of calcium at $50^{\circ}9$ , .	6·51	100
Nitrate of lime at $51^{\circ}5$ , .	6·54	100·46

While at the higher temperatures, namely,  $63^{\circ}8$  for the chloride of calcium, and  $64^{\circ}1$  for the nitrate of lime, the results for the different proportions of salt are—



Chloride of calcium, 1 per cent., .	7.92	100
Nitrate of lime, 1 per cent., .	7.66	96.72
Chloride of calcium, 2 per cent., .	15.35	100
Nitrate of lime, 2 per cent., .	15.01	97.79
Chloride of calcium, 4 per cent., .	30.78	100
Nitrate of lime, 4 per cent., .	29.04	94.35
Chloride of calcium, 8 per cent., .	61.56	100
Nitrate of lime, 8 per cent., .	55.10	89.51

The correspondence between the 1 and 2 per cent. solutions of chloride and nitrate is sufficiently close, but in the 4 and 8 per cent. the salts diverge, as happens also with hydrochloric and nitric acids themselves. The nitrate in both cases falls off, while the chloride sustains throughout the high diffusibility of the lower proportions.

#### 19. *Chloride of Manganese.*

Time of diffusion 11.43 days. The salt diffused was estimated by means of nitrate of silver.

The 1 per cent. solution, of density 1.0085, gave at 50° 8, in eight cells, 6.67, 6.26, 6.79, and 6.81 grs.; mean 6.63 for two cells.

#### 20. *Nitrate of Magnesia.*

Time of diffusion 11.43 days. The salt diffused was estimated as sulphate.

The 1 per cent. solution, of density 1.0073, gave at 50° 8, in eight cells, 6.29, 6.39, 6.52, and 6.76 grs.; mean 6.49 for two cells.

#### 21. *Nitrate of Copper.*

Time of diffusion 11.43 days. The salt diffused was estimated from the oxide of copper obtained by ignition.

The 1 per cent. solution, of density 1.0075, in eight cells, at 50° 8, gave 6.52, 6.36, 6.18, and 6.70 grs.; mean 6.44 for two cells.

Comparing the preceding salts with chloride of calcium diffused at the same temperature, 50° 8, we have the following results:—

Chloride of calcium, . . .	6.51	100
Chloride of manganese, . . .	6.63	101.85
Nitrate of magnesia, . . .	6.49	99.69
Nitrate of copper, . . .	6.44	98.92

This group of salts, belonging to the same isomorphous family of bases, the magnesian, again correspond closely in diffusibility.



The following additional magnesian chlorides were diffused, all 1 per cent. solutions, either in six or in eight cells. The salt diffused was estimated by means of nitrate of silver.

22. *Chloride of Zinc* at  $51^{\circ}$ , solution of density 1.0091, gave 6.55, 6.20, 6.21, and 6.28 grs.; mean 6.29 for two cells.

23. *Chloride of Magnesium* at  $50^{\circ}6$ , density 1.0077, gave 6.40, 5.84, and 6.29; mean 6.17 for two cells.

24. *Chloride of Copper* at  $50^{\circ}6$ , solution of density 1.0093, gave 6.08, 6.08, and 6.02 grs.; mean 6.06 for two cells.

The results referred to chloride of calcium, at nearly the same temperature,  $50^{\circ}8$ , are as follows:—

Chloride of calcium,	.	.	6.51	100
Chloride of zinc,	.	.	6.29	96.61
Chloride of magnesium,	.	.	6.17	94.77
Chloride of copper,	.	.	6.06	93.08

These salts present a greater latitude in their diffusibility, if belonging to the same class, than is usual.

#### 25. *Protochloride of Iron.*

A solution of this salt of 1.023 per cent. was diffused at  $53^{\circ}5$ , a somewhat higher temperature than the corresponding chlorides. It gave 6.45, 6.48, 6.48, and 6.28 grs. in two cells; mean 6.44 or 6.30 for 1 per cent. in two cells. This salt appears therefore to belong to the last group.

#### 26. *Sesquichloride of Iron.*

A full series of observations was made upon the diffusion of the different proportions of this salt from 1 to 8 per cent., but in all of them decomposition was determined by the diffusion, with turbidity also in the solution phial except in the 8 per cent. solution.

The mean diffusion from the 1 per cent. solution in 11.43 days, at  $63^{\circ}3$ , was 4.13 grs. of sesquichloride of iron with 1.28 gr. of free hydrochloric acid, in two cells. This result indicates that one-half nearly of the sesquichloride of iron is decomposed in the diffusion.

The mean diffusion from the 8 per cent. solution, at  $63^{\circ}3$ , was 55.88 grs. of sesquichloride of iron, with 6.66 grs. of free hydrochloric acid, in two cells. It appears from this experiment that perchloride of iron approaches the chloride of calcium in diffusibility. That the proto- and persalts of the magnesian metals should have a similar rate of diffusion is not unlikely from other analogies which they exhibit.



27. *Sulphate of Magnesia.*

The time chosen for the diffusion of this salt, namely 16·166 days, is a multiple by 2 of the time of sulphate of potash, and by 4 of the time of hydrate of potash. The diffusate was evaporated to dryness and weighed.

1. 1·012 per cent. of anhydrous sulphate of magnesia, density 1·0108, diffused at 65°·4, in eight cells, 7·34, 7·66, 7·43, 7·18; mean 7·40 grs. for two cells; calculated for 1 per cent., 7·31 grs. of sulphate of magnesia in two cells at 65°·4.

2. 2·024 per cent. of sulphate of magnesia, density 1·02089, diffused at 65°·4, in eight cells, 12·91, 13·13, 12·83, 12·93; mean 12·95 grs. for two cells; calculated for 2 per cent., 12·79 grs. of sulphate of magnesia in two cells at 65°·4.

3. 4·048 per cent. of sulphate of magnesia, density 1·04033, diffused at 65°·4, in four cells, 12·06, 12·56, 10·63, 12·24; mean 11·87 grs. for one cell; calculated for 4 per cent. 11·73 grs. of sulphate of magnesia in one cell at 65°·4.

4. 8·096 per cent. of sulphate of magnesia, density 1·07830, diffused at 65°·4, in four cells, 22·25, 20·56, 21·80, 22·06; mean 21·67 grs. for one cell; calculated for 8 per cent., 21·41 grs. of sulphate of magnesia in one cell at 65°·4.

5. 8·07 per cent. of sulphate of magnesia, density 1·07830, diffused at 62°·8, in four cells, 21·12, 21·20, 22·13, 21·77; mean 21·55 grs. for one cell; calculated for 8 per cent., 21·33 grs. of sulphate of magnesia in one cell at 62°·8.

6. 16·14 per cent. of sulphate of magnesia, density 1·15054, diffused at 62°·8, in four cells, 37·08, 38·39, 38·65, 37·50; mean 37·90 grs. for one cell; calculated for 16 per cent., 37·53 grs. of sulphate of magnesia in one cell at 62°·8.

7. 24·22 per cent. of sulphate of magnesia, density 1·21882, diffused at 62°·8, in four cells, 49·38, 50·40, 53·36, 53·00; mean 51·53 grs. for one cell; calculated for 24 per cent., 51·02 grs. of sulphate of magnesia in one cell at 62°·8.

Diffusion of Sulphate of Magnesia in 16·16 days at 65°·4; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . .	7·31	1·144
From 2 per cent. solution, . . .	12·79	2
From 4 per cent. solution, . . .	23·46	3·671
From 8 per cent. solution, . . .	42·82	6·701
From 8 per cent. solution at 62°·8, . .	42·66	1
From 16 per cent. solution at 62°·8, . .	75·06	1·759
From 24 per cent. solution at 62°·8, . .	102·04	2·340



28. *Sulphate of Zinc.*

Time of diffusion 16·166 days. The diffused salt was evaporated to dryness and weighed.

1. 1·001 per cent. of anhydrous sulphate of zinc, density 1·01093, diffused at  $65^{\circ}4$ , in eight cells, 6·66, 6·76, 6·51, 6·80; mean 6·68 grs. for two cells; calculated for 1 per cent., 6·67 grs. of sulphate of zinc in two cells at  $65^{\circ}4$ .

2. 2·002 per cent. sulphate of zinc, density 1·02120, diffused at  $65^{\circ}4$ , in eight cells, 12·16, 12·19, 12·52, 12·05; mean 12·23 grs. for two cells; calculated for 2 per cent., 12·22 grs. of sulphate of zinc in two cells at  $65^{\circ}4$ .

3. 4·005 per cent. of sulphate of zinc, density 1·04146, diffused at  $65^{\circ}4$ , in four cells, 11·63, 11·70, 11·00, 11·95; mean 11·57 grs. for one cell; calculated for 4 per cent., 11·56 grs. of sulphate of zinc in one cell at  $65^{\circ}4$ .

4. 8·01 per cent. of sulphate of zinc, density 1·08063, diffused at  $65^{\circ}4$ , in four cells, 21·22, 20·52, 21·06, 21·84; mean 21·16 grs. for one cell; calculated for 8 per cent., 21·13 grs. of sulphate of zinc in one cell at  $65^{\circ}4$ .

5. 8·04 per cent. of sulphate of zinc, density 1·08084, diffused at  $62^{\circ}8$ , in four cells, 20·70, 18·57, 20·32, 20·36; mean 19·99 grs. for one cell; calculated for 8 per cent., 19·81 grs. of sulphate of zinc in one cell at  $62^{\circ}8$ .

6. 16·08 per cent. of sulphate of zinc, density 1·15734, diffused at  $62^{\circ}8$ , in four cells, 36·70, 37·15, 37·51, 38·21; mean 37·39 grs. for one cell; calculated for 16 per cent., 37·20 grs. of sulphate of zinc in one cell at  $62^{\circ}8$ .

7. 24·11 per cent. of sulphate of zinc, density 1·23156, diffused at  $62^{\circ}8$ , in three cells, 51·12, 50·14, 51·66; mean 50·97 grs. for one cell; calculated for 24 per cent., 50·71 grs. of sulphate of zinc in one cell at  $62^{\circ}8$ .

Diffusion of Sulphate of Zinc in 16·16 days at  $65^{\circ}4$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . .	6·67	1·091
From 2 per cent. solution, . . .	12·22	2
From 4 per cent. solution, . . .	23·12	3·784
From 8 per cent. solution, . . .	42·26	6·916
From 8 per cent. solution at $62^{\circ}8$ , . .	39·62	1
From 16 per cent. solution at $62^{\circ}8$ , . .	74·40	1·878
From 24 per cent. solution at $62^{\circ}8$ , . .	101·42	2·560

It will be remarked that the diffusion of these two isomorphous



salts, sulphate of magnesia and sulphate of zinc, differs so much, in the 1 per cent. solution, as 7.31 to 6.67, that is, as 100 to 91.25; or 8.75 per cent. This, I have no doubt, however, is an accidental error, the disturbances from changes of temperature and other causes of dispersion being in direct proportion to the duration of the experiment, and therefore much increased with these long times; while the 1 per cent. solution also appears to be generally the proportion most exposed to such errors. The sulphate of zinc appears to be the truest throughout, in its diffusion, of these two salts. The approach to equality becomes close in the 4 per cent. and larger proportions of salt, particularly with the unusually high proportions of 16 and 24 per cent., which were observed in these salts. The diffusion of both salts falls off remarkably in the higher proportions. The result of the comparison of these two magnesian sulphates is no doubt favourable to the similarity of diffusion of isomorphous salts.

### 29. *Sulphate of Alumina.*

The time of diffusion chosen was 16.166 days, or the same as that for sulphate of magnesia. The usual number of eight cells of the 1 and 2 per cent. solutions were diffused, and four cells of the 4 and 8 per cent. solutions. The whole diffusates of each proportion were then mixed together and the quantities of alumina and sulphuric acid, diffused for two cells, determined separately.

1. 1.045 per cent. of sulphate of alumina, density 1.01160, diffused at  $65^{\circ}4$ , gave 1.80 gr. of alumina and 3.93 grs. of sulphuric acid, in all 5.73 grs. for two cells. Calculated for 1 per cent., 1.72 gr. alumina and 3.76 grs. sulphuric acid, in all 5.48 grs. of sulphate of alumina in two cells at  $65^{\circ}4$ .

2. 2.091 per cent. of sulphate of alumina, density 1.02251, diffused at  $65^{\circ}4$ , gave 3.32 grs. of alumina and 7.35 grs. of sulphuric acid, in all 10.67 grs. for two cells. Calculated for 2 per cent., 3.18 grs. of alumina and 7.03 grs. of sulphuric acid, in all 10.21 grs. of sulphate of alumina for two cells at  $65^{\circ}4$ .

3. 4.182 per cent. of sulphate of alumina, density 1.0438, diffused at  $65^{\circ}4$ , gave 3.17 grs. of alumina and 6.91 grs. of sulphuric acid, in all 10.08 grs. for one cell. Calculated for 4 per cent., 3.03 grs. of alumina and 6.61 grs. of sulphuric acid, in all 9.64 grs. of sulphate of alumina for one cell at  $65^{\circ}4$ .

4. 8.364 per cent. of sulphate of alumina, density 1.08518, diffused at  $65^{\circ}4$ , gave 5.37 grs. of alumina and 12.15 grs. of sulphuric acid, in all 17.52 grs. for one cell. Calculated for 8 per cent., 5.14 grs. of alumina and 11.62 grs. of sulphuric acid, in all 16.76 grs. of sulphate of alumina for one cell at  $65^{\circ}4$ .



Diffusion of Sulphate of Alumina in 16·166 days at  $65^{\circ}4$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . .	5·48	1·074
From 2 per cent. solution, . . .	10·21	2
From 4 per cent. solution, . . .	19·28	3·780
From 8 per cent. solution, . . .	33·52	6·572

The diffusion of sulphate of alumina, it will be observed, is very sensibly less than that of sulphate of zinc at the same temperature.

### 30. Nitrate of Silver.

Time of diffusion seven days. The quantity of salt diffused was ascertained by precipitation with hydrochloric acid, and weighing the chloride of silver formed.

1. Nitrate of silver, 0·996 per cent.; density 1·0089. Diffusion at  $51^{\circ}4$ , in eight cells, 5·39, 5·39, 5·74, 5·50; mean 5·50 grs. for two cells; calculated for 1 per cent., 5·52 grs. at  $51^{\circ}4$  for two cells.

2. Nitrate of silver, 1·98 per cent.; density 1·0161. Diffusion at  $53^{\circ}$ , in eight cells, 11·27, 11·16, 11·05, 11·06; mean 11·13 grs. for two cells; calculated for 2 per cent., 11·24 grs. at  $53^{\circ}$  for two cells.

3. Nitrate of silver, 1·967 per cent.; density 1·01696. Diffusion at  $63^{\circ}41$ , in eight cells, 13·85, 13·29, 13·70, 12·73; mean 13·39 grs. for two cells; calculated for 2 per cent., 13·61 grs. at  $63^{\circ}4$  for two cells.

4. Nitrate of silver, 3·93 per cent.; density 1·032. Diffusion at  $63^{\circ}4$ , in four cells, 13·27, 12·70, 12·90, 12·90; mean 12·94 grs. for one cell; calculated for 4 per cent., 13·17 grs. at  $63^{\circ}4$  for one cell.

5. Nitrate of silver, 7·88 per cent.; density 1·066. Diffusion at  $63^{\circ}4$ , in four cells, 26·45, 25·49, 24·57, 25·73; mean 25·56 grs. for one cell; calculated for 8 per cent., 25·94 grs. at  $63^{\circ}4$  for one cell.

A rise of  $10^{\circ}4$  of temperature, or from  $53^{\circ}$  to  $63^{\circ}4$ , increases the diffusibility of this salt from 11·24 to 13·61, or from 100 to 121·2; which is an increase of 2·04 per cent. for  $1^{\circ}$ .

Diffusion of Nitrate of Silver for seven days at  $63^{\circ}4$ ; two cells.

	Grs.	Ratio.
From 2 per cent. solution, . . .	13·61	2
From 4 per cent. solution, . . .	26·34	3·87
From 8 per cent. solution, . . .	51·88	7·62

### 31. Nitrate of Soda.

Time of diffusion seven days. The quantity of salt diffused was ascertained by evaporation to dryness.



1. Nitrate of soda, 1.987 per cent.; density 1.0130. Diffusion at  $53^{\circ}$ , in eight cells, 11.37, 10.44, 10.76, 10.40; mean 10.74 grs. for two cells; calculated for 2 per cent., 10.81 grs. for two cells.

2. Nitrate of soda, 1.998 per cent. Diffusion at  $63^{\circ}4$ , in eight cells, 12.53, 12.38, 12.39, 12.06; mean 12.34 grs. for two cells; calculated for 2 per cent., 12.35 grs. for two cells.

3. Nitrate of soda, 3.98 per cent.; density 1.027. Diffusion at  $63^{\circ}4$ , in four cells, 12.21, 11.32, 12.10, 11.31; mean 11.73 grs. for one cell; calculated for 4 per cent., 11.78 grs. for one cell.

4. Nitrate of soda, 7.96 per cent.; density 1.053. Diffusion at  $63^{\circ}4$ , in four cells, 24.96, 22.53, 23.16, 24.38; mean 23.76 grs. for one cell; calculated for 8 per cent., 23.87 grs. for one cell.

A rise of temperature from  $53^{\circ}$  to  $63^{\circ}4$  increases the diffusibility of nitrate of soda from 10.81 to 12.35, or from 100 to 114.3, which is an increase of 1.37 per cent. for  $1^{\circ}$ . The increase on the nitrate of silver for the same rise of temperature appeared to be considerably greater, namely, 2.04 per cent. for  $1^{\circ}$ .

Diffusion of Nitrate of Soda in seven days at  $63^{\circ}4$ ; two cells.

	Grs.	Ratio.
From solution of 2 per cent., .	12.35	2
From solution of 4 per cent., .	23.56	3.82
From solution of 8 per cent., .	47.74	7.73

The ratios of the last column of the preceding Table are sensibly the same as those already obtained for nitrate of silver. But the diffusibility of nitrate of soda appears to be increased less rapidly by temperature than nitrate of silver. Hence the diffusibility of these two salts appears more similar at low than high temperatures.

Diffusion from 2 per cent. solutions in seven days at  $53^{\circ}$ .

Nitrate of silver, . . .	11.24	100
Nitrate of soda, . . .	10.81	96.17

Diffusion from 2 per cent. solutions in seven days at  $63^{\circ}4$ .

Nitrate of silver, . . .	13.61	100
Nitrate of soda, . . .	12.35	90.74

### 32. Chloride of Sodium.

Time of diffusion seven days. The salt diffused was treated with nitrate of silver, and the chloride of silver weighed.

1. Chloride of sodium, 1 per cent. Diffused at  $50^{\circ}5$ , in eight cells, 5.96, 5.69, 5.54, 5.50; mean 5.70 grs. of chloride of sodium for two cells.



2. Chloride of sodium, 0.985 per cent. Diffused at  $53^{\circ}4$ , in eight cells, 5.86, 5.86, 5.77, 5.76; mean 5.81 grs. for two cells; calculated for 1 per cent., 5.89 grs. at  $53^{\circ}4$  for two cells.

3. Chloride of sodium, 1 per cent.; density 1.00776. Diffused at  $63^{\circ}4$ , in eight cells, 6.30, 6.18, 6.52, 6.30; mean 6.32 grs. for two cells.

4. Chloride of sodium, 2 per cent.; density 1.01483. Diffused at  $63^{\circ}4$ , in eight cells, 12.37, 12.08, 12.45, 12.53; mean 12.37 grs. for two cells.

5. Chloride of sodium, 4 per cent.; density 1.02879. Diffused at  $63^{\circ}4$ , in four cells, 12.56, 12.65, 12.55, 12.17; mean 12.48 grs. for one cell.

6. Chloride of sodium, 8 per cent.; density 1.0562. Diffused at  $63^{\circ}4$ , in four cells, 25.11, 25.36, 22.82, 23.59; mean 24.22 grs. for one cell.

The rise of temperature from  $50^{\circ}5$  to  $63^{\circ}4$  increases the diffusion of the 1 per cent. solution of chloride of sodium from 5.70 to 6.32, or from 100 to 110.9, which is an increase of 0.843 per cent. for  $1^{\circ}$ .

Diffusion of Chloride of Sodium in seven days at  $63^{\circ}4$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	6.32	1.023
From 2 per cent. solution, .	12.37	2
From 4 per cent. solution, .	24.96	4.036
From 8 per cent. solution, .	48.44	7.832

These numbers resemble closely those obtained in the diffusion of chloride of barium during the longer period of 8.57 days.

The chloride of sodium and nitrate of soda will be seen to exhibit the usual approach to parallelism between the chloride and nitrate of the same metal, by the following comparison:—

Diffusion of Chloride of Sodium and Nitrate of Soda, both at  $63^{\circ}4$ .

Chloride of sodium, 2 per cent., .	12.37	100
Nitrate of soda, 2 per cent., . .	12.35	99.83
Chloride of sodium, 4 per cent., .	24.96	100
Nitrate of soda, 4 per cent., . .	23.58	94.48
Chloride of sodium, 8 per cent., .	48.44	100
Nitrate of soda, 8 per cent., . .	47.74	98.55

As usual the chloride is slightly more rapid in its diffusion than the nitrate.

### 33. Chloride of Potassium.

Time of diffusion 5.71 days. The salt diffused was treated with nitrate of silver, and the chloride of silver weighed.



1. Chloride of potassium, 1 per cent.; density 1.00697. Diffused at 62°, in eight cells, 6.70, 6.75, 6.53, 6.77; mean 6.69 grs. of chloride of potassium for two cells.

2. Chloride of potassium, 2 per cent.; density 1.01333. Diffused at 62°, in 8 cells, 13.36, 13.35, 13.60, 12.96; mean 13.32 grs. for two cells.

3. Chloride of potassium, 4 per cent.; density 1.0258. Diffused at 62°, in four cells, 12.51, 13.21, 13.46, 12.71; mean 12.97 grs. for one cell.

4. Chloride of potassium, 8 per cent.; density 1.0503. Diffused at 62°, in four cells, 26.88, 26.64, 26.15, 27.63; mean 26.82 grs. for one cell.

Diffusion of Chloride of Potassium in 5.71 days at 62°; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . .	6.69	1.005
From 2 per cent. solution, . . .	13.32	2
From 4 per cent. solution, . . .	25.94	3.895
From 8 per cent. solution, . . .	53.64	8.054

The ratios are in remarkably close accordance with the proportions of salt diffused.

The times 5.71 and seven days chosen for the chloride of potassium and sodium, it will be observed, are as the square roots of 2 and 3. A certain deviation from this ratio of the times of equal diffusion, appears on comparing the experimental results obtained at present for these salts.

Diffusion of Chloride of Potassium in 5.71 days at 62°, and of Chloride of Sodium in 7 days at 63° 4.

Chloride of potassium, 1 per cent., . . .	6.69	100
Chloride of sodium, 1 per cent., . . .	6.32	94.47
Chloride of potassium, 2 per cent., . . .	13.32	100
Chloride of sodium, 2 per cent., . . .	12.37	92.86
Chloride of potassium, 4 per cent., . . .	25.94	100
Chloride of sodium, 4 per cent., . . .	24.96	96.23
Chloride of potassium, 8 per cent., . . .	53.64	100
Chloride of sodium, 8 per cent., . . .	48.44	90.30

The difference would be about 1 per cent. greater if the diffusion of both salts were reduced to the same temperature. The chloride of potassium deviates of course from the nitrate of soda in a similar manner. But chloride of potassium corresponds more closely with nitrate of silver than with chloride of sodium and nitrate of soda, at the temperature of the experiments.



Diffusion of Chloride of Potassium for 5·71 days at 62°, and of Nitrate of Silver for 7 days at 63°·4.

Chloride of potassium, 2 per cent.,	13·32	100
Nitrate of silver, 2 per cent.,	13·61	102·18
Chloride of potassium, 4 per cent.,	25·94	100
Nitrate of silver, 4 per cent.,	26·34	101·54
Chloride of potassium, 8 per cent.,	53·64	100
Nitrate of silver, 8 per cent.,	51·88	96·71

The coincidence in rate would appear even closer in the 2 and 4 per cent. solutions, if the diffusion of the nitrate of silver was diminished about 1 per cent., on account of its higher temperature. It might thus be supposed that the nitrate of silver followed the sodium rate more accurately than the nitrate of soda and chloride of sodium themselves do.

A series of observations were made upon the diffusion of the 1 per cent. solution of chloride of potassium at a nearly constant temperature of 56°, but for different times, varying from five days to eight days, and eighteen hours, to discover the progression, which proved to be pretty similar to that of the 2 per cent. solution of hydrochloric acid. Six cells were diffused for each period, of which the mean result is given: the times advance by ten hours.

Diffusion of Chloride of Potassium, 1 per cent. solution; two cells.

Time.	Temperature. °	Diffusion in two cells.	Differences.
5 days.	55·71	5·89	
5 days 10 hours.	55·90	6·25	0·36
5 days 20 hours.	55·79	6·55	0·30
6 days 6 hours.	55·79	6·71	0·16
6 days 16 hours.	55·90	6·95	0·24
7 days 2 hours.	55·9	7·48	0·53
7 days 12 hours.	55·9	7·58	0·10
7 days 22 hours.	56·03	8·08	0·50
8 days 8 hours.	56·28	8·34	0·26
8 days 18 hours.	56·15	8·60	0·26

When the quantities of chloride of potassium are placed beside the same quantities of hydrochloric acid in the former Table, it is found that the times of diffusion of the salt and acid exhibit an approximately constant ratio. The squares of these times of equal diffusion are as 1 to 2·04 for the shortest period of the chloride of potassium, and as 1 to 2·10 for the longest period but one. The variation in the differences towards the middle of the Table is too great to be explained, except, I



fear, by some error of observation, although no ordinary precaution was neglected in the execution of this laborious series of experiments.

### 34. *Iodides and Bromides of Potassium and Sodium.*

*Iodide of Potassium.*—Time of diffusion 5·716 days. The diffusate was estimated by means of nitrate of silver.

(1.) Iodide of potassium, 1·977 per cent. ; density 1·0145. Diffused at 53°·5, in eight cells, 11·415, 11·506, 10·942, and 11·062 grs. ; mean 11·24 for two cells, and 11·36 for two per cent.

Comparing this salt with the isomorphous chloride of potassium, we have—

Diffusion of 2 per cent. solutions in 5·716 days.

Chloride of potassium at 55°, . .	11·48	100
Iodide of potassium at 53°·5, . .	11·36	99·65

The diffusion of the iodide would slightly exceed that of the chloride, instead of falling below it as in the Table, if the temperatures were made equal.

(2.) Again, iodide of potassium 1·971 per cent. ; observed density 1·01486. Diffused at 59°·8, in eight cells, and the mean diffusate of the whole cells determined, it gave 12·33 grs. of iodide of potassium for two cells ; or 12·51 grs. for a 2 per cent. solution.

*Bromide of Potassium.*—Time of diffusion and mode of estimating diffusate as above. The solution contained 1·975 per cent. of salt, and had a density of 1·014850. Diffused at 59°·8, in eight cells, it gave a mean diffusate of 12·30 grs. for two cells ; or 12·46 grs. for 2 per cent.

For comparison, a solution of *chloride of Potassium*, containing exactly 2 per cent. of salt and having the density 1·0133, was diffused in the same circumstances of time and temperature as the two preceding salts. The mean diffusate of eight cells was 12·24 grs. for two cells.

Hence the following result of the diffusion of three isomorphous salts :—

Diffusion of 2 per cent. solutions in 5·716 days, at 59°·8.

	Gr.	Ratio.
Chloride of potassium, . . .	12·24	100
Bromide of potassium, . . .	12·46	101·80
Iodide of potassium, . . .	12·51	102·21
Mean,	12·40	

*Iodide of Sodium.*—Time of diffusion seven days, temperature 59°·8. A solution of 2·011 per cent. and density 1·01618, diffused in eight cells,



gave a mean diffusate of 12.24 grs. for two cells; that is, 12.18 grs. for 2 per cent. solution.

*Bromide of Sodium.*—Time of diffusion and temperature as above. A solution of 2.146 per cent., of density 1.01726, diffused in eight cells, gave a mean diffusate of 12.80 grs.; that is, 11.93 grs. for 2 per cent.

A comparative experiment was made with a solution of *chloride of sodium*, containing 1.917 per cent. of salt and of density 1.01376, in eight cells, at 60°. The diffusates for four pairs of cells were 11.65, 11.75, 11.63, and 11.47 grs.; mean 11.63 grs., which gives by proportion 12.14 grs. for a 2 per cent. solution. As the present salt differs only 0°.2 Fahr. in diffusion-temperature from the two preceding salts, which is inadequate to produce an assignable difference of diffusion, the three salts may be supposed to be diffused at the same temperature, without sensible error.

Diffusion of 2 per cent. solutions for 7 days.

	Grs.	Ratio.
Chloride of sodium at 60°, .	12.14	100
Bromide of sodium at 59°.8, .	11.93	98.27
Iodide of sodium at 59°.8, .	12.18	100.33
Mean,	12.08	

In both these isomorphous groups of salts of potassium and sodium, there is certainly a near approach to equality of diffusion. The times for the salts of the two bases being in the empirical proportion of the square roots of 2 and 3, the mean diffusates also approach pretty closely; namely, 12.40 grs. for the salts of potassium and 12.08 grs. for the salts of sodium, which are as 100 to 97.42. Here the members of each group are certainly very similar to each other in density, and probably other physical properties, which was not the case with the equidiffusive group containing the hydrogen acids of the same salt-radicals (p. 499).

### 35. *Chloride of Ammonium.*

Time of diffusion 5.716 days. The salt diffused was estimated by means of nitrate of silver.

Solution 0.988 per cent.; density 1.0036. Diffused at 53°, in eight cells, 6.09, 6.07, 5.67, 5.87; mean 5.92 grs., and 5.99 for one per cent. in two cells. This is somewhat more than 5.68, one-half of the diffusate of the 2 per cent. solution of iodide of potassium, at nearly the same temperature. The diffusion, however, of the small proportions of salts of ammonium, such as the 1 per cent. solution, is apt to be given in excess, from their low density.



36. *Dichloride of Copper.*

Time of diffusion seven days, or that of chloride of sodium. The salt diffused was obtained by evaporation to dryness, in an air-bath, after treating the liquid with an excess of chlorine, in the form of chloride, from which the dichloride was calculated.

It was an object of interest to discover whether the dichloride of copper ( $\text{Cu}_2\text{Cl}$ ), which should be isomorphous with the chloride of sodium, may separate from the protochloride of copper and other magnesian salts, and assume the high diffusibility of the salts of alkaline metals. But the salt in question is entirely insoluble in water. A solution, however, was obtained by dissolving an equivalent quantity of the red suboxide of copper recently precipitated, in hydrochloric acid, of density 1.033, so as to give one grain of dichloride in every hundred water-grain measures of the solution. This acid solution did not precipitate by dilution with water. The salt was diffused into pure water at a mean temperature of  $53^\circ.2$ .

1. Dichloride of copper diffused, 6.66, 6.57, 7.01, and 6.48 grs.; mean 6.68 grs. in two cells. Chloride of sodium at  $53^\circ.4$ , nearly the same temperature, gave 5.90 grs. in the same time. Reducing the result to temperature of  $51^\circ$  by an approximative correction, we should have 6.48 grs. of dichloride of copper for that temperature, at which chloride of calcium gave 6.51 grs. in 11.43 days, and protochloride of copper ( $\text{Cu Cl}$ ) 6.06 grs. at nearly the same temperature, also in 11.43 days.

So far as we can judge from an experiment at a single temperature, it would appear that the diffusion of dichloride of copper is more rapid than that of the chloride ( $\text{Cu Cl}$ ), in a proportion which supposes the former compound to possess half the "solution density" of the latter, the times of equal diffusion, 7 and 11.43 days, being when squared as 1 to 2.

With the view of discovering whether the large proportion of hydrochloric acid, amounting to 7 per cent., present in the preceding solution of dichloride of copper, modified the diffusion of the salt, a portion of the same acid solution was treated with chlorine gas, to convert the copper salt into chloride, and diffused into water, after the excess of chlorine was removed by agitation of the solution with air. The proportion of salt present was thus increased in weight from 1 to 1.36 per cent. The time of diffusion was 11.43 days, and the temperature  $53^\circ$ .

2. Chloride of copper diffused from a 1.36 per cent. solution of the salt in hydrochloric acid, 5.83, 5.66, and 5.30 grs. in two cells; mean 5.60 grs.

The corresponding diffusion from a 1 per cent. solution may be supposed to be less than 5.6 grs., in the proportion of 1.36 to 1, without any



great error. The results thus become chloride of copper diffused, 3.98, 3.85, and 3.58 grs.; mean 3.80 grs. in two cells.

It hence appears that the diffusion of chloride of copper is much diminished by the presence of a great excess of hydrochloric acid in the same solution. Different causes suggest themselves for this result, such as the possibility of a combination existing of chloride of copper with chloride of hydrogen, in the acid solution; or the influence which must be admitted of the more soluble substance, in a mixture of two similar substances, in repressing the diffusion of the less soluble. The present result, however, is entirely opposed to the idea that the high diffusibility of the dichloride of copper, observed before, is due to the hydrochloric acid present.

3. The diffusion of chloride of sodium also appears to be repressed by contact with a large excess of hydrochloric acid. One per cent. of chloride of sodium raised the density of dilute hydrochloric acid from 1.035 to 1.0408. Diffused into pure water for seven days at  $52^{\circ}9$ , in eight cells, the diffusates of chloride of sodium were 3.80, 3.87, 4.00, and 3.86 grs.; mean 3.88 for two cells. The diffusion of chloride of sodium is thus reduced in a corresponding measure with that of chloride of copper by association with seven times its weight of hydrochloric acid.

These results are interesting in a very different point of view. I have always watched for the appearance of some absorbent or imbibing power on the part of the acids, more analogous to an endosmotic attraction for water, as usually conceived. If such an attraction existed, it would complicate the phenomena of diffusion, for the volume of water absorbed by the acid would displace and project a portion of the latter into the reservoir, the phial not being extensible. The high diffusibility of hydrochloric and nitric acids would be thus explained. But by such a mechanical displacement the chloride of sodium would be thrown out in the preceding experiment, as well as the hydrochloric acid, which is not the case.

4. Even in hydrochloric acid of density 1.124 (25 per cent.), the diffusion of 1 per cent. of chloride of sodium for seven days, at  $56^{\circ}6$ , was found to amount to 4.7 grs. only in two cells, and is less than from a solution in pure water.

5. In comparing the influence of nitric acid with that of hydrochloric acid upon the diffusion of chloride of sodium, it was found that in a 7 per cent. solution of nitric acid, the chloride of sodium (1 per cent.) was entirely decomposed in the diffusive process, at  $56^{\circ}6$ , and gave hydrochloric acid in the full diffusive equivalent of that acid, together with nitrate of soda.



37. *Bicarbonate of Potash.*

Time of diffusion 8.083 days, or double that of hydrate of potash. The water of the jars was partially charged with carbonic acid gas, to prevent the decomposition of this and the other bicarbonates in the act of diffusion. The usual number of eight cells of the 1 and 2 per cent. solutions were diffused, and four cells of the 4 and 8 per cent. solutions. The whole diffusates of each proportion were then mixed together, and the quantity of bicarbonate of potash diffused for two cells, converted into the chloride of potassium, evaporated to dryness and weighed.

1. 1.059 per cent. of bicarbonate of potash ( $\text{HO} \cdot \text{CO}_2 + \text{KO} \cdot \text{CO}_2$ ), density 1.00788, diffused at  $68^\circ 2$ , gave 7.66 grs. for two cells. Calculated for 1 per cent., 7.23 grs. of bicarbonate of potash in two cells.

2. 2.12 per cent. of bicarbonate of potash, density 1.01489, diffused at  $62^\circ 2$ , gave 14.88 grs. for two cells. Calculated for 2 per cent., 14.05 grs. of bicarbonate of potash in two cells.

3. 4.236 per cent. of bicarbonate of potash, density 1.0288, diffused at  $68^\circ 2$ , gave 14.15 grs. for one cell. Calculated for 4 per cent., 13.36 grs. of bicarbonate of potash in one cell.

4. 8.472 per cent. of bicarbonate of potash, density 1.05600, diffused at  $68^\circ 2$ , gave 27.55 grs. for one cell. Calculated for 8 per cent., 26.01 grs. of bicarbonate of potash in one cell.

Diffusion of Bicarbonate of Potash in 8.08 days at  $68^\circ 2$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	7.23	1.029
From 2 per cent. solution, .	14.05	2
From 4 per cent. solution, .	26.72	3.806
From 8 per cent. solution, .	52.01	7.408

38. *Bicarbonate of Ammonia.*

Time of diffusion 8.083 days. The usual number of eight cells of the 1 and 2 per cent. solutions of this substance were diffused, and four cells of the 4 and 8 per cent. solutions. The whole diffusates of each proportion were then mixed together, and the quantity of bicarbonate of ammonia, diffused for two cells, determined by an alkalimetical experiment, which was always repeated twice.

1. 1.109 per cent. of bicarbonate of ammonia ( $\text{HO} \cdot \text{CO}_2 + \text{NH}_4\text{O} \cdot \text{CO}_2$ ), density 1.00553, diffused at  $68^\circ 2$ , gave 7.66 grs. for two cells. Calculated for 1 per cent., 6.91 grs. of bicarbonate of ammonia in two cells.

2. 2.218 per cent. of bicarbonate of ammonia, density 1.01056, diffused at  $68^\circ 2$ , gave 15.14 grs. for two cells. Calculated for 2 per cent., 13.65 grs. of bicarbonate of ammonia in two cells.



3. 4.436 per cent. of bicarbonate of ammonia, density 1.02000, diffused at  $68^{\circ}2$ , gave 14.98 grs. for one cell. Calculated for 4 per cent., 13.50 grs. of bicarbonate of ammonia in one cell.

4. 8.872 per cent. of bicarbonate of ammonia, density 1.03856, diffused at  $68^{\circ}2$ , gave 27.78 grs. for one cell. Calculated for 8 per cent., 25.05 grs. of bicarbonate of ammonia in one cell.

Diffusion of Bicarbonate of Ammonia in 8.08 days at  $68^{\circ}2$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	6.91	1.013
From 2 per cent. solution, .	13.65	2
From 4 per cent. solution, .	27.00	3.959
From 8 per cent. solution, .	50.10	7.346

The amount and progression of the diffusion of this salt correspond well, for all the proportions diffused, with the preceding isomorphous bicarbonate of potash.

### 39. Bicarbonate of Soda.

Time of diffusion 9.875 days. The usual number of eight cells of the 1 and 2 per cent. solutions were diffused, and four cells of the 4 and 8 per cent. solutions. The whole diffusates of each proportion were then mixed together, and the quantity of bicarbonate of soda, diffused for two cells, converted into chloride of sodium, evaporated to dryness and weighed.

1. 1.135 per cent. of bicarbonate of soda,  $\text{HO} \cdot \text{CO}_2 + \text{NaO} \cdot \text{CO}_2$ , density 1.00892, diffused at  $68^{\circ}1$ , gave 8.30 grs. for two cells. Calculated for 1 per cent., 7.31 grs. of bicarbonate of soda in two cells.

2. 2.27 per cent. of bicarbonate of soda, density 1.01703, diffused at  $68^{\circ}1$ , gave 15.68 grs. for two cells. Calculated for 2 per cent., 13.81 grs. of bicarbonate of soda in two cells.

3. 4.54 per cent. of bicarbonate of soda, density 1.03306, diffused at  $68^{\circ}1$ , gave 15.16 grs. for one cell. Calculated for 4 per cent., 13.35 grs. of bicarbonate of soda in one cell.

4. 9.08 per cent. of bicarbonate of soda, density 1.06386, diffused at  $68^{\circ}1$ , gave 29.73 grs. for one cell. Calculated for 8 per cent., 26.19 grs. of bicarbonate of soda in one cell.

Diffusion of Bicarbonate of Soda in 9.87 days at  $68^{\circ}1$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	7.31	1.059
From 2 per cent. solution, .	13.81	2
From 4 per cent. solution, .	26.70	3.869
From 8 per cent. solution, .	52.38	7.590



A remarkable approach to equality in the diffusion of the bicarbonates of potash and soda, in the times chosen, is observed equally in all the proportions of salt from 1 to 8 per cent.

The results for the three bicarbonates may be stated as follows, the diffusate of the 2 per cent. solution of bicarbonate of potash being made equal to 200, as a standard of comparison.

Diffusion of Bicarbonates of Potash and Ammonia in 8·08 days, at 68°·2, and of Bicarbonate of Soda in 9·875 days, at 68°·1 :—

	Bicarbonate of potash.	Bicarbonate of ammonia.	Bicarbonate of soda.
From 1 per cent. solution .....	102·9	98·3	104·0
From 2 per cent. solution .....	200·0	194·3	196·4
From 4 per cent. solution .....	380·6	384·3	380·0
From 8 per cent. solution .....	740·8	712·6	748·3

Or, making the diffusate from each proportion of the bicarbonate of potash equal to 100 :—

	Bicarbonate of potash.	Bicarbonate of ammonia.	Bicarbonate of soda.
From 1 per cent. solution .....	100	95·53	101·07
From 2 per cent. solution .....	100	97·15	98·20
From 4 per cent. solution .....	100	100·97	99·84
From 8 per cent. solution .....	100	96·19	101·03

The bicarbonate of ammonia is slightly lower in general than the bicarbonate of potash, possibly from a small loss of the former salt by evaporation in the different operations. The times chosen for these two bicarbonates is to that of the bicarbonate of soda, as the square root of 2 to the square root of 3, and the remarkable agreement observed in the diffusion of these salts gives support therefore to that relation. In alluding to this relation, however, it is proper to add that the carbonates of potash and soda deviate from it in a sensible degree, and the hydrates of potash and soda very considerably. If the relation therefore has a real foundation, it must be masked in the salts last named by differences existing between them in certain properties, the discovery and investigation of which is of the last importance for the theory of liquid diffusion.

#### 40. *Hydrochlorate of Morphine.*

Time of diffusion 11·43 days. The crystallized salt was assumed to be of the composition  $C_{34}H_{18}NO_6 \cdot HCl + 6HO$ , with the equivalent



374.5. The quantity diffused was determined from the chlorine, which was precipitated as chloride of silver in an acid solution. Hydrochlorate of morphine, 1.88 per cent. of the salt supposed anhydrous, diffused at  $64^{\circ}1$ , in six cells, 11.03, 10.72, 11.01; mean 10.92 grs. of the anhydrous salt for two cells. Calculated for 2 per cent., 11.60 grs. at  $64^{\circ}1$  for two cells.

#### 41. *Hydrochlorate of Strychnine.*

Time of diffusion 11.43 days. The crystallized salt was assumed to be of the composition  $C_{42}H_{22}N_2O_4 \cdot HCl + 3HO$ , with the equivalent 397.5. Hydrochlorate of strychnine, 2 per cent., density 1.0065, diffused at  $64^{\circ}1$ , in six cells, 11.54, 11.62, 11.31; mean 11.49 grs. for two cells. The quantities refer to anhydrous salt, and were estimated from the chlorine, as with hydrochlorate of morphine.

These two analogous salts appear to approach very closely in diffusibility.

Diffusion from 2 per cent. solutions at  $64^{\circ}1$ ; two cells.

Hydrochlorate of morphine, .	11.60	100
Hydrochlorate of strychnine, .	11.49	99.05

For a similar period of 11.43 days, but at a lower temperature,  $53^{\circ}4$ , the 1 per cent. solution of hydrochlorate of morphine gave a mean result of 5.49 grs. from two cells, and the hydrochlorate of strychnine 5.77 grs. from two cells. But the weights of chloride of silver from which these numbers are deduced were too small to admit of much precision.

The diffusion of these salts of organic bases in 11.43 days, is exceeded by the diffusion of chloride of ammonium or potassium in 5.71 days, or half the former time. The vegeto-alkalies appear thus to be divided from ammonia and potash.

The new observations of the present paper are favourable to the existence of a relation amounting to close similarity or equality in diffusibility between certain classes of substances.

The chlorides and nitrates of the same metal generally exhibit this correspondence, as in the chloride of calcium and nitrate of lime, the chloride of sodium and nitrate of soda, and also in hydrochloric and nitric acids.

Isomorphous salts exhibit the same relation, as has been observed in the chlorides, bromides and iodides of potassium, sodium and hydrogen, in various salts of baryta, strontia and lead, in numerous magnesian salts, in the salts of silver, soda, and probably those of suboxide of copper, and in several additional salts of potash and ammonia.



Corresponding salts of two of the vegeto-alkalies are found also to be equidiffusive.

Before discussing the relations between the different groups of equidiffusive substances which are thus formed, it will be necessary to examine their diffusion at widely different temperatures, a subject attended with considerable difficulty.

#### ADDITIONAL OBSERVATIONS ON THE DIFFUSION OF LIQUIDS.<sup>1</sup>

The experiments on diffusion to be presently described are in continuation of those detailed in my last publication on the subject, the same method of observing being followed without change. The diffusion is generally made from solutions in four different proportions, so as to exhibit pretty fully the characters of the property in question for each salt, so far as is possible at a constant temperature. The salts operated upon are of two bases only, potash and soda; but the acids are considerably varied, so as to include hydrates, carbonates, sulphates, sulphites, hyposulphites, sulphovinates, oxalates, acetates, and tartrates. Salts of almost every class of acids come thus to be represented, either in the present or former series of experiments on diffusion, while at the same time much information is elicited respecting the diffusive relation of the two important bases named.

##### *Comparison of Salts of Potash and Soda.*

*Hydrate of Potash.*—Time of diffusion 4·041 days. The usual number of eight cells of the 1 and 2 per cent. solutions of this substance were diffused, and four cells of the 4 and 8 per cent. solutions. The whole diffusates of each proportion were then mixed together, and the quantity of hydrate of potash diffused for two cells determined by an alkalimetric experiment, which was always repeated twice.

1. One per cent. of hydrate of potash, density 1·00978, diffused at 63°·4, gave 6·56 grs. of hydrate of potash for two cells.

2. 2·005 per cent. of hydrate of potash, density 1·01878, diffused at 63°·4, gave 12·88 grs. for two cells; calculated for 2 per cent., 12·84 grs. of hydrate of potash in two cells.

3. 4·01 per cent. of hydrate of potash, density 1·0366, diffused at 63°·4, gave 12·56 grs. for one cell; calculated for 4 per cent., 12·52 grs. of hydrate of potash in one cell.

4. 8·02 per cent. of hydrate of potash, density 1·07069, diffused at 63°·4, gave 26·20 grs. for one cell; calculated for 8 per cent., 26·12 grs. of hydrate of potash in one cell.

<sup>1</sup> Third Memoir, *Phil. Trans.* 1851. Received March 27,—Read May 22, 1851.



Diffusion of Hydrate of Potash in 4.04 days at  $63^{\circ}4$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . .	6.56	1.022
From 2 per cent. solution, . . .	12.84	2
From 4 per cent. solution, . . .	25.04	3.900
From 8 per cent. solution, . . .	52.24	8.137

*Hydrate of Soda.*—Time of diffusion 4.9497 days; the times chosen as hitherto for the corresponding potash and soda salts being always, when squared, in the proportion of 2 to 3. The usual number of eight cells of the 1 and 2 per cent. solutions were diffused, and four cells of the 4 and 8 per cent. solutions. The whole diffusates of each proportion were then mixed together, and the quantity of hydrate of soda diffused for two cells determined by alkalimetric experiments.

1. 1.043 per cent. of hydrate of soda, density 1.01256, diffused at  $63^{\circ}3$ , gave 6.06 grs. for two cells; calculated for 1 per cent., 5.81 grs. of hydrate of soda in two cells.

2. 2.087 per cent. of hydrate of soda, density 1.0242, diffused at  $63^{\circ}3$ , gave 11.58 grs. for two cells; calculated for 2 per cent., 11.09 grs. of hydrate of soda in two cells.

3. 4.177 per cent. of hydrate of soda, density 1.04666, diffused at  $63^{\circ}3$ , gave 10.90 grs. for one cell; calculated for 4 per cent., 10.43 grs. of hydrate of soda in one cell.

4. 8.35 per cent. of hydrate of soda, density 1.08846, diffused at  $63^{\circ}3$ , gave 21.10 grs. for one cell; calculated for 8 per cent., 20.22 grs. of hydrate of soda in one cell.

Diffusion of Hydrate of Soda in 4.95 days at  $63^{\circ}3$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . .	5.81	1.048
From 2 per cent. solution, . . .	11.09	2
From 4 per cent. solution, . . .	20.86	3.765
From 8 per cent. solution, . . .	40.44	7.30

The nearest approach to equality of diffusion in the hydrates of potash and soda, is exhibited by the 1 per cent. solutions, which are as 6.56 to 5.81, or as 100 to 88.57, being a difference of so much as 11.43 per cent.

Comparative Diffusion of Hydrate of Potash in 4.041 days at  $63^{\circ}4$ , and of Hydrate of Soda in 4.95 days at  $63^{\circ}3$ .

	From solutions of			
	1 per cent.	2 per cent.	4 per cent.	8 per cent.
Hydrate of potash .....	100	100	100	100
Hydrate of soda .....	88.57	86.37	83.30	77.41



The marked departure from the usual ratio of diffusion, here exhibited, must not be overlooked in considering the relation between potash and soda salts.

*Carbonate of Potash.*—Time of diffusion 8·083 days, or double the time of hydrate of potash. The usual number of eight cells of the 1 and 2 per cent. solutions were diffused, with four cells of the 4 and 8 per cent. solutions, and the diffusates of each proportion determined by alkalimetric experiments as with the preceding alkaline hydrates.

1. 1·002 per cent. of carbonate of potash, density 1·00957, diffused at 63°·7, gave 6·15 grs. for two cells; calculated for 1 per cent., 6·13 grs. of carbonate of potash in two cells.

2. 2·005 per cent. of carbonate of potash, density 1·01843, diffused at 63°·7, gave 11·95 grs. for two cells; calculated for 2 per cent., 11·92 grs. of carbonate of potash in two cells.

3. 4·01 per cent. of carbonate of potash, density 1·03577, diffused at 63°·7, gave 11·48 grs. for one cell; calculated for 4 per cent., 11·44 grs. of carbonate of potash in one cell.

4. 8·02 per cent. of carbonate of potash, density 1·06935, diffused at 63°·7, gave 22·79 grs. for one cell; calculated for 8 per cent., 22·72 grs. of carbonate of potash in one cell.

5. 2·005 per cent. of carbonate of potash, density 1·01843, diffused at 68°·2, gave 12·64 grs. for two cells; calculated for 2 per cent., 12·62 grs. of carbonate of potash in two cells.

Diffusion of Carbonate of Potash in 8·08 days at 63°·7; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	6·13	1·028
From 2 per cent. solution, .	11·92	2
From 4 per cent. solution, .	22·88	3·839
From 8 per cent. solution, .	45·44	7·624

Comparative Diffusion of Hydrate of Potash in 4·04 days at 63°·4, and Carbonate of Potash in 8·08 days at 63°·7.

	From solutions of			
	1 per cent.	2 per cent.	4 per cent.	8 per cent.
Hydrate of potash .....	100	100	100	100
Carbonate of potash.....	93·48	92·81	91·36	86·97

The diffusion of hydrate of potash appears to be excessive when compared with the carbonate of potash, as well as when compared with the hydrate of soda.



*Carbonate of Soda.*—Time of diffusion 9·8994 days. The usual number of eight cells of the 1 and 2 per cent. solutions of this substance were diffused, and four cells of the 4 and 8 per cent. solutions, and the diffusates determined by alkalimetric experiments.

1. 1·003 per cent. of carbonate of soda, density 1·01120, diffused at  $63^{\circ}4$ , gave 6·04 grs. for two cells; calculated for 1 per cent., 6·02 grs. of carbonate of soda in two cells.

2. 2·007 per cent. of carbonate of soda, density 1·0216, diffused at  $63^{\circ}4$ , gave 11·74 grs. for two cells; calculated for 2 per cent., 11·70 grs. of carbonate of soda in two cells.

3. 4·015 per cent. of carbonate of soda, density 1·04156, diffused at  $63^{\circ}4$ , gave 10·74 grs. for one cell; calculated for 4 per cent., 10·71 grs. of carbonate of soda in one cell.

4. 8·03 per cent. of carbonate of soda, density 1·0800, diffused at  $63^{\circ}4$ , gave 19·93 grs. for one cell; calculated for 8 per cent., 19·87 grs. of carbonate of soda in one cell.

In the two following additional experiments the diffusate was treated with hydrochloric acid, and estimated from the weight of chloride of sodium produced.

5. 2·007 per cent. of carbonate of soda, density 1·02166, diffused at  $68^{\circ}1$ , gave 12·06 grs. for two cells; calculated for 2 per cent., 12·02 grs. of carbonate of soda in two cells at  $68^{\circ}1$ .

6. 2·13 per cent. of carbonate of soda, density 1·02246, diffused at  $59^{\circ}6$  in eight cells, 11·12, 11·34, 11·17, 11·58; mean 11·38 grs. for two cells; calculated for 2 per cent., 10·65 grs. of carbonate of soda in two cells at  $59^{\circ}6$ .

Diffusion of Carbonate of Soda in 9·9 days at  $63^{\circ}4$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	6·02	1·028
From 2 per cent. solution, .	11·70	2
From 4 per cent. solution, .	21·42	3·661
From 8 per cent. solution, .	39·74	6·792

The similarity of diffusion between the carbonates of potash and soda is remarkable in the 1 per cent. solution, which are as 6·13 to 6·02, or as 100 to 98·2; also in the 2 per cent. solutions, which were observed at two different temperatures.

Diffusion of 2 per cent. solutions of Carbonate of Potash in 8·083 days, and Carbonate of Soda in 9·9 days.

	Grs.	Ratio.
Carbonate of potash at $63^{\circ}7$ , .	11·92	100
Carbonate of soda at $63^{\circ}4$ , .	11·70	98·15
Carbonate of potash at $68^{\circ}2$ , .	12·62	100
Carbonate of soda at $68^{\circ}1$ , .	12·02	95·24



Comparative Diffusion of Carbonate of Potash in 8·083 days at  $63^{\circ}7$ ,  
and Carbonate of Soda in 9·9 days at  $63^{\circ}4$ .

	From solutions of			
	1 per cent.	2 per cent.	4 per cent.	8 per cent.
Carbonate of potash .....	100	100	100	100
Carbonate of soda.....	98·20	98·15	93·63	87·44

The carbonate of soda appears to preserve more analogy to the hydrate of soda in its diffusion than the carbonate of potash to the hydrate of potash.

Comparative Diffusion of Hydrate of Soda in 4·937 days at  $63^{\circ}3$ , and  
Carbonate of Soda in 9·9 days at  $63^{\circ}4$ .

	From solutions of			
	1 per cent.	2 per cent.	4 per cent.	8 per cent.
Hydrate of soda .....	100	100	100	100
Carbonate of soda.....	103·62	105·50	102·68	98·27

Here we have a nearly equal diffusion with the times as 1 to 2 for the hydrate and carbonate of soda respectively.

*Sulphate of Potash.*—Time of diffusion 8·083 days. The solution of diffused salt was evaporated to dryness and weighed.

1. 1·005 per cent. of sulphate of potash, density 1·00844, diffused at  $60^{\circ}3$ , in eight cells, 6·11, 6·21, 6·12, 6·32; mean 6·19 grs. in two cells; calculated for 1 per cent., 6·16 grs. of sulphate of potash in two cells.

2. 2·01 per cent. of sulphate of potash, density 1·01653, diffused at  $60^{\circ}3$ , in eight cells, 11·61, 11·58, 11·50, 11·97; mean 11·66 grs. in two cells; calculated for 2 per cent., 11·60 grs. of sulphate of potash in two cells.

3. 4·02 per cent. of sulphate of potash, density 1·03240, diffused at  $60^{\circ}3$ , in four cells, 10·80, 11·33, 11·20, 12·07; mean 11·35 grs. for one cell; calculated for 4 per cent., 11·35 grs. of sulphate of potash in one cell.

4. 8·04 per cent. of sulphate of potash, density 1·06306, diffused at  $60^{\circ}3$ , in four cells, 21·91, 21·93, 22·00, 22·47; mean 22·08 grs. for one cell; calculated for 8 per cent., 21·96 grs. of sulphate of potash in one cell.



Diffusion of Sulphate of Potash in 8·083 days at 60°·3; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	6·16	1·062
From 2 per cent. solution, .	11·60	2
From 4 per cent. solution, .	22·70	3·914
From 8 per cent. solution, .	43·92	75·72

The diffusion of sulphate of potash above, at 60°·3, appears to be similar to that of carbonate of potash at 63°·7, a higher temperature by 3°·4 (p. 533). The numbers for the sulphate of potash and hydrate of potash (p. 531) would probably correspond closely at the same temperature, the times of diffusion of the two substances being taken as 2 to 1.

*Sulphate of Soda.*—Time of diffusion 9·9 days. The diffusate was evaporated to dryness and weighed.

1. One per cent. of sulphate of soda, density 1·00940, diffused at 59°·9, in eight cells, 6·31, 6·47, 6·21, 6·32; mean 6·33 grs. for two cells.

2. 1·995 per cent. of sulphate of soda, density 1·01832, diffused at 59°·9, in eight cells, 12·02, 12·10, 11·66, 12·16; mean 11·98 grs. for two cells; calculated for 2 per cent., 12·00 grs. of sulphate of soda in two cells at 59°·9.

3. 3·99 per cent. of sulphate of soda, density 1·03594, diffused at 59°·9, in four cells, 10·00, 10·80, 11·53, 11·53; mean 10·96 grs. for one cell; calculated for 4 per cent., 10·98 grs. of sulphate of soda in one cell at 59°·9.

4. 7·98 per cent. of sulphate of soda, density 1·06960, diffused at 59°·9, in four cells, 20·50, 21·36, 20·01, 20·68; mean 20·64 grs. for one cell; calculated for 8 per cent., 20·69 grs. of sulphate of soda in one cell at 59°·9.

Diffusion of Sulphate of Soda in 9·9 days at 59°·9; two cells.

	Grs.	Ratio.
From 1 per cent. solution, .	6·33	1·055
From 2 per cent. solution, .	12·00	2
From 4 per cent. solution, .	21·96	3·66
From 8 per cent. solution, .	41·38	6·896

The 2 per cent. solution of sulphate of soda above, at 59°·9, appears to be more diffusive than the corresponding solution of carbonate of soda at 59°·6, as 12·00 to 10·65 grs., or as 100 to 88·75.

The assumed relation in the times of equal diffusion for salts of potash and soda appears to derive support from the sulphates, particularly in the lower proportions of salt.



Comparative Diffusion of Sulphate of Potash in 8·083 days at 60°·3, and Sulphate of Soda in 9·9 days at 59°·9.

	From solutions of			
	1 per cent.	2 per cent.	4 per cent.	8 per cent.
Sulphate of potash .....	100	100	100	100
Sulphate of soda .....	102·74	103·45	96·74	94·21

Another set of experiments made upon these two salts, simultaneously with certain oxalates and acetates which follow, may be placed here to illustrate the same relation. The preceding times of diffusion were observed.

5. 2·013 per cent. of sulphate of potash, diffused at 59°·8, in eight cells, gave 11·90, 11·94, 11·41, 11·71; mean 11·74 grs. for two cells; calculated for two per cent., 11·67 grs. of sulphate of potash in two cells.

6. Two per cent. of sulphate of soda, density 1·01846, diffused at 59°·6, in eight cells, gave 11·58, 11·56, 11·94, 11·97; mean 11·76 grs. of sulphate of soda in two cells.

The present results, from 2 per cent. solutions of these salts, are as follows:—

Sulphate of potash in 8·083 days at 59°·8,	11·67	100
Sulphate of soda in 9·9 days at 59°·6,	11·76	100·94

The diffusion in the selected times appears therefore to be, as nearly as possible, equal at the present temperatures.

Another experiment may be recorded at present, of which the object was to ascertain the influence of free sulphuric acid upon the diffusion of sulphate of soda.

7. Sulphate of soda, 2·02 per cent., to which an equivalent quantity of sulphuric acid was added, had the density 1·02703. This solution, diffused into pure water, in eight cells, at 59°·6, for the same time as the preceding sulphate of soda, gave a diffusate of 9·70, 10·06, 10·17, and 10·29 grs. of sulphate of soda; mean 10·05 grs. in two cells; calculated for 2 per cent., this diffusate becomes 9·95 grs. The presence of one equivalent of sulphuric acid appears therefore to diminish the diffusion of sulphate of soda considerably, namely, from 11·76 to 9·95 grs., or from 100 to 84·61. The free sulphuric acid diffused in the experiment was not determined.

*Sulphite of Potash.*—It was curious to observe how far this and other salts of the oxygen acids of sulphur correspond with the sulphates. Time of diffusion 8·083 days. The diffusate was treated with sulphuric acid and estimated in the form of neutral sulphate of potash.



1.90 per cent. of sulphite of potash, density 1.01753, diffused at  $59^{\circ}5$ , in eight cells, gave 11.36, 10.72, 11.22, and 10.90 grs. in two cells; mean 11.05 grs. in two cells; calculated for 2 per cent., 11.63 grs.

Making the comparison for 2 per cent. solutions we have—

Sulphate of potash at $60^{\circ}3$ , . . .	11.60	100
Sulphite of potash at $59^{\circ}5$ , . . .	11.63	100.26

The two salts appear to have the same diffusibility.

*Sulphite of Soda.*—Time of diffusion 9.9 days. The diffusate was estimated in the same manner as the preceding salt.

2.26 per cent. of sulphite of soda, density 1.02330, diffused at  $59^{\circ}6$ , in eight cells, gave 12.93, 13.35, 13.56, and 13.62 grs. in two cells; mean 13.37 grs. in two cells; calculated for 2 per cent., 11.83 grs.

The comparative diffusion of the sulphites of the two bases is as follows:—

Sulphite of potash in 8.083 days at $59^{\circ}5$ ,	11.63	100
Sulphite of soda in 9.9 days at $59^{\circ}6$ , . .	11.83	100.72

The sulphites of potash and soda appear therefore to exhibit the usual relation of these two bases.

*Hyposulphite of Potash.*—Time of diffusion 8.083 days. The diffusate was evaporated to dryness with sulphuric acid, ignited and estimated from the sulphate produced.

1.925 per cent. of anhydrous hyposulphite of potash, density 1.0150, diffused at  $59^{\circ}8$ , in eight cells, gave 11.66, 11.67, 12.01, 12.26 grs.; mean 11.90 grs. for two cells; calculated for 2 per cent., 12.37 grs. of hyposulphite of potash in two cells.

Comparing this salt with the sulphate of the same base, we have—

Sulphate of potash at $60^{\circ}3$ , . . .	11.60	100
Hyposulphite of potash at $59^{\circ}8$ , . . .	12.37	106.44

A slight error in excess may possibly have been introduced from the circumstance that the hyposulphite of potash employed was not absolutely free from sulphate.

*Hyposulphite of Soda.*—Time of diffusion 9.9 days. The diffusate was estimated in the same manner as the preceding salt.

2.136 per cent. of anhydrous hyposulphite of soda, density 1.01778, diffused at  $59^{\circ}9$ , in eight cells, gave 13.11, 12.77, 12.92, 11.99 grs.; mean 12.70 grs. for two cells; calculated for 2 per cent., 11.89 grs. of hyposulphite of soda in two cells.

The comparative diffusion of the salts of potash and soda appears thus:—



Hyposulphite of potash in 8.083 days at 59°8,	12.37	100
Hyposulphite of soda in 9.9 days at 59°9, .	11.89	96.21

The relation of the sulphate and hyposulphite of soda appears still closer.

Sulphate of soda at 59°6, .	11.76	100
Hyposulphite of soda at 59°9, .	11.89	101.10

*Sulphovinate of Potash.*—Time of diffusion 8.083 days. The diffusate was evaporated to dryness and ignited with sulphuric acid.

1.966 per cent. of sulphovinate of potash, of density 1.00977, diffused at 59°8, in eight cells, gave 12.57, 12.48, 12.12, and 12.39 grs.; mean 12.39 grs. for two cells; calculated for 2 per cent., 12.60 grs. of sulphovinate of potash in two cells.

The diffusion of this salt appears in excess when compared with sulphate of potash.

Sulphate of potash at 60°3, .	11.60	100
Sulphovinate of potash at 59°8, .	12.60	108.62

*Sulphovinate of Soda.*—Time of diffusion 9.9 days. The diffusate was estimated in the same manner as the preceding salt.

2.063 per cent. of sulphovinate of soda, of density 1.00944, diffused at 59°6, in eight cells, gave 13.32, 13.50, 13.78, and 13.15 grs.; mean 13.44 grs. for two cells; calculated for 2 per cent., 13.03 grs. of sulphovinate of soda in two cells.

Comparing the two sulphovinates together, we have—

Sulphovinate of potash in 8.083 days at 59°8,	12.60	100
Sulphovinate of soda in 9.9 days at 59°6, .	13.03	103.41

Neither of these sulphovinates appeared to suffer decomposition in the act of diffusion, at least to any considerable extent. But the experiments on both of these salts are less precise than usual, from the difficulty of obtaining them entirely free from sulphates.

*Oxalate of Potash.*—Time of diffusion 8.083 days. The diffusate was evaporated to dryness, ignited, and then converted into chloride of potassium.

1. 0.981 per cent. of anhydrous oxalate of potash, density 1.00775, diffused at 59°8, in eight cells, 6.24, 6.22, 5.91, 5.97; mean 6.08 grs. for two cells; calculated for 1 per cent., 6.20 grs. of oxalate of potash in two cells.

2. 1.92 per cent. of oxalate of potash, density 1.01463, diffused at 59°9, in eight cells, 11.54, 11.63, 11.94, 11.63; mean 11.68 grs. for two cells; calculated for 2 per cent., 12.17 grs. of oxalate of potash, in two cells.



3. 3.84 per cent. of oxalate of potash, density 1.02864, diffused at  $59^{\circ}9$ , in four cells, 11.10, 11.16, 11.09, 10.92; mean 11.07 grs. for one cell; calculated for 4 per cent., 11.52 grs. of oxalate of potash in one cell.

4. 7.68 per cent. of oxalate of potash, density 1.05604, diffused at  $59^{\circ}9$ , in four cells, 20.45, 20.63, 20.99, 20.15; mean 20.55 grs. for one cell; calculated for 8 per cent., 21.41 grs. of oxalate of potash in one cell.

Diffusion of Oxalate of Potash in 8.083 days at  $59^{\circ}9$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution,	6.20	1.019
From 2 per cent. solution,	12.17	2
From 4 per cent. solution,	23.04	3.789
From 8 per cent. solution,	42.82	7.042

The oxalate of potash corresponds well with sulphate of potash,

Comparative diffusion in 8.083 days of Sulphate of Potash at  $60^{\circ}3$ , and Oxalate of Potash at  $59^{\circ}9$ .

	From solutions of			
	1 per cent.	2 per cent.	4 per cent.	8 per cent.
Sulphate of potash .....	100	100	100	100
Oxalate of potash.....	100.65	104.91	101.50	97.47

The sensible excess in the diffusion of the 2 per cent. solution of oxalate of potash is, I believe, to be accounted for by this proportion having been estimated in the form of carbonate of potash instead of chloride of potassium.

*Oxalate of Soda.*—Time of diffusion 9.9 days. The diffusate was evaporated to dryness, ignited, and then converted into chloride, as with the preceding oxalate of potash.

1. 0.925 per cent. of oxalate of soda, density 1.00882, diffused at  $59^{\circ}9$ , in eight cells, 5.99, 5.81, 5.69, 5.59; mean 5.77 grs. for two cells; calculated for 1 per cent., 6.24 grs. of oxalate of soda in two cells.

It was found impossible to form a 2 per cent. solution of this salt from its sparing solubility, so that the observations respecting it are limited to the lowest proportion of salt.

The comparative diffusion from 1 per cent. solutions of these alkaline oxalates is as follows:—

Oxalate of potash in 8.083 days at $59^{\circ}9$ ,	6.20	100
Oxalate of soda in 9.9 days at $59^{\circ}9$ , .	6.24	100.65



Here again a nearly equal diffusion is observed in times of which the squares are as 2 to 3.

*Acetate of Potash*.—Time of diffusion 8·083 days. The diffusate was converted into chloride of potassium and weighed in that form.

1. 0·951 per cent. of anhydrous acetate of potash, density 1·00540, diffused at 60°·3, in eight cells, 6·01, 6·18, 6·27, 6·06; mean 6·13 grs. for two cells; calculated for 1 per cent., 6·44 grs. of acetate of potash in two cells.

2. 1·903 per cent. of acetate of potash, density 1·00976, diffused at 60°·3, in eight cells, 11·90, 11·91, 11·65, 12·24; mean 11·92 grs. for two cells; calculated for 2 per cent., 12·52 grs. of acetate of potash in two cells.

3. 3·807 per cent. of acetate of potash, density 1·01928, diffused at 60°·3, in four cells, 10·91, 11·08, 11·48, 11·18; mean 11·16 grs. for one cell; calculated for 4 per cent., 11·72 grs. of acetate of potash in one cell.

4. 7·614 per cent. of acetate of potash, density 1·03743, diffused at 60°·3, in four cells, 22·62, 21·72, 23·23, 22·42; mean 22·50 grs. for one cell; calculated for 8 per cent., 23·63 grs. of acetate of potash in one cell.

Diffusion of Acetate of Potash in 8·08 days at 60°·3; two cells.

	Grs.	Ratio.
From 1 per cent. solution,	6·44	1·028
From 2 per cent. solution,	12·52	2
From 4 per cent. solution,	23·44	3·744
From 8 per cent. solution,	47·26	7·549

The acetate will be found to exceed sensibly the sulphate and oxalate of potash in diffusibility at the preceding temperature.

Comparative diffusion of Sulphate and Acetate of Potash in 8·083 days, at 60°·3.

	From solutions of			
	1 per cent.	2 per cent.	4 per cent.	8 per cent.
Sulphate of potash .....	100	100	100	100
Acetate of potash.....	104·55	107·93	103·26	107·58

The acetate of potash appears to possess that increased diffusibility which is observed in bicarbonate of potash. But a parallelism still holds between the acetate and sulphate, and the diffusion of the two salts would probably coincide if that of the acetate were observed at a temperature 3° or 4° lower than the sulphate.



*Acetate of Soda.*—Time of diffusion 9.9 days. The diffusate was converted into chloride of sodium and weighed in that form.

1. 0.958 per cent. of anhydrous acetate of soda, density 1.00530, diffused at  $59^{\circ}6$ , in eight cells, 6.33, 6.56, 6.63, 6.05; mean 6.39 grs. for two cells; calculated for 1 per cent., 6.67 grs. of acetate of soda in two cells.

2. 1.917 per cent. of acetate of soda, density 1.01032, diffused at  $59^{\circ}6$ , in eight cells, 11.70, 12.04, 11.90, 12.19; mean 11.96 grs. for two cells; calculated for 2 per cent., 12.46 grs. of acetate of soda in two cells.

3. 3.835 per cent. of acetate of soda, density 1.02039, diffused at  $59^{\circ}6$ , in four cells, 12.19, 11.74, 12.15, 11.93; mean 12.00 grs. for one cell; calculated for four per cent., 12.52 grs. of acetate of soda in one cell.

4. 7.67 per cent. of acetate of soda, density 1.03968, diffused at  $59^{\circ}6$ , in four cells, 23.49, 22.26, 23.87, 22.49; mean 23.03 grs. for one cell; calculated for 8 per cent., 24.02 grs. of acetate of soda in one cell at  $59^{\circ}9$ .

Diffusion of Acetate of Soda in 9.9 days at  $59^{\circ}6$ ; two cells.

	Grs.	Ratio.
From 1 per cent. solution, . . . . .	6.67	1.070
From 2 per cent. solution, . . . . .	12.46	2
From 4 per cent. solution, . . . . .	25.04	4.019
From 8 per cent. solution, . . . . .	48.04	7.711

The diffusion of acetate of soda presents a general parallelism to that of acetate of potash for the times chosen, the temperatures of the two series of experiments differing only  $0^{\circ}7$ .

Comparative diffusion of Acetate of Potash in 8.083 days at  $60^{\circ}3$ , and Acetate of Soda in 9.9 days at  $59^{\circ}6$ .

	From solutions of			
	1 per cent.	2 per cent.	4 per cent.	8 per cent.
Acetate of potash .....	100	100	100	100
Acetate of soda .....	103.57	99.52	106.82	101.65

*Tartrate of Potash.*—Time of diffusion 8.08 days. The diffusate was evaporated to dryness, ignited, and then converted into chloride of potassium.

1.82 per cent. of anhydrous tartrate of potash, density 1.01227, diffused at  $59^{\circ}9$ , in eight cells, 9.96, 10.02, 10.06, 9.87; mean  $9^{\circ}98$  grs. for two cells; calculated for 2 per cent., 10.96 grs. of tartrate of potash in two cells.



*Tartrate of Soda.*—Time of diffusion 9·9 days. The diffusate was evaporated to dryness, ignited, and then converted into chloride of sodium.

2·03 per cent. of anhydrous tartrate of soda, density 1·01460, diffused at 59°·6, in eight cells, 10·84, 10·77, 10·81, 10·82; mean 10·81 grs. for two cells; calculated for 2 per cent., 10·65 grs. of tartrate of soda in two cells.

Diffusion of 2 per cent. solutions of Tartrate of Potash in 8·08 days at 59°·9, and Tartrate of Soda in 9·9 days at 59°·6.

Tartrate of potash, . . . .	10·96	100
Tartrate of soda, . . . .	10·65	97·18

The tartrate of soda happens to correspond absolutely with the carbonate of soda, the diffusate of the latter salt obtained at the same temperature being also 10·65 grs. (p. 534).

The double *Tartrate of Potash and Soda* afforded an interesting instance of decomposition produced by diffusion. Instead of the usual diffusion cells, a single plain cylindrical jar was employed about 5 inches in diameter and 10 inches in height. A portion of a 4 per cent. solution of Rochelle salt, amounting to 5000 grs. of liquid, was covered over by nine times as much pure water, in this jar, and the salt allowed to diffuse upwards for three weeks at 56°. The upper third of the fluid column, amounting to 17,000 grs. of liquid, was then drawn off, evaporated to dryness, and the salt ignited and converted, by the addition of hydrochloric acid, into chloride, which weighed 3·14 grs. The salt proved to be a mixture of the two chlorides in the proportion of 2·43 grs. of chloride of potassium and 0·71 gr. of chloride of sodium. This gives the following as the composition of the diffusate:—

Tartrate of potash, . . . .	3·68
Tartrate of soda, . . . .	1·17
	<hr/> 4·85

It hence follows that the proportion of potash, or of tartrate of potash, in the diffusate is nearly three times greater than existed in the original Rochelle salt. It will be recollected that the salt decomposed is, strictly speaking, a bibasic tartrate of potash and soda, and not a double tartrate of potash and soda. The diffusate was observed to be exactly neutral to test-paper. This mode of diffusing upwards in water from the lower part of a deep jar obviously gives the greatest degree of separation attainable in consequence of unequal diffusibility.

I may confine myself at present to the conclusion that of the nine pairs of potash and soda salts, of which the diffusion is compared in this



paper, the potash salt uniformly exceeds in diffusibility the corresponding soda salt; that the ratio between the two classes is always sensibly the same, or exhibits only a small range of variation at the temperature of the experiments, which was near  $60^{\circ}$ ; with the peculiar exception of the hydrates of potash and soda.

## XIII.

ON THE APPLICATION OF LIQUID DIFFUSION TO  
PRODUCE DECOMPOSITIONS.

From *Chem. Soc. Journ.* vol. iii. p. 60, 1851.

THE experiments to be described in the sequel of this paper were conducted in the same manner as those contained in a late communication to the Royal Society.<sup>1</sup> A set of phials, of nearly equal capacity,



were made use of, all cast in the same mould, and further adjusted by grinding to a uniform size of aperture. The dimensions for a phial, (see Fig.) were 3.8 inches in height, with a neck 0.5 inch in depth; aperture 1.25 inch in diameter, and capacity to base of the neck, 2080 grains of water, or between 4 and 5 ounces. For each phial a plain glass jar was also provided, 4 inches in diameter and 7 inches in

depth. The method of observing the diffusion of a salt will be best explained by an example.

For my present object, it was necessary to observe the spontaneous diffusion into pure water of several salts, already dissolved in 100 times their weight of water. The phial was filled with such a solution of sal-ammoniac, for instance, to the base of the neck, or, more correctly, to a distance of exactly 0.5 inch from the ground surface of the lip. The neck of the phial was then filled up with distilled water, a light float being placed on the surface of the solution, and care taken to avoid agitation, after the phial had been placed within the jar. The latter was then filled up with distilled water, so as to cover the open phial to the depth of an inch, which required about twenty ounces of water. The saline liquid in the "solution-phial" is thus allowed to communicate freely with the water of the "water-jar." The water of the latter forms an atmosphere into which salts spread or diffuse, escaping from the solution-phial with different degrees of velocity. The phial and jar

<sup>1</sup> "On the Diffusion of Liquids." Read December 21, 1849.



together form the "diffusion-cell." The diffusion is interrupted by placing a small plate of ground glass upon the mouth of the phial, and raising the latter out of the jar. The amount of salt diffused, or the "diffusion-product," is learned by evaporating the water of the jar to dryness, or with this and the following chlorides, by precipitating with nitrate of silver.

The diffusion was always allowed to proceed for a period of exactly seven days, unless another time is expressly mentioned. The experiments were conducted in a vault, of which the temperature did not vary more than one degree on either side  $50^{\circ}$  F.

The 1 per cent. solution of sal-ammoniac, in the solution-phial, would contain 20.8 grains of salt. Of this quantity of salt, 3.49 grs. were found to diffuse out into the water-jar in the time mentioned, in one experiment, and 3.36 grains in another experiment. The mean of these two diffusion-products is 3.42 grs., which is, therefore, the quantity of hydrochlorate of ammonia diffused out of the solution-phial, containing a 1 per cent. solution of that salt, in a period of seven days.

The diffusion of a 1 per cent. solution of chloride of sodium, in similar circumstances, gave, in eight cells, the following products: 3.02, 2.83, 2.86, 2.68, 2.74, 2.70, 2.80, and 2.94 grs., of which the mean is 2.85 grs. These results for the chlorides of ammonium and sodium approach to the theoretical ratio of 1.4142 to 1.7320, that is, of the square root of 2 to the square root of 3.

Anhydrous chloride of calcium gave 2.01 and 2.04 grs. in two experiments; mean 2.02 grs.

Anhydrous chloride of magnesium gave 2.15 and 1.90 grs.; mean 2.03 grs. These two earthy chlorides appear, therefore, to be equally diffusible. I may place along with these results, the diffusion-products which the alkaline hydrates, and a few other salts would have afforded in similar circumstances, the latter numbers being deduced from experiments detailed in the paper on the diffusion of liquids already referred to.

Salt Diffused from a 1 per cent. Solution in Equal Times.

Hydrate of potash,	.	.	.	.	4.84 grs.
„ soda,	.	.	.	.	4.03 „
Chloride of ammonium,	.	.	.	.	3.42 „
„ potassium,	.	.	.	.	3.42 „
„ sodium,	.	.	.	.	2.85 „
Sulphate of soda,	.	.	.	.	2.35 „
Chloride of calcium,	.	.	.	.	2.02 „
„ magnesium,	.	.	.	.	2.03 „
Sulphate of lime,	.	.	.	.	1.21 „
„ magnesia,	.	.	.	.	1.21 „



The alkaline hydrates have the highest diffusibility, being twice as diffusive as the sulphates of the same bases, and four times as diffusive as the sulphates of magnesia and lime. The salts of potash and ammonia, of the same acid, have an equal diffusibility, which is greater than the diffusibility of the corresponding salts of soda.

Now it has been shown that, when two salts are dissolved together in the solution-phial, they diffuse independently, each salt maintaining its own rate of diffusion. Hence the possibility of separating salts to a certain extent, by diffusion, in a manner analogous to the separation of substances of unequal volatility by distillation. Further, decompositions may be effected by diffusion, such as the decomposition of alum, the sulphate of potash being separated from the sulphate of alumina, from the higher diffusibility of the former substance.

It appeared probable, also, that, in a mixture of several salts, the acids and bases would have a tendency to arrange themselves so as to form the most diffusive compounds, when an opportunity for diffusion was presented. This would be analogous to the sublimation of carbonate of ammonia, when carbonate of lime and hydrochlorate of ammonia are heated together. As the order of affinity is often determined in mixed salts by volatility or insolubility, according to the canons of Berthollet, so it may be regulated and determined, in a similar sense, by diffusibility.

The application which I have particularly in view, is the possible decomposition of the sulphates of potash and soda, and of the chlorides of potassium and sodium, by means of lime, when the affinity of that base for an acid is aided by the high diffusibility of the hydrate of potash or of soda.

1. A solution was made of 1 part of sulphate of potash in 100 parts of lime-water, with which six phials were filled, and placed to diffuse in jars containing lime-water, instead of water simply, for the usual period of seven days. To obtain the salts diffused, the fluid of the jars was treated with an excess of bicarbonate of ammonia and evaporated twice to dryness. The filtered liquid contained only sulphate and carbonate of potash, without a trace of lime. The proportions of these salts found, indicated a diffusion-product from two phials of—

Hydrate of potash,	.	.	1.08	grs.	23.69
Sulphate of potash,	.	.	3.48	„	76.31
			4.56	„	100.00

The diffusion-product of the remaining four cells was similar :

Hydrate of potash,	.	.	2.19	grs.	21.66
Sulphate of potash,	.	.	7.94	„	78.34
			10.13	„	100.00



More than a fifth part of the diffused salt appears thus to be hydrate of potash, and a considerable decomposition of the sulphate of potash has therefore taken place.

2. Sulphate of soda dissolved in lime-water, was diffused into lime-water, in a precisely similar series of experiments.

The diffusion-product obtained in a set of four cells, appeared to consist of—

Hydrate of soda, . . . .	0.90 grs.	11.45
Sulphate of soda, . . . .	6.87 „	88.55
	<hr/>	<hr/>
	7.77 „	100.00

Of another set of four cells, the diffusion-product was represented by—

Hydrate of soda, . . . .	0.93 grs.	13.22
Sulphate of soda, . . . .	6.10 „	86.78
	<hr/>	<hr/>
	7.03	100.00

The hydrate of soda formed and diffused, is very sensible, amounting on an average to about 12 per cent. of the whole diffused salt.

It may be remarked that, although sulphate of soda may be justly supposed to require a less powerful affinity to decompose it than sulphate of potash, still the latter salt appears to yield to the action of the lime to a greater extent than the former, in these experiments; the weight of hydrate of potash diffused being fully double that of the hydrate of soda. The result in question may be confidently referred to the superior diffusibility of the hydrate of potash, and establishes, beyond doubt, the nature of the agency by which the decomposition, in both cases, is principally, if not wholly, effected.

The low diffusibility of the sulphate of lime (one fourth of that of hydrate of potash) retains a large proportion of that salt behind in the solution-phial, where, indeed, it was deposited in crystals. It is proper to remark, that a similar deposition of sulphate of lime took place in lime-water containing so much as 1 per cent. of sulphate of potash or sulphate of soda, in the course of two or three days, in a close vessel, quite irrespective of diffusion. One of the solution-phials was found to contain so much as 2.04 grains of hydrate of potash, formed in consequence of this deposition of sulphate of lime, without any diffusion, in the course of seven days. The same decomposition of sulphate of potash, with deposition of sulphate of lime, was observed by Scheele, and afterwards referred, by Berthollet, to the insolubility of the latter salt, which enables the affinity of lime for sulphuric acid to prevail over that of potash for the same acid.



3. Similar solutions, of 1 per cent. of chlorides of potassium and sodium in lime-water, were diffused into lime-water.

Eight cells of chloride of potassium gave 25.51 grains of diffused salt, containing only 0.04 grain of hydrate of potash.

Eight cells of chloride of sodium gave 20.77 grains of diffused salt, containing no more than 0.08 grain of hydrate of soda.

The decomposition of the alkaline chlorides is so small as to be barely sensible, not exceeding, in the most favourable case, more than  $\frac{1}{250}$ th part of the salt diffused. Lime, therefore, appears incapable, although aided by diffusion, to decompose the chlorides of potassium and sodium to a sensible extent.

4. Solutions in lime-water were diffused of 0.25 and 0.5 per cent. of the alkaline sulphates, not with the view of increasing the product of alkali, but for the purpose of observing the diffusion, where no deposition of sulphate of lime is possible, owing to the dilute condition of the solutions. The experiments, however, come to be more liable to derangement from currents produced by small changes of temperature, and other accidental causes of dispersion, where the solution in the phial differs so little in density from the water of the jar.

One set of four cells, containing the quarter per cent. solution of sulphate of potassa in lime-water, gave 0.321 gr. of hydrate of potash. Another similar set gave 0.614 gr. of hydrate of potash. The hydrate of soda diffused from four cells of the quarter per cent. solution of sulphate of soda was 0.260 gr. The diffusion was always into lime-water.

The half per cent. solution of sulphate of potash in lime-water gave 0.62 gr. hydrate of potash in two cells; or twice as much alkali as the quarter per cent. solution. The diffusion-product was altogether 2.60 grs., so that 23.85 per cent. of the salt diffused consisted of hydrate of potash. No sulphate of lime crystallized, or was deposited in the phial or jar, in any of these experiments, so that the decomposition of the sulphate of potash by lime cannot be referred in any degree to the insolubility of sulphate of lime, but must be ascribed entirely to the high diffusibility of hydrate of potash.

5. Carbonate of lime dissolved in carbonic acid water, or a saturated solution of bicarbonate of lime, was now applied to form a 1 per cent. solution of sulphates of potash and soda. These solutions were diffused from the phials into pure water, as the liquid atmosphere of the jars. Decomposition of the alkaline sulphate always took place, and without any visible deposit of sulphate of lime, but to a less extent than in the preceding experiments with hydrate of lime. The proportion of potash salts diffused in two pairs of cells was 4.86 and 5.84 grs.; of which 0.26 and 0.30 gr. was carbonate of potash, or 5.35 and 6.2 per cent. of carbonate of potash.



The proportion of soda-salts diffused in two pairs of cells was 3.40 and 3.78 grs., of which 0.26 and 0.29 gr. was carbonate of soda; or 7.65 and 7.67 per cent. of carbonate of soda. The excess of carbonate of soda diffused over the carbonate of potash, in these experiments, is probably accidental.

The experiments on the decomposition of an alkaline sulphate by means of carbonate of lime, aided by diffusion, are chiefly interesting, as they illustrate a decomposition which may occur among the salts of the soil, and with the formation of an alkaline carbonate, from a reaction between carbonate of lime and an alkaline sulphate, although the solutions may be too dilute to admit of any separation of sulphate of lime in the solid state.

But the decomposition of the chlorides of potassium and sodium is a more important problem than that of the sulphates of potash and soda. The direct diffusion of these chlorides with hydrate of lime appears to be inadequate to produce this effect, for no more than a trace of fixed alkali was obtained in the experiments already described. It was further observed, that a saturated solution of the chlorides of potassium and sodium in lime-water did not afford the smallest appreciable quantity of alkali by diffusion. Bicarbonate of lime had no greater effect upon the alkaline chlorides. But the conjoint action of lime-water and the sulphate of lime upon these chlorides gave better results.

6. Lime-water and solution of sulphate of lime, both saturated solutions, were mixed together in equal volumes, and the liquid was employed to dissolve 1 per cent. of chloride of sodium. The phials charged with this solution were allowed to diffuse into pure water. After separating the hydrate of lime from the water of the jars, the latter exhibited only the faintest possible alkaline reaction due to soda. The proportion of alkali was too minute to be appreciated by the alkali-metrical method, although a quantity so small as 0.01 gr. could be determined. To enable the hydrate and sulphate of lime to act upon the chloride of sodium, it was found necessary first to heat the solution before diffusion.

7. The solution of sulphate of lime, with an addition of 2 per cent. of chloride of sodium, was kept at the boiling point for half an hour. No deposition of sulphate of lime occurred then, or after the liquid cooled. Two or three days afterwards, this solution was mixed with an equal volume of lime-water, and diffused into pure water, for the short period of three and a half days. The liquid of the jars was evaporated to dryness, as usual, with an excess of pure carbonate of ammonia, to precipitate the salts of lime. The hydrate of soda diffused in three cells amounted to 0.234 gr., and the sulphuric acid to 0.209 gr. Allow-



ing the sulphuric acid to have diffused as sulphate of soda, and putting out of consideration the undecomposed chloride of sodium which was also diffused, we have a diffusion-product of—

Hydrate of soda, . . .	0·234 gr.
Sulphate of soda, . . .	0·371 „
	<hr/>
	0·605 „

These quantities are necessarily small, from the form of the experiment, but could easily be increased by enlarging the diffusing surface, which is at present limited to the area of the aperture of the solution-phial. They are amply sufficient, however, to establish the fact that the united affinities of hydrate and sulphate of lime are sufficient to decompose chloride of sodium, when aided by diffusion of the hydrate of soda formed. Of chloride of potassium, we have reason to believe that the decomposition would be more considerable in similar circumstances.

Two phials of the same liquid, as in the last experiment, were diffused into water for the longer period of seven days and eighteen hours. The whole lime found afterwards in the water-jar, and precipitated by the addition of carbonate of ammonia, was represented by 1·01 grain of carbonate of lime. The soluble salts filtered from the last amounted to 6·14 grains, and contained carbonate of soda equivalent to 0·646 gr. of hydrate of soda, and sulphuric acid equivalent to 0·373 gr. of sulphate of soda. It is difficult to decide in what form the lime reached the water-jar, but this earth was probably diffused out of the solution-phial, partly as hydrate of lime, partly as sulphate of lime, but principally as chloride of calcium. The last two salts would destroy a portion of free alkali in the evaporation, but the hydrate of soda obtained, even after this deduction, amounted to 10·52 per cent. of the whole salts diffused. With a smaller quantity of chloride of sodium than 2 per cent. in the original mixture, the alkali, although not increased in absolute quantity, might no doubt come to form a considerably larger proportion of the diffusion-product.

The experiments also throw a curious light upon the condition of mixed salts. It follows, from the absence of hydrate of soda in the diffusion product of the first experiments, that cold solutions of sulphate of lime and chloride of sodium may be mixed without decomposition, or without any sensible formation of sulphate of soda. But on heating, this change is induced, and it is permanent; sulphate of soda is formed, and continues to exist in the cold solution: for it is the decomposition of that salt alone, by hydrate of lime, which appears to afford the diffused hydrate of soda. More than one condition of equilibrium is therefore possible for mixed solutions of sulphate of lime and



chloride of sodium. It would be interesting to submit such a mixture to a diffusion experiment, after being kept for different periods. The effects of time and temperature are so often convertible, that we might anticipate a gradual formation of sulphate of soda. If such be the case, we have an agency in the soil, by which the alkaline carbonates required by plants may be formed from the chlorides of potassium and sodium, as well as from the sulphates of potash and soda; for the sulphate of lime generally present will convert those chlorides into sulphates.

The mode in which the soil of the earth is moistened by rain is peculiarly favourable to separations by diffusion. The soluble salts of the soil may be supposed to be carried down together, to a certain depth, by the first portion of rain which falls, while they find afterwards an atmosphere of nearly pure water, in the moisture which falls last and occupies the surface stratum of the soil. Diffusion of the salts upwards into this water, with its separations and decompositions, must necessarily ensue. The salts of potash and ammonia, which are most required for vegetation, possess the highest diffusibility, and will rise first. The pre-eminent diffusibility of the alkaline hydrates may also be called into action in the soil by hydrate of lime, particularly as quicklime is applied for a top-dressing to grass lands.

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#### XIV.

#### ON THE CONCENTRATION OF ALCOHOL IN SÖMMERING'S EXPERIMENTS.

From *Brit. Assoc. Rep.* 1854 (Pt. ii.), p. 69.

THE author stated that when an open vessel is filled with a mixture of alcohol and water and exposed to the air, the alcohol goes off first and leaves the water; but if, as in Sömmering's experiments, a bladder be completely filled with dilute alcohol, the liquid will decrease in bulk, and the water pass through the membrane, leaving a much larger percentage of alcohol in the bladder. Sömmering describes the action of membrane to be improved by coating it with isinglass. Prof. Graham removed the membrane entirely, and made use of a septum of gelatin itself. Cotton calico was coated several times with a solution of isinglass and allowed to dry. A retentive vessel was thus prepared, in which alcohol in different states of dilution was placed, and kept between



100° and 12° Fahr. for twenty-four hours. Evaporation took place, which was uniformly attended by concentration of the spirit :—

180	grammes of alcohol	0·860	gave	150	grms. of	0·854
180	„	„	0·860	gave	146	„ of 0·852
180	„	„	0·880	gave	146	„ of 0·871
180	„	„	0·900	gave	154	„ of 0·888

or, the septum of gelatin alone acted exactly like the coats of bladder. Further, it was observed that dry gelatin (isinglass) placed in alcohol 0·860 increased 11 per cent. in weight, and at the same time lowered the gravity of the spirit to 0·857. There can be no doubt, therefore, that gelatin *per se* separates water from alcohol, and the colliferous tissues possess the same property. In the bladder experiment, the water thus absorbed by the membrane evaporates from the outer surface, and its place being constantly supplied from the dilute alcohol within, the latter comes to be rapidly concentrated.

## XV.

### LIQUID DIFFUSION APPLIED TO ANALYSIS.<sup>1</sup>

From *Phil. Trans.* 1861, pp. 183-224. [*Roy. Soc. Proc.* xi. 1860-62, pp. 243-247 ; *Annal. de Chimie*, lxxv. 1862, pp. 129-207 ; *Chemical News*, iv. 1861, pp. 86, 87 ; *Chem. Soc. Journ.* xv. 1862, pp. 216-270 ; Liebig, *Annal.* cxxi. 1862, pp. 1-77, cxxiii. 1862, pp. 90-112 ; *Nuovo Cimento*, xv. 1862, pp. 92-94 ; *Paris Comptes Rendus*, liii. 1861, pp. 275-279 ; *Phil. Mag.* xxiii. 1862, pp. 204-223, 290-306, 368-380 ; Poggend. *Annal.* cxiv. 1861, pp. 187-192.]

THE property of volatility, possessed in various degrees by so many substances, affords invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the Diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it. The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapour tensions. Thus hydrate of potash may be said to possess double the velocity of diffusion of sulphate of potash, and sulphate of potash again double the velocity of sugar, alcohol, and sulphate of magnesia. But the substances named belong all, as regards diffusion,

<sup>1</sup> Received May 8,—Read June 13, 1861.



to the more "volatile" class. The comparatively "fixed" class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme. Among the latter are hydrated silicic acid, hydrated alumina, and other metallic peroxides of the aluminous class, when they exist in the soluble form; with starch, dextrin and the gums, caramel, tannin, albumen, gelatine, vegetable and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to, appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatine appears to be its type, it is proposed to designate substances of the class as *colloids*, and to speak of their peculiar form of aggregation as the *colloidal condition of matter*. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as *crystalloids*. The distinction is no doubt one of intimate molecular constitution.

Although chemically inert in the ordinary sense, colloids possess a compensating activity of their own arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloids as can exist at a high temperature. Hence a wide sensibility on the part of colloids to external agents. Another and eminently characteristic quality of colloids, is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloids appear to have always a *pectous*<sup>1</sup> modification; and they often pass under the slightest influences from the first into the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point.

<sup>1</sup> Πηκτός, *curdled*. As fibrin, casein, albumen. But certain liquid colloid substances are capable of forming a jelly and yet still remain liquefiable by heat and soluble in water. Such is gelatine itself, which is not pectous in the condition of animal jelly; but may be so as it exists in the gelatiferous tissues.



For the mineral forms of silicic acid, deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition (H. Rose). The colloidal is, in fact, a dynamical state of matter; the crystalloidal being the statical condition. The colloid possesses *ENERGIA*. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element), may the characteristic protraction of chemico-organic changes also be referred.

A simple and easily applicable mode of effecting a diffusive separation is to place the mixed substance under a column of water, contained in a cylindrical glass jar of five or six inches in depth. The mixed solution may be conducted to the bottom of the jar by the use of a fine pipette, without the occurrence of any sensible intermixture. The spontaneous diffusion, which immediately commences, is allowed to go on for a period of several days. It is then interrupted by siphoning off the water from the surface in successive strata, from the top to the bottom of the column. A species of cohobation has been the consequence of unequal diffusion, the most rapidly diffusive substance being isolated more and more as it ascended. The higher the water column, sufficient time being always given to enable the most diffusive substance to appear at the summit, the more completely does a portion of that substance free itself from such other less diffusive substances as were originally associated with it. A marked effect is produced even where the difference in diffusibility is by no means considerable, such as the separation of chloride of potassium from chloride of sodium, of which the relative diffusibilities are as 1 to 0.841. Supposing a third metal of the potassium group to exist, standing above potassium in diffusibility as potassium stands above sodium, it may be safely predicted that the new metal would admit of being separated from the other two metals by an application of the jar-diffusion above described.

A certain property of colloid substances comes into play most opportunely in assisting diffusive separations. The jelly of starch, that of animal mucus, of pectin, of the vegetable gelose of Payen, and other solid colloidal hydrates, all of which are, strictly speaking, insoluble in cold water, are themselves permeable when in mass, as water is, by the more highly diffusive class of substances. But such jellies greatly resist the passage of the less diffusive substances, and cut off entirely other colloid substances like themselves that may be in solution. They resemble animal membrane in this respect. A mere film of the jelly has the separating effect. Take for illustration the following simple experiment.

A sheet of very thin and well-sized letter-paper, of French manufacture, having no porosity, was first thoroughly wetted and then laid



upon the surface of water contained in a small basin of less diameter than the width of the paper, and the latter depressed in the centre so as to form a tray or cavity capable of holding a liquid. The liquid placed upon the paper was a mixed solution of cane-sugar and gum-arabic, containing 5 per cent. of each substance. The pure water below and the mixed solution above were therefore separated only by the thickness of the wet sized paper. After twenty-four hours the upper liquid appeared to have increased sensibly in volume, through the agency of osmose. The water below was found now to contain three-fourths of the whole sugar, in a condition so pure as to crystallize when the liquid was evaporated on a water-bath. Indeed the liquid of the basin was only in the slightest degree disturbed by sub-acetate of lead, showing the absence of all but a trace of gum. Paper of the description used is sized by means of starch. The film of gelatinous starch in the wetted paper has presented no obstacle to the passage of the crystalloid sugar, but has resisted the passage of the colloid gum. I may state at once what I believe to be the mode in which this takes place.

The sized paper has no power to act as a filter. It is mechanically impenetrable, and denies a passage to the mixed fluid as a whole. Molecules only permeate this septum, and not masses. The molecules also are moved by the force of diffusion. But the water of the gelatinous starch is not directly available as a medium for the diffusion of either the sugar or gum, being in a state of true chemical combination, feeble although the union of water with starch may be. The hydrated compound itself is solid, and also insoluble. Sugar, however, with all other crystalloids, can separate water, molecule after molecule, from any hydrated colloid, such as starch. The sugar thus obtains the liquid medium required for diffusion, and makes its way through the gelatinous septum. Gum, on the other hand, possessing as a colloid an affinity for water of the most feeble description, is unable to separate that liquid from the gelatinous starch, and so fails to open the door for its own passage outwards by diffusion.

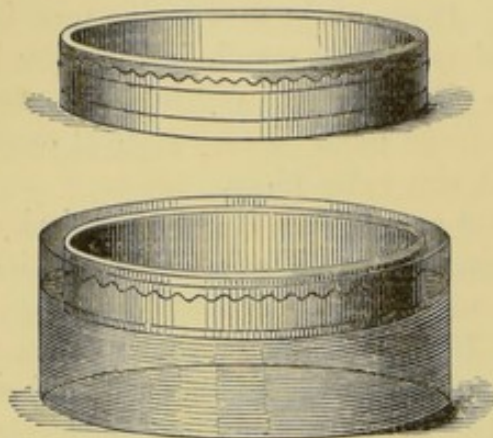
The separation described is somewhat analogous to that observed in a soap-bubble inflated with a gaseous mixture composed of carbonic acid and hydrogen. Neither gas, as such, can penetrate the water-film. But the carbonic acid, being soluble in water, is condensed and dissolved by the water-film, and so is enabled to pass outwards and reach the atmosphere; while hydrogen, being insoluble in water, or nearly so, is retained behind within the vesicle.

It may perhaps be allowed to me to apply the convenient term *dialysis* to the method of separation by diffusion through a septum of gelatinous matter. The most suitable of all substances for the dialytic septum appears to be the commercial material known as vegetable



parchment or parchment-paper, which was first produced by M. Gaine, and is now successfully manufactured by Messrs. De la Rue. This is unsized paper, altered by a short immersion in sulphuric acid, or in chloride of zinc, as proposed by Mr. T. Taylor. Paper so metamorphosed acquires considerable tenacity, as is well known; and when wetted it expands and becomes translucent, evidently admitting of hydration. A slip of 25 inches in length was elongated 1 inch in pure water, and 1·2 inch in water containing 1 per cent. of carbonate of potash. In the wetted state parchment-paper can easily be applied to a light hoop of wood, or, better, to a hoop made of sheet gutta percha, 2 inches in depth and 8 or 10 inches in diameter, so as to form a vessel like a sieve in

FIG. 1. —Hoop Dialyser.



form (fig. 1.). The disc of parchment-paper used should exceed in diameter the hoop to be covered by 3 or 4 inches, so as to rise well round the hoop. It may be bound to the hoop by string, or by an elastic band, but should not be firmly secured. The parchment-paper must not be porous. Its soundness will be ascertained by sponging the upper surface with pure water, and then observing that no wet spots show themselves

on the opposite side. Such defects may be remedied by applying liquid albumen, and then coagulating the same by heat. Mr. De la Rue recommends the use of albumen in cementing parchment-paper, which thus may be formed into cells and bags very useful in dialytic experiments. The mixed fluid to be dialysed is poured into the hoop upon the surface of the parchment-paper to a small depth only, such as half an inch. The vessel described (*dialyser*) is then floated in a basin containing a considerable volume of water, in order to induce the egress of the diffusive constituents of the mixture. Half a litre of urine, dialysed for twenty-four hours, gave its crystalloidal constituents to the external water. The latter, evaporated by a water-bath, yielded a white saline mass. From this mass urea was extracted by alcohol in so pure a condition as to appear in crystalline tufts upon the evaporation of the alcohol.

### 1. *Jar-diffusion.*

The mode of diffusing more lately followed, which I have already alluded to as jar-diffusion, is extremely simple, and gives results of more precision than could possibly be anticipated. The salt is allowed to rise



from below into a cylindrical column of water, and after a fixed time, the proportion of salt which has risen to various heights in the column is observed. The water was contained in a plain cylindrical glass jar, of about 152 millimetres (6 inches) in height and 87 millimetres (3.45 inches) in width. In operating, seven-tenths of a litre of water were first placed in the jar, and then one-tenth of a litre of the liquid to be diffused was carefully conveyed to the bottom of the jar by means of a fine pipette. The whole fluid column then measured 127 millimetres (5 inches) in height. So much as five or six minutes of time were occupied in emptying the pipette at the bottom of the jar, and extremely little disturbance was occasioned in the superincumbent water, as could be distinctly seen when the liquid introduced by the pipette was coloured. The jar was then left undisturbed, to allow diffusion to proceed; the experiments being always conducted in an apartment of constant, or nearly constant, temperature. When a certain time had elapsed, the diffusion was interrupted by drawing off the liquid from the top, by means of a small siphon, slowly and deliberately as the liquid had been first introduced, in portions of 50 cubic centimetres, or one-sixteenth of the whole volume. The open end of the short limb of the siphon was kept in contact with the surface of the liquid in the jar, and the portion of liquid drawn off was received in a graduated measure. By evaporating each fraction separately, the quantity of salt which had risen into equal sections of the liquid column was ascertained. From the bottom of two jars, A and B for instance, a 10 per cent. solution of chloride of sodium was diffused for a period of fourteen days. The whole quantity of salt present in each jar was 10 grammes, which was found at the end to be distributed as follows in the different sectional strata of fluid, numbering them from the top downwards:—

In the first or highest stratum, 0.103 and 0.105 gramme of salt in A and B respectively; in the second stratum, 0.133 and 0.125; in the third stratum, 0.165 and 0.158; in the fourth stratum, 0.204 and 0.193; in the fifth stratum, 0.273 and 0.260; in the sixth stratum, 0.348 and 0.332; in the seventh stratum, 0.440 and 0.418; in the eighth stratum, 0.545 and 0.525; in the ninth stratum, 0.657 and 0.652; in the tenth stratum, 0.786 and 0.747; in the eleventh stratum, 0.887 and 0.875; in the twelfth stratum, 0.994 and 0.984; in the thirteenth stratum, 1.080 and 1.000; in the fourteenth stratum, 1.176 and 1.198; in the fifteenth and sixteenth strata together, 2.209 and 2.324 grammes. With differences so moderate in amount between corresponding strata in the two experiments, this method of observing diffusion may claim a considerable degree of precision.

In similar experiments made at the same time and temperature with sugar, gum-arabic and tannin of nut-galls, the final distribution of each



substance was different in each case, and the results may be placed together in illustration of unequal diffusibility, as exhibited by this method of observation. Two experiments were made on each substance, as with chloride of sodium, but the mean result only need be stated.

TABLE I.—Diffusion of 10 per cent. solutions (10 grammes of substance in 100 cub. cent. of fluid) into pure water, after fourteen days, at 10° (50° Fahr.)

Number of stratum (from above downwards).	Chloride of sodium.	Sugar.	Gum.	Tannin.
1	·104	·005	·003	·003
2	·129	·008	·003	·003
3	·162	·012	·003	·004
4	·198	·016	·004	·003
5	·267	·030	·003	·005
6	·340	·059	·004	·007
7	·429	·102	·006	·017
8	·535	·180	·031	·031
9	·654	·305	·097	·069
10	·766	·495	·215	·145
11	·881	·740	·407	·288
12	·991	1·075	·734	·556
13	1·090	1·435	1·157	1·050
14	1·187	1·758	1·731	1·719
15 and 16	2·266	3·783	5·601	6·097
	9·999	10·003	9·999	9·997

The superimposed column of water being 111 millimetres (4·38 inches) in height, the chloride of sodium, it will be observed, has diffused in sensible quantity to the top, and could have risen higher; the upper layer being found to contain 0·104 gramme of salt, or 1 per cent. of the whole quantity present. The apex of the diffusion column of sugar appears to have just reached the top of the liquid in the fourteen days of the experiment, for ·005 gramme only of that substance is found in the first stratum, followed by ·008, ·012, ·016, and ·030 in the following strata. Again, no gum appears to be carried by diffusion higher than the seventh stratum (2·2 inches), which stratum contains ·006 gramme, followed by ·031 gramme in the eighth stratum. The minute quantities of substance shown in the first to the sixth stratum, and which do not altogether exceed ·020 gramme, are no doubt the result of accidental dispersion, arising probably from a movement of the upper fluid occasioned by slight inequalities of temperature. The diffusion of tannin is even less advanced than that of gum; but the former numbers are apparently influ-



enced by a partial decomposition, to which tannin is known to be liable, and which gives rise to new and more highly diffusible substances.

Experiments continued, like those last described, for a constant time, do not exhibit the exact relative diffusibilities, although these could be obtained by proceeding to ascertain, by repeated trial, the various times required to bring about a similar distribution and equal amount of diffusion in all the salts. The numbers observed, however, may afford data for the deduction of the relative diffusibilities by calculation.

A particular advantage of the new method is the means which it affords of ascertaining the absolute rate or velocity of diffusion. It becomes possible to state the distance which a salt travels per second in terms of the metre. It is easy to see that such a constant must enter into all the chronic phenomena of physiology, and that it holds a place in vital science not unlike the time of the falling of heavy bodies in the physics of gravitation. It may therefore be not amiss to place here in a short tabular form the results observed of the diffusion of a few more substances, conducted in the same manner as the preceding.

TABLE II.—Diffusion of 10 per cent. solutions for 14 days.

Number of stratum (from above downwards).	Sulphate of magnesia, at 10°.	Albumen, at 13° to 13°·5.	Caramel, at 10° to 11°.
1	·007		
2	·011		
3	·018		
4	·027		
5	·049		
6	·085	.....	·003
7	·133	.....	·005
8	·218	·010	·010
9	·331	·015	·023
10	·499	·047	·033
11	·730	·113	·075
12	1·022	·343	·215
13	1·383	·855	·705
14	1·803	1·892	1·725
15 and 16	3·684	6·725	7·206
	10·000	10·000	10·000

The sulphate of magnesia was anhydrous. The albumen was purified by Wurtz's method. The caramel was partly purified by precipitation by alcohol, as recommended by Frémy, and further by other means which will again be referred to. It will be remarked that the diffusion of sulphate of magnesia exhibited above is very similar to that of sugar in a former Table, but is slightly less advanced. The similarity in



diffusibility of these two substances had already been observed in the experiments of former papers. The fall in rate on passing from these crystalloids to the colloids tannin, albumen, and caramel, is very striking. The elevation in the liquid column attained by albumen or by caramel is moderate indeed compared with that of crystalline substances. Of albumen, which will be looked upon with most interest, no portion whatever was found in the seven higher strata. It appeared to the extent of 0.010 gramme in the eighth stratum, 0.015 in the ninth stratum, 0.047 in the tenth stratum, 0.113 in the eleventh stratum, 0.343 in the twelfth stratum; while the great mass of this substance remained in the four lower strata. The diffused albumen did not appear to lose its coagulability, or to be otherwise altered. It will be seen immediately that the diffusion of sugar advances as much in two days as the albumen above in fourteen days (Table IV.).

The diffusion of caramel is the slowest of all, and does not much exceed in fourteen days the diffusion of sugar in a single day.

It was considered useful to possess examples of the progress of diffusion, in one or two selected substances, for successive periods of time, so as to exemplify the continuous progress of diffusion in these substances. Such a chronological progress of diffusion in a particular substance becomes a standard of comparison for single experiments on the diffusion of other substances. The substances selected were chloride of sodium and cane-sugar.

TABLE III.—Diffusion of a 10 per cent. solution of Chloride of Sodium in different times.

Number of stratum.	In four days, at 9° to 10°.	In five days, at 11°-75.	In seven days, at 9°.	In fourteen days, at 10°.
1	·004	·004	·013	·104
2	·004	·006	·017	·129
3	·005	·011	·028	·162
4	·011	·020	·051	·198
5	·023	·040	·081	·267
6	·040	·075	·134	·340
7	·080	·134	·211	·429
8	·145	·233	·318	·535
9	·261	·368	·460	·654
10	·436	·589	·640	·766
11	·706	·762	·850	·881
12	1·031	1·090	1·057	·991
13	1·416	1·357	1·317	1·090
14	1·815	1·697	1·527	1·187
15 and 16	4·023	3·613	3·294	2·266
	10·000	9·999	9·998	9·999



TABLE IV.—Diffusion of a 10 per cent. solution of Cane-sugar in different times.

Number of stratum.	In one day, at 10°-75.	In two days, at 10°.	In six days, at 9°.	In seven days, at 9°.	In eight days, at 9°.	In fourteen days, at 10°.
1	.....	.....	·001	·002	·002	·005
2	.....	.....	·002	·002	·003	·008
3	.....	.....	·002	·003	·003	·012
4	.....	.....	·002	·004	·004	·016
5	.....	.....	·003	·004	·007	·030
6	.....	.....	·005	·007	·012	·059
7	.....	.....	·011	·020	·031	·102
8	·002	·002	·024	·051	·072	·180
9	·002	·008	·071	·121	·154	·305
10	·005	·027	·170	·260	·304	·495
11	·024	·107	·376	·507	·555	·740
12	·133	·344	·727	·897	·858	1·075
13	·597	·930	1·282	1·410	1·365	1·435
14	1·850	1·940	1·930	1·950	1·955	1·758
15 and 16	7·386	6·641	5·392	4·760	4·674	3·783
	9·999	9·999	9·998	9·998	9·999	10·003

The scheme of the diffusion of the chloride of sodium may afford terms of comparison for the metallic salts, acids and other highly diffusible substances, while the scheme of sugar will be found more useful in appreciating the diffusion of organic and other less diffusible substances. In comparing the two Tables together, it appears that a fourteen days' diffusion of sugar is greater in amount than a four days' diffusion of chloride of sodium, but less than a five days' diffusion of the same substance. The diffusion of chloride of sodium appears to be pretty nearly three times greater (or more rapid) than that of sugar.

The following experiments were made upon hydrochloric acid and chloride of sodium at a somewhat lower temperature and for times which are different, but which give a nearly equal diffusion for each substance.

TABLE IV. *bis.*—



TABLE IV. *bis.*—10 per cent. solutions.

Number of stratum.	Hydrochloric acid, in grammes. Three days at 5°.	Chloride of sodium, in grammes. Seven days at 5°.
1	·003	·003
2	·006	·009
3	·012	·010
4	·022	·026
5	·043	·055
6	·086	·082
7	·162	·165
8	·308	·270
9	·406	·403
10	·595	·595
11	·837	·823
12	1·080	1·085
13	1·163	1·270
14	1·578	1·615
15 and 16	3·699	3·589
	10·000	10·000

The diffusion of hydrochloric acid in three days corresponds closely with the diffusion of chloride of sodium in seven days. The times of equal diffusion for these two substances, at the temperature of the experiment, appear accordingly to be 1 (hydrochloric acid) and 2·33 (chloride of sodium). Hydrochloric acid and the allied hydracids, with other monobasic acids, are the most diffusive substances known. The general results of several series of experiments may be expressed approximately by the following numbers :—

*Approximate times of equal diffusion.*

Hydrochloric acid,	.	.	.	1
Chloride of sodium,	.	.	.	2·33
Sugar,	.	.	.	7
Sulphate of magnesia,	.	.	.	7
Albumen,	.	.	.	49
Caramel,	.	.	.	98

It is curious to observe the effect of changing the liquid atmosphere in which diffusion takes place, which is water in all these experiments, and replacing it by another fluid, namely alcohol. Two substances were diffused in the usual manner, but with this difference, that the substances were dissolved in alcohol, and the solutions placed under a column of the same liquid in the jar. The alcohol was of sp. gr. 0·822 (90 per cent.)



TABLE V.—Diffusion in Alcohol of 10 per cent. solutions of Iodine and of Acetate of Potash in seven days.

Number of stratum.	Iodine at 14°.	Acetate of potash, at 14° to 15°.
1	·028	·055
2	·033	·057
3	·046	·061
4	·038	·063
5	·037	·064
6	·039	·066
7	·081	·070
8	·143	·071
9	·263	·072
10	·417	·095
11	·637	·285
12	·936	·619
13	1·235	1·157
14	1·506	1·907
15 and 16	4·561	5·358
	10·000	10·000

TABLE V. *bis.*—Diffusion in Alcohol of a 10 per cent. solution of Resin, for seven days, at 14°·5.

Number in stratum.	Diffusate, in grammes.
1	·017
2	·017
3	·018
4	·017
5	·019
6	·020
7	·022
8	·024
9	·025
10	·080
11	·210
12	·498
13	·992
14	1·700
15 and 16	6·341
	10·000



The experiments were conducted in the absence of light, and there is no reason to believe that the iodine acted chemically upon the alcohol. The diffusion is more advanced in the iodine than in the acetate of potash, but in both is moderate in amount, confirming the early experiments with phials, which appeared to show that the diffusion process was several times slower in alcohol than in water. The small quantities of iodine found in each of the six superior strata are nearly equal, and were no doubt accidentally elevated by the mobility of this fluid, arising from its high dilatability by heat compared with that of water at the same low temperature. The diffusion may be considered then as confined to the nine lower strata, and considerably resembles that of sugar in water for eight days.

The diffusion of acetate of potash is still less advanced than that of iodine, and is probably confined to the six lower strata, the salt found in the higher strata presenting in its distribution the appearance of having been carried there by a movement of the fluid consequent upon heat-dilatation, and not by diffusion. The diffusion of acetate of potash in alcohol observed during seven days approximates to that of sugar in water during six days (Table IV.)

I now proceed to observations of the simultaneous diffusion of two substances in the same fluid. The great object of this class of experiments was to separate salts of unequal diffusibility, and to test the application of diffusion as an analytical process. A mixture of two salts being placed at the bottom of the jar, it may be expected that the salts will diffuse pretty much as they do when they are diffused separately; the more diffusive salt travelling most rapidly, and showing itself first and always most largely in the upper strata. The early experiments of diffusion from phials had shown indeed that inequality of diffusion is increased by mixture, and the actual separation is consequently greater than that calculated from the relative diffusibilities of the mixed substances. Chlorides of potassium and sodium diffuse nearly in the proportion of 1 to 0·841, according to the earlier experiments. They may afford, therefore, the means of observing the amount of separation that may be produced by a very moderate difference in diffusibility. A mixture of 5 grammes of each salt in the usual 100 cub. cent. of water was diffused.



TABLE VI.—Diffusion of a mixture of 5 per cent. of Chloride of Potassium and 5 per cent. of Chloride of Sodium, for seven days, at 12° to 13°.

Number of stratum.	Chloride of potassium.	Chloride of sodium.	Total diffusate.
1	·018	·014	·032
2	·025	·015	·040
3	·044	·014	·058
4	·075	·017	·092
5	·101	·034	·135
6	·141	·063	·204
7	·185	·104	·289
8	·252	·151	·403
9	·330	·212	·542
10	·349	·351	·700
11	·418	·458	·876
12	·511	·559	1·070
13	·552	·684	1·236
14	·615	·772	1·387
15 and 16	1·385	1·551	2·936
	5·001	4·999	10·000

In the upper part of the Table chloride of potassium always appears in excess, but not in so large a proportion in the first three strata as in the fourth. This inequality may be partly owing to mechanical dispersion of the mixed solution, but is to be referred chiefly, I believe, to errors of analysis from a loss of the chloride of potassium difficult to avoid in the determination of minute proportions of that salt by means of chloride of platinum. Of 92 milligrammes of salt found in the fourth stratum, 75 milligrammes, or 81·5 per cent., are chloride of potassium. The first six strata contain together 561 milligrammes, of which 404 milligrammes, or 72 per cent., that is nearly three-fourths, are chloride of potassium. We have to descend to the tenth stratum before the salts are found in equal proportions. The progression is then inverted, and chloride of sodium comes to preponderate in the lower strata.

It is evident that the preceding experiment might be so conducted as to diffuse away the chloride of potassium and leave below a mixture containing chloride of sodium in relative excess, to as great an extent as the chloride of potassium is found above, in the last experiment.

Further, the mixture in which chloride of potassium was concentrated in the experiment described, so as to form 72 per cent. of the whole mixture, might be subjected again to diffusion in the same manner. In an experiment upon a mixture of 7·5 grammes of chloride



of potassium and 2.5 grammes of chloride of sodium, the six upper strata gave 640 milligrammes of salt, of which 610 milligrammes, or 95.3 per cent., were chloride of potassium. It is obvious that by repeating this diffusive rectification a sufficient number of times, a portion of the more diffusive salt might be obtained at last in a state of sensible purity.

The preceding example illustrates the separation of unequally diffusive metals or bases; the following example, on the other hand, the separation of unequally diffusive acids united with a common base. Chloride of sodium and sulphate of soda diffuse separately in the phial experiments in the proportion of 1 to 0.707.

TABLE VII.—Diffusion of 5 per cent. of Chloride of Sodium and 5 per cent. of anhydrous Sulphate of Soda, for seven days, at  $10^{\circ}$  to  $10^{\circ}.75$ .

Number of stratum.	Chloride of sodium, in grammes.	Sulphate of soda, in grammes.	Total diffusate, in grammes.
1	.009	.....	.009
2	.013	.001	.014
3	.024	.002	.026
4	.038	.003	.041
5	.060	.006	.066
6	.095	.012	.107
7	.141	.029	.170
8	.203	.059	.262
9	.278	.115	.393
10	.360	.205	.565
11	.473	.317	.790
12	.560	.507	1.067
13	.637	.694	1.331
14	.718	.909	1.627
15 and 16	1.390	2.141	3.531
	4.999	5.000	9.999

Here the separation is still more sensible than before with the bases. The six upper strata contain 263 milligrammes of salt, of which 239 milligrammes, that is 90.8 per cent., are chloride of sodium. The salt of the upper eight strata amounts to 695 milligrammes, of which 583 milligrammes, or 83.9 per cent., are chloride of sodium.

How long the diffusion should be continued in a liquid column of limited height, such as in these experiments, so as to produce the greatest separation, is a question of some interest, which can only



be answered by experiment. The last diffusion was accordingly repeated, with the difference that it was continued for double the former time.

TABLE VIII.—Diffusion of 5 per cent. of Chloride of Sodium and 5 per cent. of Sulphate of Soda, for fourteen days, at  $10^{\circ}$  to  $11^{\circ}$ .

Number of stratum.	Chloride of sodium, in grammes.	Sulphate of soda, in grammes.	Total diffusate, in grammes.
1	·077	·005	·082
2	·089	·009	·098
3	·105	·014	·119
4	·130	·026	·156
5	·161	·044	·205
6	·199	·072	·271
7	·240	·111	·351
8	·289	·173	·462
9	·337	·241	·578
10	·392	·334	·726
11	·433	·433	·866
12	·487	·539	1·026
13	·525	·646	1·171
14	·555	·745	1·300
15 and 16	·979	1·609	2·588
	4·998	5·001	9·999

The salt contained in the three upper strata amounts to 299 milligrammes, of which 271, or 90·6 per cent. of the whole, are chloride of sodium. The upper five strata yield 660 milligrammes of salt, of which 562 milligrammes, or 85·1 per cent., are chloride of sodium. These proportions are not dissimilar to those deduced from the former Table, and show that little is gained in the way of separation by extending the diffusion-period from seven to fourteen days; unless indeed the column of fluid be increased in height at the same time.

It might be worth observing whether the separation of two unequally diffusive metals can be favoured by varying the acid, or form of combination; whether, for instance, the hydrates of potash and soda would not separate to a greater extent than has been observed of the chlorides of potassium and sodium, the separate diffusibilities of the former substances being as 1 to 0·7, while that of the latter are as 1 to 0·841. I have not, however, pursued this branch of the subject.

The separation of the same metals from each other may possibly be favoured in another manner. In the preceding experiments (Table VI.) the two metals were in union with the same acid, or rather both were



in the state of chloride. But the metals might be used in combination with different acids, and these acids themselves might be of equal or of unequal diffusibility. If of equal diffusibility, such as nitric and hydrochloric acids, no reason appears why the acids should affect the amount of separation. But if the acids are unlike in diffusibility, the case is not so clear. If, for instance, the potassium were in the form of chloride and the sodium of that of sulphate, might not the diffusion of the potassium be promoted by the highly diffusive chlorine with which it is associated, and the diffusion of the soda, on the other hand, be retarded by its association with the slowly diffusive sulphuric acid? Will, in fine, the separation of the metals be greater from a mixture of chloride of potassium and sulphate of soda, or even from sulphate of potash and chloride of sodium, than from the two chlorides, or from the two sulphates? The inquiry, it will be remarked, raises the whole question of the distribution of acid and base in solutions of mixed salts. It will be illustrated by a comparison of the diffusion of chloride of potassium mixed with sulphate of soda, with the diffusion of sulphate of potash mixed with the chloride of sodium, the salts being taken in equivalent proportions.

TABLE IX.—Diffusion of a mixture of 5·12 per cent. of Chloride of Potassium and 4·88 per cent. of Sulphate of Soda (equivalent proportions), for seven days, at 14°.

Number of stratum.	Potassium, in grammes.	Sulphuric acid, in grammes.	Total diffusate, in grammes.
1	·028	·002	·024
2	·035	·002	·030
3	·048	·004	·045
4	·064	·009	·066
5	·092	·016	·097
6	·128	·032	·149
7	·174	·058	·215
8	·242	·105	·316
9	...	...	·441
10	...	...	·615
11	...	...	·815
12	...	...	1·042
13	...	...	1·290
14	...	...	1·517
15 and 16	...	...	3·346
			10·008



TABLE X.—Diffusion of a mixture of 4.01 per cent. of Chloride of Sodium and 5.99 per cent. of Sulphate of Potash (equivalent proportions), for seven days, at 14°.

Number of stratum.	Potassium, in grammes.	Sulphuric acid, in grammes.	Total diffusate, in grammes.
1	.028	.002	.023
2	.034	.002	.030
3	.049	.004	.044
4	.064	.009	.065
5	.092	.015	.096
6	.128	.031	.149
7	.172	.059	.219
8	.242	.104	.315
9	...	...	.435
10	...	...	.600
11	...	...	.797
12	...	...	1.025
13	...	...	1.261
14	...	...	1.480
15 and 16	...	...	3.467
			10.016

The weight of the mixed salt was always 10 grammes. The diffusions exhibited in the two Tables are strikingly similar, and indeed may be considered as identical. It thus appears that the diffusion of the metals is not affected by the acid with which they are in combination. The result is quite in harmony with Berthollet's view, that the acids and bases are indifferently combined, or that a mixture of chloride of potassium and sulphate of soda is the same thing as a mixture of sulphate of potash and chloride of sodium, when the mixtures are in a state of solution. With two acids very unequal in their affinity for bases, the result possibly might be very different.

## 2. *Effect of Temperature on Diffusion.*

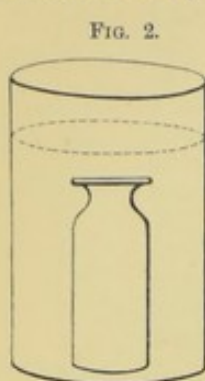
Diffusion is promoted by heat, and separations may accordingly be effected in a shorter time at high than at low temperatures. In a series of observations made upon hydrochloric acid, the diffusion of that substance was carefully determined at 15.5 (60° F.), and at three higher points, advancing by 11.11 (20° F.). The ratios of the diffusions observed were as follows:—

Diffusion of hydrochloric acid at 15.55 (60° F.), 1	
„ „ at 26.66 (80° F.), 1.3545	
„ „ at 37.77 (100° F.), 1.7732	
„ „ at 48.88 (120° F.), 2.1812	



The increments of diffusibility, 0.3545, 0.4187, and 0.408 for equal increments of temperature, are probably affected by small errors of observation, but they appear to indicate that the diffusion increases at a higher, although not greatly higher, rate than the temperature. The average increase of diffusibility for the whole range of temperature observed is 0.03543, or  $\frac{1}{28}$  for each degree (0.01969, or  $\frac{1}{50}$  nearly for 1° F.)

The preceding experiments were made by diffusing a 2 per cent. solution of hydrochloric acid from wide-mouth phials immersed in a jar



of water, as in my former experiments.<sup>1</sup> The times were observed in which an equal amount of the acid (0.777 gramme from three phials) was diffused out. These times of equal diffusion were 72 hours at 15°·55 (60° F.); 53.15 hours at 26°·66 (80° F.); 40.6 hours at 37°·77 (100° F.); and 33 hours at 48°·88 (120° F.)

The diffusate from a 2 per cent. solution of chloride of potassium in similar circumstances was 0.6577 gramme,

In 101.75 hours, at 15°·55 (60° F.); and

In 41.93 hours, at 48°·88 (120° F.)

The diffusate from a 2 per cent. solution of chloride of sodium was 0.6533 gramme,

In 124.75 hours, at 15°·55 (60° F.);

In 49.60 hours, at 48°·88 (120° F.).

In equal times the diffusate would be

For chloride of potassium at 15°·55 (60° F.), 1

„ „ at 48°·88 (120° F.), 2.426

For chloride of sodium at 15°·55 (60° F.), 1

„ „ at 48°·88 (120° F.), 2.5151.

As the ratio between the diffusates of hydrochloric acid, at the same two temperatures, was 1 to 2.1812, it appears that the acid is less increased in diffusibility than the salts at the higher temperature; chloride of sodium also is slightly more increased than chloride of potassium. The more highly diffusive the substance the less does it appear to gain by heat. Chloride of sodium appears to be sensibly  $2\frac{1}{2}$  times more diffusible at 48°·88 (120° F.) than at 15°·55 (60° F.): this gives an average increase of 0.014, or  $\frac{1}{71}$  for 1 degree (0.025 for 1° F., or  $\frac{1}{40}$ . The inequality of diffusion which the three substances referred to exhibit at a low temperature becomes therefore less at high temperatures; and it would

<sup>1</sup> *Philosophical Transactions*, 1850, p. 25.



appear to be the effect of a high temperature to assimilate diffusibilities. Heat, then, although it quickens the operation of diffusion, does not appear otherwise to promote the separation of unequally diffusive substances.

The results in such experiments are less disturbed by changes of temperature, if at all gradual, than might be supposed. A sensible separation was obtained of hydrochloric acid and chloride of sodium from each other, in a solution containing 2 per cent. of each substance, when the water-jar was heated up from  $15^{\circ}55$  to  $95^{\circ}$  C. in two hours, and maintained at the latter temperature during four hours more. Diffusion appeared to be accelerated about six times at the higher temperature.

At low temperatures, again, diffusion is proportionally slow. The ratio of diffusibility of the following salts at two different temperatures appeared to be,—

For chloride of potassium	at $5^{\circ}3$ ( $41^{\circ}5$ F.), 1 ; at $16^{\circ}6$ ( $62^{\circ}$ F. ),	1.4413
For chloride of sodium	at $5^{\circ}3$ ( $41^{\circ}5$ F.), 1 ; at $17^{\circ}4$ ( $63^{\circ}4$ F.),	1.4232
For nitrate of soda	at $5^{\circ}3$ ( $41^{\circ}5$ F.), 1 ; at $17^{\circ}4$ ( $63^{\circ}4$ F.),	1.4475
For nitrate of silver	at $5^{\circ}3$ ( $41^{\circ}5$ F.), 1 ; at $17^{\circ}4$ ( $63^{\circ}4$ F.),	1.3914

The salts are unequally affected to a sensible extent; and it will be observed that the superiority of chloride of potassium over chloride of sodium, in diffusibility, is increased at the low temperature.

Within the range of temperature of the preceding experiments, the diffusibility of chloride of sodium being taken as 1 at  $17^{\circ}4$  ( $63^{\circ}4$  F.), it becomes 0.7026 at  $5^{\circ}3$  ( $41^{\circ}5$  F.); or it diminishes 0.0246, or  $\frac{1}{40.7}$ , for a depression of  $1^{\circ}$  (0.0136, or  $\frac{1}{73.5}$ , for a depression of  $1^{\circ}$  F.)

### 3. Dialysis.

Passing from liquid diffusion in the water-jar, I may advert first to the diffusion of crystalloids through a gelatinous or colloid mass, the circumstance of the experiment being varied as little as possible from those of jar-diffusion.

Ten grammes of chloride of sodium and 2 grammes of the Japanese gelatine, or gelose of Payen, were dissolved together in so much hot water as to form 100 cub. cents. of fluid. Introduced into the empty diffusion-jar and allowed to cool, this fluid set into a firm jelly, occupying the lower part of the jar, and containing of course 10 per cent. of chloride of sodium. Instead of placing pure water over this jelly, it was covered by 700 cub. cents. of a solution containing 2 per cent. of the same gelose, cooled so far as to be on the point of gelatinizing; the jar at the same time being placed in a cooling mixture, in order to expedite that change. The jar with its contents was now left undis-



turbed for eight days at the temperature  $10^{\circ}$ . After the lapse of this time the jelly was removed from the jar in successive portions of 50 cub. cents. each from the top, and the proportion of chloride of sodium in the various strata ascertained. The results were very similar to those obtained in diffusing the same salt in a jar of pure water. The diffusion in the gelose appeared more advanced in eight days than diffusion in water for seven days, as will be seen by comparing the gelose experiment below with a water experiment on chloride of sodium which had been conducted at nearly the same temperature (Table III.)

TABLE XI.—Diffusion of a 10 per cent. solution of Chloride of Sodium in the jelly of gelose, for eight days, at  $10^{\circ}$ .

Number of stratum.	Diffusate, in grammes.
1	·015
2	·015
3	·026
4	·035
5	·082
6	·130
7	·212
8	·350
9	·486
10	·630
11	·996
12	1·172
13	1·190
14	1·203
15 and 16	3·450
	9·992

Diffusion of a crystalloid thus appears to proceed through a firm jelly with little or no abatement of velocity. With a coloured crystalloid, such as bichromate of potash, the gradual elevation of the salt to the top of the jar is beautifully illustrated. On the other hand, the diffusion of a coloured colloid such as caramel through the jelly, appears scarcely to have begun after eight days had elapsed. The diffusion of a salt into the solid jelly may be considered as cementation in its most active form.

Numerous experiments were made on the diffusion of crystalloids through various dialytic septa, such as gelatinous starch, coagulated albumen, gum-tragacanth, besides animal mucus, and parchment-paper, which all tended to prove how little the diffusive process was interfered with by the intervention of colloid matter. Salts appeared to preserve their usual relative diffusibility unchanged. The same partial separa-



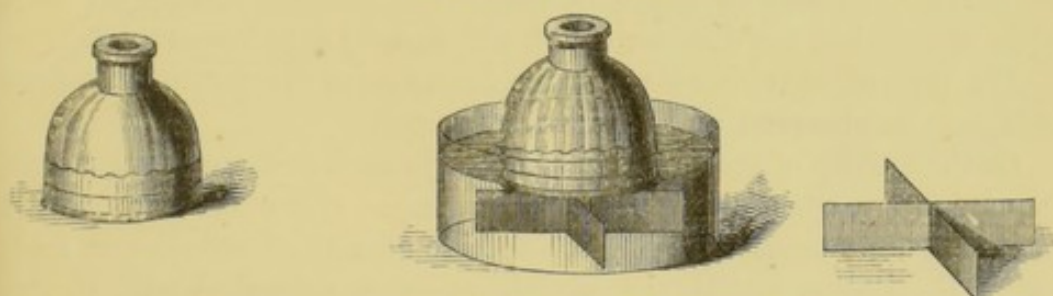
tion of mixed salts was observed as in the water-jar. With a mixture, for instance, of equal parts of chlorides of potassium and sodium in the dialyser, the first tenth part of the mixture which passed through was found to consist of 59.17 per cent. of chloride of potassium and 40.83 per cent. of chloride of sodium. Double salts also, such as alum, and the sulphate of copper and potash, which admit of being resolved into pairs of unequally diffusive salts, were largely decomposed upon the dialyser, as they are in the water-jar. The effect of heat in promoting diffusion appeared, however, to be diminished in dialysis, at least with a parchment-paper septum. Thus the diffusion from a 2 per cent. solution of chloride of sodium in a constant period of three hours was,—

			Ratio.
At 10,	.	0.738 grm.	1
At 20,	.	0.794 grm.	1.07
At 30,	.	0.892 grm.	1.20
At 40,	.	1.017 grm.	1.37

The rate of diffusion in water alone, without the septum, would have been doubled by an equal rise of temperature instead of being increased one-third only as above.

The small glass bell-jar (fig. 3) formerly used as an osmometer, was

FIG. 3.—Bulb Dialyser.



conveniently applied to dialytic experiments. Two sizes of the bulb were employed, 3.14 and 4.44 inches in diameter respectively, and of which the dialytic septa possessed an area very nearly of  $\frac{1}{100}$ th and  $\frac{1}{200}$ th of a square metre (15.6 and 7.8 square inches). With 100 cub. cents. of fluid in the osmometer (the volume usually employed), the septum of the smaller instrument was covered to a depth of about 20 millimetres (0.8 inch), and the septum of the larger to a depth of 10 millimetres (0.4 inch). The thinner the stratum, the more exhaustive the diffusion in a given time. It is generally unadvisable to cover

the septum deeper than 10 or 12 millimetres (half an inch), where a considerable diffusion is desired within twenty-four hours. The following



practical observations may be found useful in applying the dialyser to actual cases of analysis. They refer to the parchment-paper septum, which is much the most convenient for use.

With a 2 per cent. solution of chloride of sodium, containing 2 grammes of the salt, and covering a septum of nearly 0.01 square metre (15.6 square inches) in area, to a depth of 10 millimetres, the salt which diffused in five hours amounted to 0.75 gramme, and in twenty-four hours to 1.657 gramme, leaving behind 0.343 gramme, or 17.1 per cent. of the original salt. The following experiments, made with the same osmometer and solution, show the effect of reducing the volume of liquid placed in the dialyser. The proportion of salt which diffused out in twenty-four hours was—

From 100 cub. cents. of solution 86 per cent.

From 50 cub. cents. of solution 92 per cent.

From 25 cub. cents. of solution 96 per cent.

In all cases the volume of water outside into which the salt escaped was ample, being from five to ten times greater than the volume of fluid placed in the dialyser, and it was changed during the continuance of the experiment. A much less volume of external water suffices, provided it is changed at intervals of a few hours. The temperature was 10° to 12°. It will be observed that these volumes correspond to a depth of liquid in the dialyser of 0.4, 0.2, and 0.1 inch respectively.

The time of travelling through the thickness of the parchment-paper itself may be observed, and is worthy of remark.

Of the quality of parchment-paper always used in these experiments, a square metre, when dry, weighed 67 grammes; and when charged with water, 108.6 grammes. Taking the specific gravity of cellulose at 1.46, that of the lighter woods, the parchment-paper described will, in the humid state, have a thickness of 0.0877 millimetre, or  $\frac{1}{11.41}$  of a millimetre. Wet parchment-paper so thin is highly translucent. Gelatinous starch, slightly coloured with blue litmus, was applied by a brush to one side of the wet parchment-paper. Immediately afterwards a drop of water, containing  $\frac{1}{1000}$ th part of *hydrochloric acid*, was applied on the point of the finger to the other (the lower) side of the paper. The time required by the acid to affect the litmus, in five successive trials, was 6 seconds, 5.5 seconds, 6 seconds, and 5 seconds. The mean is 5.7 seconds, which is therefore the time required by hydrochloric acid, diluted already 1000 times, to travel a distance of 0.0877 of a millimetre, by the agency of diffusion. The temperature was 15°.

With hydrochloric acid diluted twice as much as before (water containing 0.0005 dry acid), the average time of passage was 10.4 seconds, or nearly double the preceding time.

Water containing  $\frac{1}{1000}$ th of sulphuric acid (an acid less rapidly



diffused than hydrochloric acid) reddened the litmus in 9.1 seconds, and when doubly diluted in 16.5 seconds.

These results are not affected, it is believed, by any sensible diffusive movement on the part of the litmus. The diffusion of that colouring matter, in a colloid medium, is so slow that it may be entirely disregarded. The acid, therefore, is not met in its way by the litmus, but really travels the entire distance expressed by the thickness of the parchment-paper. The first experiments related give a diffusive velocity, in water, to hydrochloric acid, already diluted one thousand times, of 0.0154 millimetre per second, and 0.924 millimetre in one minute.

The few following dialytic experiments may be recorded for the sake of the practical points which they bring out. They were made in the smaller osmometer, with 100 cub. cents. of a solution containing 10 grammes of each of the various substances. The area of the parchment-paper septum was 0.005 square metre, and the depth of the stratum of fluid placed upon it 20 millimetres. The substances diffused were all crystalloids, with the exception of gum-arabic.

TABLE XII.—Dialysis through Parchment-paper during twenty-four hours, at 10° to 15°.

Ten per cent. solutions.	Diffusate, in grammes.	Relative diffusate.	Osmose, in grammes of water.	Relative osmose.
Gum-arabic, . . . . .	0.029	.004	5.0	.263
Starch-sugar, . . . . .	2.000	.266	17.0	.894
Cane-sugar, . . . . .	1.607	.214	15.3	.805
Milk-sugar, . . . . .	1.387	.185	15.0	.789
Mannite, . . . . .	2.621	.349	17.6	.926
Glycerine, . . . . .	3.300	.440	17.6	.926
Alcohol, . . . . .	3.570	.476	7.6	.400
Starch-sugar (second experiment),	2.130	.284	16.8	.884
Chloride of sodium, . . . . .	7.500	1	19.0	1

The experiments were all made through the same portion of parchment-paper, and in the order of the Table; gum-arabic first, and chloride of sodium last. After every experiment the bulb was immersed in water for twenty-four hours, to purify the septum, before it was again used. The diffusion of starch-sugar was repeated early and late in the series of experiments, with little change in the result, showing considerable uniformity in the action of the parchment-paper; the first diffusate of starch-sugar being 2 grammes, and the second 2.13 grammes. Yet the parchment-paper had been in contact with water or some solution for a whole fortnight between the two observations referred to.

A layer of animal mucus, taken from the stomach of the pig, 12 millimetres in thickness (10 grammes of humid mucus being spread over 0.005 square metre of surface), was applied, between two discs of



calico, to the diffusion-bulb used above, the parchment-paper being first removed.

TABLE XIII.—Dialysis through Animal Mucus during twenty-five hours, at  $10^{\circ}$  to  $15^{\circ}$ .

Ten per cent. solutions.	Diffusate, in grammes.	Proportional diffusate.	Osmose, in grammes of water.
Gum-arabic, . . . . .	·023	·004	+ 29
Starch-sugar, . . . . .	1·821	·360	+ 7·6
Cane-sugar, . . . . .	1·753	·347	+ 4·6
Milk-sugar, . . . . .	1·328	·262	+ 7·1
Mannite, . . . . .	1·895	·375	+ 5·0
Alcohol, . . . . .	2·900	·573	+ 7·2
Starch-sugar, . . . . .	1·765	·349	+ 7·0
Glycerine, . . . . .	2·554	·505	+ 7·5
Chloride of sodium, . . . . .	5·054	1	- 0·2

The relative diffusibilities of the different substances present a considerable degree of similarity in the two Tables, and are equally analogous to the diffusibilities of the same substances observed in pure water. The intervention of a colloid septum cannot be said to have impeded much the diffusion of any of these substances except the colloid gum.

The dialysis through parchment-paper of several other organic substances, both crystalloids and colloids, may be brought together, in comparison with the chloride of sodium as a standard. The larger osmometer bulb was used, and the parchment paper was now changed in each experiment. The substance in solution amounted to 2 grammes, the depth of fluid in the dialyser to 10 millimetres (0·4 of an inch), and the surface of the septum to 0·01 square metre (15·6 square inches).

TABLE XIV.—Dialysis through Parchment-paper during twenty-four hours, at  $12^{\circ}$ .

Two per cent. solutions.	Diffusate in grammes.	Proportional diffusate.
Chloride of sodium, . . . . .	1·657	1
Picric acid, . . . . .	1·690	1·020
Ammonia, . . . . .	1·404	·847
Thein, . . . . .	1·166	·703
Salicin, . . . . .	·835	·503
Cane-sugar, . . . . .	·783	·472
Amygdalin, . . . . .	·517	·311
Extract of quercitron, . . . . .	·305	·184
Extract of logwood, . . . . .	·280	·168
Catechu, . . . . .	·265	·159
Extract of cochineal, . . . . .	·086	·051
Gallo-tannic acid, . . . . .	·050	·030
Extract of litmus, . . . . .	·033	·019
Purified caramel, . . . . .	·009	·005



Picric acid and thein were actually diffused from 1 per cent. solutions, and the numbers observed are multiplied by 2. The crystallizable principles, thein, salicin, and amygdalin, appear greatly more diffusible than gallo-tannic acid, or than gum, as has been already seen. Such inequality of rate is likely to facilitate the separation of vegetable principles by the agency of dialysis.

#### 4. *Preparation of Colloid Substances by Dialysis.*

The purification of many colloid substances may be effected with great advantage by placing them on the dialyser. Accompanying crystalloids are eliminated, and the colloid is left behind in a state of purity. The purification of soluble colloids can rarely be effected by any other known means, and dialysis is evidently the appropriate mode of preparing such substances free from crystalloids.

*Soluble Silicic Acid.*—A solution of silica is obtained by pouring silicate of soda into diluted hydrochloric acid, the acid being maintained in large excess. But in addition to hydrochloric acid, such a solution contains chloride of sodium, a salt which causes the silica to gelatinize when the solution is heated, and otherwise modifies its properties. Now such soluble silica, placed for twenty-four hours in a dialyser of parchment-paper, to the usual depth of 10 millimetres, was found to lose in that time 5 per cent. of its silicic acid, and 86 per cent. of its hydrochloric acid. After four days on the dialyser, the liquid ceased to be disturbed by nitrate of silver. All the chlorides were gone, with no further loss of silica. In another experiment 112 grammes of silicate of soda, 67.2 grammes of dry hydrochloric acid, and 1000 cub. cents. of water were brought together, and the solution placed upon a hoop dialyser, 10 inches in diameter. After four days the solution had increased to 1235 cub. cents., by the action of osmose; colloid bodies being generally highly osmotic. The solution now gave no precipitate with nitrate of silver, and contained 60.5 grammes of silica, 6.7 grammes of that substance having been lost. The solution contained 4.9 per cent. of silicic acid.

The pure solution of silicic acid so obtained may be boiled in a flask, and considerably concentrated, without change; but when heated in an open vessel, a ring of insoluble silica is apt to form round the margin of the liquid, and soon causes the whole to gelatinize. The pure solution of hydrated silicic acid is limpid and colourless, and not in the least degree viscous, even with 14 per cent. of silicic acid. The solution is the more durable the longer it has been dialysed and the purer it is. But this solution is not easily preserved beyond a few days, unless considerably diluted. It soon appears slightly opalescent, and after a time



the whole becomes pectous somewhat rapidly, forming a solid jelly transparent and colourless, or slightly opalescent, and no longer soluble in water. This jelly undergoes a contraction after a few days, even in a close vessel, and pure water separates from it. The coagulation of the silicic acid is effected in a few minutes by a solution containing  $\frac{1}{10,000}$ th part of any alkaline or earthy carbonate, but not by caustic ammonia, nor by neutral or acid salts. Sulphuric, nitric, and acetic acids do not coagulate silicic acid, but a few bubbles of carbonic acid passed through the solution produce that effect after the lapse of a certain time. Alcohol and sugar, in large quantity even, do not act as precipitants; but neither do they protect silicic acid from the action of alkaline carbonates, nor from the effect of time in pectizing the fluid colloid. Hydrochloric acid gives stability to the solution: so does a small addition of caustic potash or soda.

This pure water-glass is precipitated on the surface of a calcareous stone without penetrating, apparently from the coagulating action of soluble lime-salts. The hydrated silicic acid then forms a varnish, which is apt to scale off on drying. The solution of hydrated silicic acid has an acid reaction, somewhat greater than that of carbonic acid. It appears to be really tasteless (like most colloids), although it occasions a disagreeable persistent sensation in the mouth, after a time, probably from precipitation.

Soluble hydrated silicic acid, when dried in the air-pump receiver, at  $15^{\circ}$ , formed a transparent glassy mass of great lustre, which was no longer soluble in water. It retained 21.99 per cent. of water after being kept two days over sulphuric acid.

The colloidal solution of silicic acid is precipitated by certain other soluble colloids, such as gelatine, alumina, and peroxide of iron, but not by gum nor caramel. As hydrated silicic acid, after once gelatinizing, cannot be made soluble again by either water or acids, it appears necessary to admit the existence of two allotropic modifications of that substance, namely, soluble hydrated silicic acid, and insoluble hydrated silicic acid, the fluid and pectous forms of this colloid.

The ordinary soluble silicate of soda is not at all colloidal, but diffuses as readily through a septum as the sulphate of soda does. Several crystalline hydrated silicates of soda are known (Fritzsche).

The amorphous silicic acid obtained by drying and calcining the jelly, and the vitreous acid obtained by igneous fusion, have both a specific gravity of about 2.2, according to H. Rose,<sup>1</sup> and appear to be the same colloidal substance; while the specific gravity of crystalloidal silicic acid (rock-crystal and quartz) is about 2.6.

Soluble silicic acid forms a peculiar class of compounds, which like

<sup>1</sup> *Annales de Chimie*, 3 sér. t. lvii. p. 163.



itself are colloidal, and differ entirely from the ordinary silicates. The new compounds are interesting from their analogy to organic substances, and from appearing to contain an acid of greatly higher atomic weight than ordinary silicic acid. Like gallo-tannic acid, gummic acid, and the other organic colloidal acids, silicic acid combines with gelatine; the last substance appearing to possess basic properties. *Silicate of gelatine* falls as a flaky, white and opaque precipitate, when the solution of silicic acid is gradually added to a solution of gelatine in excess. The precipitate is insoluble in water, and is not decomposed by washing. Silicate of gelatine prepared in the manner described, contains 100 silicic acid to about 92 gelatine. This is a greater proportion of gelatine than in the gallo-tannate of gelatine, and requires for soluble silicic acid a higher equivalent than that of gallo-tannic acid. In the humid state the gelatine of this compound does not putrefy.

The acid reaction of 100 parts of soluble silicic acid is neutralized by 1.85 part of oxide of potassium, and by corresponding proportions of soda and ammonia. The *colli-silicates* or *co-silicates* thus formed are soluble and more durable than fluid silicic acid, but they are pectized by carbonic acid or by an alkaline carbonate, after standing for a few minutes. The co-silicate of potash forms a transparent hydrated film on drying *in vacuo*, which is not decomposed by water, and appears to require about ten thousand parts of water to dissolve it. The silicate of soda which Forchhammer obtained by boiling freshly precipitated silicic acid with carbonate of soda, and collecting the precipitate which falls on cooling, contains 2.74 per cent. of soda, and is represented by  $\text{NaO} + 36 \text{SiO}_2$  (Gmelin). This silicate is probably a co-silicate of soda in the pectous condition. Soluble silicic acid produces a gelatinous precipitate in lime-water, containing 6 per cent. and upwards of the basic earth. This and the other insoluble earthy co-silicates appear not to be easily obtained in a definite state. They gave out a more basic silicate to water on washing. The composition of these salts, and that also of the co-silicate of gelatine, were found to vary according as the mode of preparation was modified. When a solution of gelatine was poured into silicic acid in excess, the co-silicate of gelatine formed gave, upon analysis, 100 silicic acid with 56 gelatine, or little more than half the gelatine stated above as found in that compound prepared with the mode of mixing the solutions reversed. The gallo-tannate of gelatine is known to offer the same variability in composition.

The gelatine used in the preceding experiments was isinglass (*colle de poisson*), purified by solution in hydrochloric acid and subsequent dialysis. As the acid escapes by diffusion, a jelly is formed in the dialyser. This jelly is free from the earthy matter, amounting to about 0.4 per cent. in isinglass, and is not liable to putrefaction.



Cosilicic acid also precipitates both *albuminic acid* and pure *casein*.

*Soluble Alumina*.—We are indebted to Mr. Walter Crum for the interesting discovery that alumina may be held in solution by water alone in the absence of any acid. But two soluble modifications of alumina appear to exist, alumina and metalumina. The latter is Mr. Crum's substance.

A solution of the neutral chloride of aluminium ( $\text{Al}_2 \text{Cl}_3$ ), placed on the dialyser, appears to diffuse away without decomposition. But when an excess of hydrated alumina is previously dissolved in the chloride, the latter salt is found to escape by diffusion in a gradual manner, and the hydrated alumina, retaining little or no acid, to remain behind in a soluble state. A solution of alumina in chloride of aluminium, consisting at first of 52 parts of alumina to 48 of hydrochloric acid, after a dialysis of six days, contained 66.5 per cent. of alumina; after eleven days 76.5 per cent.; after seventeen days 92.4 per cent., and after twenty-five days the alumina appeared to be as nearly as possible free from acid, as traces only of hydrochloric acid were indicated by an acid solution of nitrate of silver. But in such experiments the alumina often pectizes in the dialyser before the hydrochloric acid has entirely escaped.

Acetate of alumina with an excess of alumina gave similar results. The alumina remained fluid in the dialyser for twenty-one days, and when it pectized was found to retain 3.4 per cent. of acetic acid, which is in the proportion of 1 equivalent of acid to 28.2 equivalents of alumina.

Soluble alumina is one of the most unstable of substances, a circumstance which fully accounts for the difficulty of preparing it in a state of purity. It is coagulated or pectized by portions, so minute as to be scarcely appreciable, of sulphate of potash and, I believe, by all other salts; and also by ammonia. A solution containing 2 or 3 per cent. of alumina was coagulated by a few drops of well-water, and could not be transferred from one glass to another, unless the glass was repeatedly washed out by distilled water, without gelatinizing. Acids in small quantity also cause coagulation; but the precipitated alumina readily dissolves in an excess of the acid. The colloids gum and caramel also act as precipitants.

This alumina is a mordant, and possesses indeed all the properties of the base of alum and the ordinary aluminous salts. A solution containing 0.5 per cent. of alumina may be boiled without gelatinizing, but when concentrated to half its bulk it suddenly coagulated. Soluble alumina gelatinizes when placed upon red litmus paper, and forms a faint blue ring about the drop, showing a feeble alkaline reaction. Soluble alumina is not precipitated by alcohol nor by sugar. No pure solution of alumina, although dilute, remained fluid for more than a few days.



Like hydrated silicic acid, then, the colloid alumina may exist either fluid or pectous, or it has a soluble and insoluble form, the latter being the gelatinous alumina as precipitated by bases. It is evident that the extraordinary coagulating action of salts upon hydrated alumina must prevent the latter substance from ever appearing in a soluble state when liberated from combination by means of a base.

Colloidal alumina possesses also, I believe, a high atomic weight, like cosilicic acid. The chloride of aluminium with excess of alumina referred to above appears to be, either in whole or in part, a colloidal hydrochlorate of alumina, containing the latter substance with its large colloidal equivalent, and may be really neutral in composition. The soluble basic persalts of iron, tin, etc., are likewise all colloidal, and have no doubt a similar constitution. Such colloidal salts are themselves slowly decomposed on the dialyser, being resolved into the crystalloidal acid which escapes and the colloidal oxide which remains behind.

*Soluble Metalumina.*—Mr. Crum first pointed out a singular relation of acetic acid to alumina, which has never been explained. Sulphate of alumina, when precipitated by acetate of lead or baryta, gives a binacetate of alumina, with one equivalent of free acetic acid; the neutral teracetate of alumina not appearing to exist. It was further observed that, by keeping a solution of this binacetate in a close vessel at the boiling-point of water for several days, nearly the whole acetic acid came to be liberated, without any precipitation of alumina occurring at the same time. Mr. Crum boiled off the free acetic acid, or the greater part of it, and thus obtained his soluble alumina. The same result may be arrived at by dialysing a solution of acetate of alumina that has been altered by heat. In three days the acetic acid was reduced on the dialyser to 11 per cent., giving 1 equiv. acetic acid to 8 equivs. alumina; in six days to 7.17 per cent. acid; in thirteen days to 2.8 per cent. acid, or 1 equiv. acid to 33 equivs. alumina. The alumina exists in an allotropic condition, being no longer a mordant; and forming, when precipitated, a jelly that is not dissolved by an excess of acid. Metalumina resembles alumina in being coagulated by minute proportions of acids, bases, and of most salts. Mr. Crum found the solution of metalumina to require larger quantities of acetates, nitrates, and chlorides to produce coagulation than of the former substances. The solution of metalumina is tasteless, and entirely neutral to test-paper, according to my own observation.

Like alumina, the present colloid has therefore a fluid and a pectous form, the liquid soluble metalumina, and the gelatinous insoluble metalumina.

*Soluble Peroxide of Iron.*—A solution of hydrated peroxide of iron may be obtained by a process exactly analogous to that for soluble alumina. Perchloride of iron in solution is first saturated with hydrated



peroxide of iron, added by small quantities at a time; or carbonate of ammonia may be added in a gradual manner to perchloride of iron, so long as the precipitated oxide continues to be redissolved on stirring. These red solutions of iron have lately been carefully investigated by Mr. Ordway (*Silliman's Journal*, 3 ser. xxxix. 197), by M. Bechamp (*Annales de Chimie*, 3 sér. lvii. 293), and by M. Scheurer-Kestner (*ib.* lv. 330). It is observed that the act of solution of the hydrated peroxide by the chloride of iron is a gradual process, demanding time. The quantity of oxide taken up will go on increasing for a long time, if digestion in the cold is continued. Mr. Ordway found chloride of iron to take up so much as 18 equivalents of peroxide of iron in the course of five months. This slowness of action is highly characteristic of colloids. Only monobasic acids, such as hydrochloric and nitric, serve for preparing such solutions; sulphuric and other polybasic acids giving insoluble subsalts with excess of ferric oxide, or of any other aluminous oxide. The red liquid so obtained is already a colloidal hydrochlorate of peroxide of iron, but requires to be dialysed for a sufficient time. Such a compound possesses an element of instability in the extremely unequal diffusibility of its constituents. Beginning with perchloride of iron, containing five or six equivalents of peroxide in solution, the whole solid matter also amounting to 4 or 5 per cent. of the liquid, and the latter forming a stratum of the usual depth of about half an inch in the dialyser, it was found that hydrochloric acid diffused out accompanied only by a small proportion of the iron. After eight days, the deep red solution in the dialyser contained peroxide of iron and hydrochloric acid, in the proportion of 97.6 per cent. of the former to 2.4 per cent. of the latter. In nineteen days the hydrochloric acid was reduced to 1.5 per cent., which gives 1 equiv. of acid to 30.3 equivs. peroxide of iron. The last solution was transferred to a phial, in which it remained fluid for twenty days, and then spontaneously pectized.

The peracetate of iron, prepared by double decomposition, is incapable of dissolving hydrated peroxide of iron, as is well known, but still may be made a source of soluble peroxide; as the salt referred to is itself decomposed to a great extent by diffusion on the dialyser. About one-half of the iron was lost by a diffusion of eighteen days, in a particular experiment, leaving on the dialyser a red liquid, in which ninety-four parts of peroxide of iron were still associated with six parts of acetic acid.

Water containing about 1 per cent. of hydrated peroxide of iron in solution has the dark red colour of venous blood. The solution may be concentrated by boiling to a certain point, and then pectizes. The red solution is coagulated in the cold by traces of sulphuric acid, alkalies, alkaline carbonates, sulphates and neutral salts in general, but not by



hydrochloric, nitric, and acetic acids, nor by alcohol or sugar. The coagulum is a deep red-coloured jelly, resembling the clot of blood, but more transparent. Indeed, the coagulation of this colloid is highly suggestive of that blood, from the feeble agencies which suffice to effect the change in question, as well as from the appearance of the product. The coagulum formed by a precipitant, or in the course of time, without any addition having been made to the solution of peroxide of iron, is no longer soluble in water, hot or cold; but it yields readily to dilute acids. It is, in short, the ordinary hydrated peroxide of iron. Here, then, again, we have a soluble and insoluble form of the same colloidal substance. Native hematite, which presents itself in mammillary concretions, is no doubt colloidal.

*Soluble Metaperoxide of Iron.*—The soluble peroxide of iron of M. Péan de Saint-Gilles<sup>1</sup> appears to be the analogue of metalumina. It was also prepared by the prolonged action of heat upon a pure solution of the acetate. The characteristic properties of this substance, which indicate its allotropic nature, are the orange-red colour and the opalescent appearance of its solution. The metaperoxide of iron is entirely precipitated of a brown ochreous appearance by a trace of sulphuric acid, or of an alkaline salt, and is insoluble in all cold acids, even when the latter are concentrated. The solubility of metaperoxide of iron in water appears to be more precarious, if possible, than that of the colloid alumina. It would no doubt be more safely prepared by diffusing away the acetic acid of the altered acetate of iron, than it is by boiling off that acid; as the solution is said to become precipitable by heat before the whole acetic acid is expelled.

*Ferrocyanide of Copper.*—Many of the insoluble ferrocyanides are crystalline precipitates, but the compound above named, and the different varieties of prussian blue, appear to be strictly colloidal.

Certain anomalous properties long observed in these compounds come thus to be explained. The ferrocyanide of copper, precipitated from ferrocyanide of potassium and sulphate of copper, is a reddish-brown gelatinous precipitate, and carries down a portion of the potash salt. It is obtained of greater purity, like the other insoluble ferrocyanides, by the use of ferrocyanic acid as the precipitant. Ferrocyanide of copper is then darker in colour, and still more highly gelatinous. It is well known that this substance appears as a transparent almost colourless jelly, when precipitated from strong solutions. This colloidal matter assumes colour on the addition of water, in consequence of further hydration, following in this respect the analogy of the crystalloid salts of copper. The ferrocyanide of copper, when once precipitated, may be washed without loss, and exhibits no symptoms of solubility. But it

<sup>1</sup> *Comptes Rendus*, 1855, p. 568.



has been remarked that the same salt, when produced by mixing the precipitating salts dissolved in not less than two or three thousand times their weight of water, gives a wine-red solution with no precipitate. This is the soluble condition of the colloid. When the red solution is placed in the dialyser the salt of potash diffuses out, and the whole ferrocyanide of copper is retained behind in solution.

Precipitated ferrocyanide of copper is not dissolved by oxalic acid, nor by oxalate of potash, but dissolves freely in about one-fourth of its weight of neutral oxalate of ammonia. The ferrocyanide of copper must be washed beforehand, to insure solubility. A solution holding 3 or 4 per cent. of ferrocyanide of copper is of a dark reddish-brown colour, intermediate in tint between the acetate and meconate of iron. The solution is transparent, but assumes a peculiar appearance of opacity when seen by light reflected from its surface. The same appearance was observed by Péan de Saint-Gilles in his metaperoxide of iron.

When a red solution, such as that described, was dialysed, the oxalate of ammonia came away in a gradual manner; 30.6 per cent. of the oxalate of ammonia were found in the colourless diffusate of the first twenty-four hours; 31 per cent. of the same salt in the diffusate of the next three days, and 18.2 per cent. in the diffusates of the following seven days, making altogether 79.8 per cent., or four-fifths of the whole oxalate of ammonia originally introduced. A small portion of the ammoniacal salt is retained with force, as might be expected from a ferrocyanide. Although the diffusate appeared colourless, it was found to contain a little oxide of copper, namely, 0.041 gramme (of which 0.022 gramme diffused out in the first twenty-four hours), from 2 grammes of ferrocyanide of copper placed in the dialyser.

The liquid ferrocyanide of copper, both before and after being dialysed, may be heated without change, but it is pectized by foreign substances with extreme facility. This effect is produced by a minute addition of nitric, hydrochloric, and sulphuric acids in the cold, and of oxalic and tartaric acids with the aid of a slight heat. It is remarkable that acetic acid does not pectize the ferrocyanide of copper and many other colloids. Sulphate of potash, sulphate of copper, and metallic salts generally appear to pectize the red liquid. The oxalate of ammonia, if any is present, remains in solution.

*Neutral Prussian Blue.*—The blue precipitate from perchloride of iron and ferrocyanide of potassium, or ferrocyanic acid, is a bulky hydrate, which dries up into gummy masses, so far resembling a colloid. The precipitate dissolves readily with the aid of a gentle heat, in one-sixth of its weight of oxalic acid, giving the well-known solution of prussian blue, used as an ink. Prussian blue is equally soluble in the oxalate and binoxalate of potash. When the solution of prussian blue in oxalic



acid was placed on the dialyser, no colouring matter came through, but 28 per cent. of the oxalic acid diffused away in the first twenty-four hours, accompanied by traces of peroxide of iron. The oxalic acid appears to leave the colloidal solution very slowly and incompletely, 8 per cent. diffusing away in the second twenty-four hours, 11 per cent. in the next four days, and 2 per cent. in the following six days. The colloidal solution of prussian blue was pectized by small additions of sulphate of zinc and several other metallic salts, but required larger quantities of the alkaline salts for precipitation.

*Ferridcyanide of Iron.*—The blue precipitate from the ferridcyanide of potassium and a protosalt of iron is soluble in oxalic acid and the binoxalate of potash, but not in the neutral oxalates. This blue liquid is quite incapable of passing through the dialyser, and is equally colloidal with ordinary prussian blue. So also is *basic prussian blue* prepared by the spontaneous oxidation of precipitated ferrocyanide of protoxide of iron. This last colloid might probably be purified with advantage upon the dialyser.

The ammonio-tartrate of iron, ammonio-citrate of iron, and similar pharmaceutical preparations are chiefly colloidal matters.

*Sucrate of Copper.*—The deep blue liquid obtained by adding potash to a mixed solution of chloride of copper and sugar appears to contain a colloidal substance. Placed on a dialyser for four days, the blue liquid became green, and no longer contained either potassium or chlorine; it in fact consisted of oxide of copper united with twice its weight of sugar. The external liquid remained colourless, and gave no indication of copper when tested with sulphuretted hydrogen. The colloidal solution of sucrate of copper was sensitive in the extreme to pectizing agents. Salts and acids generally gave a bluish-green precipitate; even acetic acid had that effect. The precipitate, or pectous sucrate, after being well washed, consisted of oxide of copper with about half its weight of sugar, and is therefore a subsucrate. When the green liquid is heated strongly, it gives a bluish-green precipitate, and does not allow the copper to be readily reduced to the state of suboxide. The subsucrate of copper possesses considerable vivacity of colour, and might be used as a pigment. A solution of sucrate of copper absorbs carbonic acid from the air with great avidity.

The sucrate of copper dries up into transparent films of an emerald green colour. These films are not altered in appearance or dissolved in cold or boiling alcohol. In water they are resolved into sugar and the pectous subsucrate of copper.

*Sucrate of Peroxide of Iron.*—The perchloride of iron with an addition of sugar is not precipitated by potash, provided the temperature is not allowed to rise. The peroxide of iron combined with the sugar is



colloidal, and remains on the dialyser without loss. At a certain stage, however, the sugar appears to leave the peroxide of iron, and a gelatinous subsucrate of iron pectizes. The subsucrate of iron thrown down from the soluble sucrate, by the addition of sulphate of potash, consisted of about 22 parts of sugar to 78 parts of peroxide of iron.

*Sucrate of Peroxide of Uranium.*—A similar solution may be obtained by adding potash to a mixture of the nitrate or chloride of uranium with sugar, avoiding heat. The solution is of a deep orange-yellow colour, and on the dialyser soon loses the whole of its acid and alkali. This fluid sucrate has considerable stability, but is readily pectized by salts, like the sucrate of copper. The subsucrate pectized has considerable solubility in pure water.

*Sucrate of Lime.*—The well-known solution of lime in sugar forms a solid coagulum when heated. It is probably, at a high temperature, entirely colloidal. The solution obtained on cooling passes through the septum, but requires a much longer time than a true crystalloid like the chloride of calcium.

The blue solution of tartrate of copper in caustic potash contains a colloidal compound, which has not been fully examined.

*Soluble Chromic Oxide.*—The definite terchloride of chromium, being a crystalloid, diffuses away entirely when placed in solution upon the dialyser. This salt dissolves, with time, a certain portion of freshly-precipitated hydrated chromic oxide, and becomes of a deeper green colour. Such a solution, after dialysis for twenty-two days, contained 8 hydrochloric acid to 92 chromic oxide; and after thirty days, 4.3 acid to 95.7 oxide, or 1 equiv. acid to 10.6 equivs. oxide. After thirty-eight days, the solution gelatinized in part upon the dialyser, and then contained 1.5 acid to 98.5 oxide, or 1 equiv. acid to 31.2 equivs. chromic oxide. This last solution, which may be taken to represent soluble chromic oxide, is of a dark green colour, and admits of being heated, and also of being diluted with pure water without change. It was gelatinized with the usual facility by traces of salts and other reagents which affect colloid solutions, and was then no longer soluble in water, even with the assistance of heat. It appeared to be the green hydrated oxide of chromium, as that substance is usually known. A metachromic oxide may possibly be obtained by heating and dialysing the acetate, but I have not attempted to form it.

Mr. Ordway succeeded in dissolving an excess of the hydrated *uranic oxide* and of *glucina* in the chloride of uranium and of glucinum respectively. The dialysis of such solutions may be reasonably expected to yield soluble uranic oxide and soluble glucina.

It appears, then, that the hydrated peroxides of the aluminous type, when free, are colloid bodies; that two species of each of these hydrated



oxides exist, of which alumina and metalumina are the types; one derived from an unchanged salt, and the other from the heated acetate of the base; further, that each of these species has two forms, one soluble and the other insoluble, or coagulated. This last species of duality should be well distinguished from the preceding allotropic variability of the same peroxide. The possession of a soluble and an insoluble (fluid and pectous) modification is not confined to hydrated silicic acid and the aluminous oxides, but appears to be very general, if not universal, among colloid substances. The double form is typified in the fibrin of blood.

The precipitated and gelatinous *peroxide of tin* is largely soluble in the bichloride of the same metal. Such a solution, when placed in the dialyser, allows the whole chlorine of the salt and a portion of the tin to diffuse away. Peroxide of tin, or stannic acid, remains behind, but not in a soluble state. It forms in the dialyser a semi-transparent gelatinous cake, which after a few days is entirely free from chlorine. The original solution, containing excess of stannic acid, was diluted to various degrees, but was dialysed always with the same result. The coagulum was insoluble in hot or cold water, but dissolved readily in dilute acids. It was evidently the peroxide of tin unaltered.

The *metastannic acid*, or nitric acid peroxide of tin of Berzelius, forms a solid compound with a small quantity of hydrochloric acid. This compound is not dissolved by an excess of acid, but is soluble in pure water. The solution placed in the dialyser is readily decomposed, and leaves behind a semi-transparent gelatinous mass of pure hydrated metastannic acid, insoluble both in water and acids. There appears, then, to be no soluble form of either hydrated stannic or metastannic acid, although both are colloidal substances.

Precipitated *titanic acid* was dissolved in hydrochloric acid and submitted to dialysis. The hydrochloric acid readily diffused away, leaving hydrated titanic acid, gelatinous and insoluble, upon the dialyser. The proportion of titanic acid, which escaped from the dialyser and was lost, amounted to 0.050 gramme out of 2.5 grammes. Titanic acid thus resembles stannic acid in not presenting itself in the form of a fluid colloid.

Metallic protoxides are not soluble in their neutral salts, and cannot therefore be submitted to dialysis in the same conditions as the preceding peroxides. It was observed, however, that oxide of copper and oxide of zinc, when dissolved in ammonia, are capable of diffusing through a colloidal septum, and are therefore not colloids themselves. The water outside the dialyser should be charged with ammonia in such an experiment.



### 5. *Dialysis of Organic Colloid Substances.*

*Tannin.*—The tannin employed was that extracted from gall-nuts by the ether process of Pelouze. A two per cent. solution of this substance, covering a surface of paper-parchment of the area of about  $\frac{1}{100}$ th of a square metre, or 15.6 square inches, to a depth of 10 millimetres, was diffused at 10° to 13° of temperature. The diffused matter amounted, in successive periods of twenty-four hours, to .073, .040, .021, .021, .024, and .024 gramme, derived from the two grammes in solution. Probably the earlier diffusates were increased by the presence of a little gallic acid, which, being a crystalloid, would no doubt be rapidly eliminated by diffusion. The latter observations indicate that tannin passes through a paper-parchment septum about 200 times less rapidly than chloride of sodium does, in similar circumstances as to temperature and strength of solution. The diffusates from the tannin solution gave a precipitate with gelatine, and therefore contained tannin unaltered. But the diffusates probably contained also throughout some products of decomposition of a crystalloid character.

To the low diffusibility of tannin may be ascribed the remarkably slow penetration of skins by that substance in the ordinary operation of tanning leather. Tannin appears to form compounds of much stability with certain other colloids, as tanno-gelatine, and the compound with albumen which appears to be the primary basis of the vegetable cell (Frémy).

*Gum.*—The diffusate obtained from a solution containing 2 grammes of gum-arabic, in experiments corresponding in their conditions with the experiments upon tannin just related, was .013 gramme per day. The power of gum to penetrate the colloid septum appears, therefore, to be one-half less than that of tannin, and 400 times less than the diffusibility of chloride of sodium. Gum gave the same amount of diffusate with a mucus septum as with parchment-paper. When substances of the crystalloid class are mixed with the gum, the diffusion of the latter appears to be still further reduced, and may even be entirely extinguished. The separation of colloids from crystalloids by dialysis is, in consequence, generally more complete than might be expected from the relative diffusibility of the two classes of substances.

Vegetable gum, which Frémy has shown to be a gummate of lime, can be purified by a dialytic method, which may be found applicable with advantage in other cases. Oxalic acid, it is known, precipitates lime from the gum very imperfectly. Hydrochloric acid may be used to separate that base from a solution of gum placed upon the dialyser, with more effect. It is only necessary to add to a strong solution of gum 4 or 5 per cent. of hydrochloric acid, and to dialyse till the gum solution gives no precipitate with nitrate of silver. In an experiment



made upon a 20 per cent. solution of gum, the ash was reduced to 0.1 per cent. of the gum in five days. The gummie acid possesses a sensible acid reaction, about equal to that of carbonic acid. This acid reaction was neutralized in 100 parts of gummie acid by 2.85 parts of potash. This amount of potash is very nearly equivalent to the lime originally present in the gum (1.72 lime, or 3.07 carbonate of lime, being equivalent to 2.89 potash). When the gummie of potash itself was dialysed without addition, the potash gradually diffused away, possibly in the state of carbonate, and left the gum again possessed of an acid reaction. Gummie acid, well dried at 100°, becomes insoluble in water, but swells up in that liquid, like gum-tragacanth. We appear to have here the pectous form of gummie acid.

It is worthy of inquiry whether such native gums as are insoluble in water are not the pectous form of soluble gum, rather than allotropic varieties of that substance. So also of the metagummie acid of Frémy, formed by the action of strong sulphuric acid on mucilage. This last substance is insoluble in water, but was found by Frémy to afford, when neutralized by lime and alkalies, a soluble gum undistinguishable from gum-arabic.

Gummie acid produces a remarkable compound with gelatine. When solutions of these two colloids are mixed, oily drops fall and form a nearly colourless jelly on standing. This jelly is very fusible, melting at 25°, or by the heat of the hand. The *gummie of gelatine* may be washed without decomposition, but is soluble to a certain extent in pure water, and still more so in a solution of gelatine. Prepared with gummie acid in excess, the compound, when dried at 100°, consisted of 100 gummie acid with 59 gelatine. The drops and the jelly contained 83.5 per cent. of water. Solution of gelatine is not precipitated by unpurified gum, nor by the gummie of potash.

*Dextrin*.—A 2 per cent. solution of dextrin, prepared from starch, was diffused in the same conditions as the preceding substances, but through a mucus septum. It gave in twenty-four hours .034 gramme of diffusate from 2 grammes, or about three times more diffusate than was given by gum-arabic.

*Caramel*.—The dialytic examination of this substance adds to the accurate information on the subject lately supplied by M. A. Gélis,<sup>1</sup> and places caramel indisputably in the colloid class. The crude caramel obtained by heating cane-sugar at 210°–220°, when placed on the dialyser, allows certain intermediate coloured substances (Caramelane and Caramelene of Gélis) to diffuse out with considerable facility, while the compound containing the largest proportion of carbon remains behind. The latter substance, as obtained by me, possessed five times the colour-

<sup>1</sup> *Annales de Chimie*, etc., sér. 3, t. lii. p. 352.



ing power of the original crude caramel, weight for weight. This highest soluble member of the caramel series may also be obtained, more quickly, by precipitation from its aqueous solution by means of alcohol. But I found it necessary to repeat the precipitation four times, or till the mass thrown down, from being plastic at first became pulverulent. A solution containing 10 per cent. of the caramel so purified is gummy; and on standing, it formed a tremulous jelly entirely soluble in hot or cold water. Evaporated *in vacuo*, the solution dries up into a black shining mass, which is tough and elastic, while it still possesses a certain proportion of water, like gum containing some water. Once thoroughly dried at a low temperature, this soluble caramel may be heated, afterwards, to  $120^{\circ}$  and retain complete solubility. But if a solution of the same caramel be directly evaporated to dryness by the heat of a water-bath, the whole matter is rendered insoluble in hot or cold water. The soluble and insoluble caramel have the same composition, and appear to illustrate the usual double form of colloids. The proportion of carbon in the fluid caramel was found as high as 54.59 per cent., which comes nearer to  $C_{24}H_{15}O_{15}$  (requiring C 55.17) than any other formula in which the oxygen and hydrogen are assumed to be present in the proportion of water. In the analysis by Gélis of his carameline, the proportion of carbon did not exceed 51.33 per cent., which does not apply to the present substance.

Fluid caramel is wholly tasteless, and appears to be neutral. It exhibits the same excessive sensibility to crystalloidal reagents which is witnessed in fluid silicic acid and alumina. The solution is precipitated or pectized by mere traces of any mineral acid, by alkaline sulphates, chloride of sodium, by most other salts, and by alcohol. The caramel then forms a brownish black pulverulent substance, insoluble in hot or cold water. The presence of sugar and of the intermediate brown substances protects fluid caramel in a remarkable way from the action of crystalloids, and accounts for the preceding properties not being observed in crude caramel. This colloid appears also to be precipitated by certain substances of its own class, such as peroxide of iron.

Pectous caramel may readily have its solubility restored. Placed in dilute potash, the caramel swells and appears gelatinous, and is dissolved on the application of heat. When this solution is dialysed, the potash is quickly reduced to the proportion of about 9 per cent., which forms a neutral compound. If an excess of acetic acid now be added, the whole potash is soon diffused away, and pure soluble caramel remains on the dialyser. Even carbonic acid will carry away the potash.

The extremely low diffusibility which has been assigned to caramel in former Tables, belongs to that substance as last described; the brown intermediate substances which accompany it in crude caramel being



considerably more diffusive, although they again are much less diffusive than any variety of crystallizable or uncrystallizable sugar. When the molasses of the cane-sugar are diffused, much the greater portion of the colouring matters remains in the dialyser.

With the parchment-paper septum the fluid caramel appeared even less dialysable than gum, the diffusate in twenty-four hours from a 2 per cent. solution of the former being .009 gramme only, while that of the latter was .013. Caramel may be stated, approximately, to be 600 times less dialysable than chloride of sodium, and 200 times less so than sugar. Hence liquids coloured with caramel, such as porter and coffee, may be dialysed for a day with the passage of very little colouring matter.

Before leaving caramel, the analogy may be referred to which the insoluble form of that substance presents to *coal*. Caramelization appears the first step in that direction,—the beginning of a colloidal transformation to be consummated in the slow lapse of geological ages.

*Albumen*.—The purification of albumen is effected with much advantage upon the dialyser. The solution of egg-albumen is mixed freely with acetic acid and then dialysed. The earthy and alkaline salts are speedily got rid of, and in three or four days the albumen burns without leaving a trace of ash. Although the acetic acid used in the process appears to diffuse off entirely, albumen prepared in the manner described has a faint acid reaction. It also coagulates milk when mixed with the latter and heated. Albumen so prepared retains its constituent sulphur.

The passage through parchment-paper of pure albumen prepared by the unobjectionable process of M. Wurtz is so slow, that several days are required to produce a sensible result. Thus the diffusate from a solution of 2 grammes of albumen in 50 grammes of water was 0.052 gramme in eleven days, which gives 0.005 gramme in a single day. Albumen, then, appears to be about  $2\frac{1}{2}$  times less dialysable than gum, and 1000 less so than chloride of sodium.

Even combination with an alkali does not appear to enable albumen to pass through the colloid septum. To half a gramme of pure albuminic acid dissolved in 50 grammes of water, .05 gramme of hydrate of soda was added (one-tenth of the weight of the albumen), and the liquid was placed upon parchment-paper. No albumen could be discovered in the diffusate of several days, but it gave .069 gramme of carbonate of soda, equivalent to .053 gramme of hydrate of soda; that is the whole soda originally added to the albumen. The separation of the soda from the albumen may possibly have been aided by the presence of carbonic acid in the water, but certainly the entire separation of the alkali from albumen by diffusion through a colloidal film is a remarkable fact.



Hydrate of potash was found to diffuse away from albumen in the same manner.

A solution of *Emulsin* is precipitated by albuminic and gummie acids, but not by unpurified albumen or gum-arabic. The precipitates are white and opaque, pulverulent, and not gelatinous. They are soluble in acetic acid.

A thin stratum of pure albumen coagulated by heat appears to intercept completely the passage of liquid albumen of the egg. Forty grammes of undiluted egg-albumen, representing 5.6 grammes of dry albumen, were placed on a dialyser of the small size, composed of two sheets of calico well impregnated with albumen and coagulated by heat of steam, as in the albumenized osmometer.<sup>1</sup> After twelve days the volume of liquid within the instrument had increased to 117 grammes by osmose, while a diffusate had passed through the dialyser of 0.243 gramme, or 4.34 per cent. of the original dry albumen. This diffusate consisted of salts chiefly, with some organic matter, but no portion of the latter was coagulable by heat.

Neither gelatinous starch, animal gelatine dissolved in water, nor extract of flesh, appears to be capable of diffusing through a colloid septum in a sensible degree, although salts and other crystallizable substances, which are mixed with the former, diffuse the septum readily, and may thus be separated from the former substances.

#### 6. *Separation of Arsenious Acid from Colloidal Liquids.*

Dialysis may be advantageously applied to the separation of arsenious acid and metallic salts from organic solutions in medico-legal inquiries. The process has the advantage of introducing no metallic substance or chemical reagent of any kind into the organic fluid. The arrangement for operating is also of the simplest nature.

The organic fluid is placed, to the depth of half an inch, on a dialyser formed of a hoop of gutta percha 10 or 12 inches in diameter, covered with parchment-paper (fig. 1, page 556). The dialyser is then floated in a basin containing a volume of water about four times greater than the volume of organic fluid in the dialyser. The water of the basin is generally found to remain colourless after the lapse of twenty-four hours, and after being concentrated by evaporation, it admits of the application of the proper reagents to precipitate and remove a metal from solution. One-half to three-fourths of the crystalloidal and diffusible constituents of the organic fluid will generally be found in the water of the basin.

In the few illustrative experiments which follow, the 4-inch bulb dialyser, having an area of 16 square inches, or about  $\frac{1}{100}$ th part of a

<sup>1</sup> *Philosophical Transactions*, 1854, p. 189.



square metre, was generally made use of (fig. 3, p. 573). The volume of liquid placed in the bulb was 50 cubic centimetres, and accordingly covered the dialyser to a depth of 5 millimetres, or about 0.2 inch. The outer volume of water (in the jar) was not less than 1 litre, or twenty times the volume of the solution on the dialyser.

1. A solution of arsenious acid, in pure water, was first placed on the dialyser, the water containing 0.5 per cent. of arsenious acid, or 0.25 gramme of that substance, for twenty-four hours. The dialyser being then removed, the outer fluid was concentrated by heat, and then precipitated by sulphuretted hydrogen. It gave 0.300 gramme of tersulphide of arsenic, equivalent to 0.241 gramme of arsenious acid. It appears, then, that about 95 per cent. of the arsenious acid had diffused from the dialyser into the water-jar in twenty-four hours.

2. Water, with one-fourth of its volume of fluid egg albumen and 0.25 gramme, or 0.5 per cent. of arsenious acid, was now placed on the dialyser as before. The diffusate gave, with sulphuretted hydrogen, after being acidulated with hydrochloric acid, 0.267 gramme of tersulphide of arsenic, equivalent to 0.214 gramme of arsenious acid.

3. The water contained 10 per cent. of gum-arabic and 1 per cent. arsenious acid, the latter amounting to 0.5 gramme. From the diffusate was derived 0.505 gramme of tersulphide of arsenic, equivalent to 0.406 gramme of arsenious acid. The dialyser still gave out arsenious acid when immersed for a second day in water. The outer fluid contained no gum.

It may be added that a similar 1 per cent. solution of arsenious acid, without the gum, gave a diffusate of 0.45 gramme arsenious acid in the same time, that is, nine-tenths of the whole acid.

4. A solution in hot water of 1 per cent. isinglass and 0.5 per cent. of arsenious acid (0.25 gramme), formed a jelly upon the dialyser on cooling. The diffusate from this jelly gave 0.260 tersulphide of arsenic, equivalent to 0.209 arsenious acid, with no gelatine. The escape of the arsenious acid appears then to have been slightly retarded by the fixing of the gelatinous solution. This is probably due to the arrest of mechanical movement within the gelatinous stratum, and not to any sensible impediment offered by the jelly to diffusion.

In another experiment, similar to the last, but continued for four days instead of twenty-four hours, the tersulphide of arsenic weighed 0.320 gramme, equivalent to 0.257 arsenious acid.

5. A quantity of white of egg, amounting to 50 grammes, to which 0.01 gramme of arsenious acid in solution had been added, was coagulated by heat. The solid mass was then cut up into small pieces and placed on the dialyser, mixed with 50 grammes of water; after the usual period of twenty-four hours, the diffusate gave 0.01 gramme



of tersulphide of arsenic, equivalent to 0.008 gramme arsenious acid. Here, of the mass upon the dialyser, the arsenious acid formed only  $\frac{1}{10,000}$ th part, yet four-fifths of it are recovered.

6. One hundred grammes of milk, charged with  $\frac{1}{10,000}$ th part of arsenious acid (0.01 gramme), and forming a stratum on the dialyser of 10 millimetres, gave a diffusate which yielded 0.010 tersulphide of arsenic, equivalent to 0.008 gramme of arsenious acid. The outer liquid was colourless, and gave no indication of casein, but it contained of course the salts and the sugar of the milk.

7. The same experiment was repeated with sized writing-paper, as the septum, applied to the same bulb. The result was a slight increase in the quantity of arsenious acid recovered.

It appears, then, that arsenious acid separates on the dialyser from gum, from gelatine, albumen, fluid or coagulated, and from casein, and is obtained in a solution fit for the application of reagents.

8. Half a litre of dark-coloured porter, with 0.05 gramme of arsenious acid added ( $\frac{1}{10,000}$ th part of arsenious acid) was placed on a hoop dialyser, 8 inches in diameter, and the whole floated in an earthenware basin containing 2 or 3 litres of water. After twenty-four hours the latter fluid had acquired a slight tinge of yellow. It yielded, when concentrated and precipitated by sulphuretted hydrogen, upwards of one-half of the original arsenious acid in a fit state for examination.

9. In a similar experiment on 200 grammes of defibrinated blood charged with  $\frac{1}{4000}$ th part of arsenious acid (0.05 gramme), and placed in a similar dialyser to the last for twenty-four hours, the diffusate of arsenious acid was recovered with the same facility, and appeared to be equally considerable.

10. Animal intestines, charged with the usual minute proportion of arsenious acid, were cut into small pieces and digested in water, about 32° C., for twenty-four hours. The whole was then thrown upon a dialyser for an equal time. Arsenious acid diffused out so free from colloidal matter that the action of reagents was not interfered with. A high temperature in digesting the intestines is quite unnecessary, and appeared indeed to increase the difficulty of diffusing out the arsenious acid afterwards.

The *tartrate of potash and antimony*, mixed in the small proportion of  $\frac{1}{10,000}$ th, with defibrinated blood and with milk, was separated by dialysis quite as effectually as arsenious acid above.

*Strychnine* also was separated from organic fluids in the same manner, a small addition of hydrochloric acid being first made to the fluid on the dialyser.

Dialysis then appears of general application in the preparation of a



liquid for examination by chemical tests, whether the poison looked for be mineral or organic. All soluble poisonous substances, whatever their origin, appear to be crystalloids, and accordingly pass through colloidal septa.

### 7. *Colloidal Condition of Matter.*

I may be allowed to advert again to the radical distinction assumed in this paper to exist between colloids and crystalloids in their intimate molecular constitution. Every physical and chemical property is characteristically modified in each class. They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organized mass.

The colloidal character is not obliterated by liquefaction, and is therefore more than a modification of the physical condition of solid. Some colloids are soluble in water, as gelatine and gum-arabic; and some are insoluble, like gum-tragacanth. Some colloids, again, form solid compounds with water, as gelatine and gum-tragacanth, while others, like tannin, do not. In such points the colloids exhibit as great a diversity of property as the crystalloids. A certain parallelism is maintained between the two classes, notwithstanding their differences.

The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow; time, indeed, appearing essential to all colloidal changes. The change of temperature, usually occurring in the act of solution, becomes barely perceptible. The liquid is always sensibly gummy or viscous when concentrated. The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced and precipitated by the addition to their solution of any substance from the other class. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa, are the most serviceable in distinguishing them from crystalloids. Colloids have feeble chemical reactions, but they exhibit at the same time a very general sensibility to liquid reagents, as has already been explained.

While soluble crystalloids are always highly sapid, soluble colloids are singularly insipid. It may be questioned whether a colloid, when tasted, ever reaches the sentient extremities of the nerves of the palate, as the latter are probably protected by a colloidal membrane, impermeable to soluble substances of the same physical constitution.

It has been observed that vegetable gum is not digested in the stomach. The coats of that organ dialyse the soluble food, absorbing



crystalloids and rejecting all colloids. This action appears to be aided by the thick coating of mucus which usually lines the stomach.

The secretion of free hydrochloric acid during digestion—at times most abundant—appears to depend upon processes of which no distinct conception has been formed. But certain colloidal decompositions are equally inexplicable upon ordinary chemical views. To facilitate the separation of hydrochloric acid from the perchloride of iron, for instance, that salt is first rendered basic by the addition of peroxide of iron. The comparatively stable perchloride of iron is transformed, by such treatment, into a feebly-constituted colloidal hydrochlorate. The latter compound breaks up under the purely physical agency of diffusion, and divides on the dialyser into colloidal peroxide of iron and free hydrochloric acid. The super-induction of the colloidal condition may possibly form a stage in many analogous organic decompositions.

A tendency to spontaneous change, which is observed occasionally in crystalloids, appears to be general in the other class. The fluid colloid becomes pectous and insoluble by contact with certain other substances, without combining with these substances, and often under the influence of time alone. The pectizing substance appears to hasten merely an impending change. Even while fluid a colloid may alter sensibly, from colourless becoming opalescent; and while pectous the degree of hydration may become reduced from internal change. The gradual progress of alteration in the colloid effected by the agency of time, is an investigation yet to be entered upon.

The equivalent of a colloid appears to be always high, although the ratio between the elements of the substance may be simple. Gummie acid, for instance, may be represented by  $C_{12}H_{11}O_{11}$ , but judging from the small proportions of lime and potash which suffice to neutralize this acid, the true numbers of its formula must be several times greater. It is difficult to avoid associating the inertness of colloids with their high equivalents, particularly where the high number appears to be attained by the repetition of a smaller number. The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the bases of colloidalness may not really be this composite character of the molecule.

With silicic acid, which can exist in combination both as a crystalloid and colloid, we have two series of compounds, silicates and cosilicates, the acid of the latter appearing to have an equivalent much greater (thirty-six times greater in one salt) than the acid of the former. The apparently small proportion of acid in a variety of metallic salts, such as certain red salts of iron, is accounted for by the high colloidal equivalent of their bases. The effect of such an insoluble colloid as prussian



blue in carrying down small proportions of the precipitating salts, may admit of a similar explanation.

Gelatine appears to hold an important place as a colloidal base. This base unites with colloidal acids, giving a class of stable compounds, of which tanno-gelatine only appears to be hitherto known. Gelatine is precipitated entirely by a solution of meta-phosphoric acid added drop by drop, 100 parts of gelatine uniting with 3.6 parts of the acid. The compound formed is a semi-transparent, soft, elastic, and stringy solid mass, presenting a startling resemblance to animal fibrin. It will be an interesting inquiry whether metaphosphoric acid is a colloid, and enters into the compound described in that character, or is a crystalloid, as the small proportion and low equivalent of the acid would suggest. Gelatine is also precipitated by carbolic acid.

The hardness of the crystalloid, with its crystalline planes and angles, is replaced in the colloid by a degree of softness, with a more or less rounded outline. The water of crystallization is represented by the water of gelatination. The water in gelatinous hydrates is aptly described by M. Chevreul as retained by "capillary affinity," that is, by an attraction partaking both of the physical and chemical character. While it is here admitted that chemical affinity of the lowest degree may shade into capillary attraction, it is believed that the character of gelatinous hydration is as truly chemical as that of crystalline hydration. Combination of a colloid with water is feeble, it is true, but so is combination in general with the colloid. Notwithstanding this, anhydrous colloids can decompose certain crystalloid hydrates. The water in alcohol of greater strength than corresponds with the density 0.926, which represents the definite hydrate  $C_4H_6O_2 + 6HO$ , is certainly in a state of chemical union. But alcohol so high as 0.906, contained in a close vessel, is concentrated in a notable degree by contact with dry mucus, gelatine, and gum, and sensibly even by dry parchment-paper. Dilute alcohol divided from the air of the atmosphere by a dry septum of mucus, gelatine, or gum, is also concentrated by evaporation, as in the well-known bladder experiment of Sömmerring. The selective power is here apparent of the colloid for water, that fluid being separated from alcohol, and travelling through the colloidal septum by combination with successive molecules of the latter, till the outer surface is reached and evaporation takes place. The penetration in this manner of a colloid by a foreign substance may be taken as an illustration of the phenomena of cementation. Iron and other substances which soften under heat, may be supposed to assume at the same time a colloidal constitution. So it may be supposed does silica when fused into a glass by heat, and every other vitreous substance.

Gelatinous hydrates always exhibit a certain tendency to aggregation,



as is seen in the jelly of hydrated silicic acid and of alumina. With some the jelly is also adhesive, as in glue and mucus. But unless they be soluble in water, gelatinous hydrates, when once formed, are not in general adhesive. Separated masses do not reunite when brought into contact. This want of adhesiveness is very remarkable in the gelose of Payen, which resembles gelatine so closely in other respects. Layers of a gelose solution, allowed to cool and gelatinize in succession in a diffusion-jar (p. 571), do not adhere together.

*Ice* itself presents colloidal characters at or near its melting-point, paradoxical although the statement may appear. When ice is formed at temperatures a few degrees under  $0^{\circ}$  C., it has a well-marked crystalline structure, as is seen in water frozen from a state of vapour, in the form of flakes of snow and hoar-frost, or in water frozen from dilute sulphuric acid, as observed by Mr. Faraday. But ice formed in contact with water at  $0^{\circ}$ , is a plain homogeneous mass with a vitreous fracture, exhibiting no facets or angles. This must appear singular when it is considered how favourable to crystallization are the circumstances in which a sheet of ice is slowly produced in the freezing of a lake or river. The continued extrication of latent heat by ice as it is cooled a few degrees below  $0^{\circ}$  C., observed by M. Person, appears also to indicate a molecular change subsequent to the first freezing. Further, ice, although exhibiting none of the viscous softness of pitch, has the elasticity and tendency to rend seen in colloids. In the properties last mentioned, ice presents a distant analogy to gum incompletely dried, to glue, or any other firm jelly. Ice further appears to be of the class of adhesive colloids. The redintegration (regelation of Faraday) of masses of melting ice, when placed in contact, has much of a colloid character. A colloidal view of the plasticity of ice demonstrated in the glacier movement will readily develop itself.

A similar extreme departure from its normal condition appears to be presented by a colloid holding so high a place in its class as albumen. In the so-called blood-crystals of Funke, a soft and gelatinous albuminoid body is seen to assume a crystalline contour. Can any facts more strikingly illustrate the maxim that in nature there are no abrupt transitions, and that distinctions of class are never absolute?

#### 8. *Osmose.*

Little has been said in the present paper respecting osmose, a subject closely connected with colloidal septa. It now appears to me that the water movement in osmose is an affair of hydration and of dehydration in the substance of the membrane or other colloid septum, and that the diffusion of the saline solution placed within the osmometer has little



or nothing to do with the osmotic result, otherwise than as it affects the state of hydration of the septum.

Osmose is generally considerable, through membranous and other highly hydrated septa, with the solution of any colloid (gum, for instance) contained in the osmometer. Yet the diffusion outwards of the colloid is always minute, and may sometimes amount to nothing. Indeed, an insoluble colloid, such as gum-tragacanth, placed in powder within the osmometer, was found to indicate the rapid entrance of water to convert the gum into a bulky gelatinous hydrate. Here no outward or double movement is possible.

The degree of hydration of any gelatinous body is much affected by the liquid medium in which it is placed. This is very obvious in fibrin and animal membrane. Placed in pure water, such colloids are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water tends to hydrate itself in a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane and reaches the inner surface, it there receives a check. The degree of hydration is lowered, and water must be given up by the inner layer of the membrane, and it forms the osmose. The contact of the saline fluid is thus attended by a continuous catalysis of the gelatinous hydrate, by which it is resolved into a lower gelatinous hydrate and free water. The inner surface of the membrane of the osmometer contracts by contact with the saline solution, while the outer surface dilates by contact with pure water. Far from promoting this separation of water, the diffusion of the salt throughout the substance of the membrane appears to impede osmose, by equalizing the condition as to saline matter of the membrane through its whole thickness. The advantage which colloidal solutions have in inducing osmose, appears to depend in part upon the low diffusibility of such solutions, and their want of power to penetrate the colloidal septum.

The substances fibrin, albumen, and animal membrane swell greatly when immersed in water containing minute proportions of acid or of alkali, as is well known. On the other hand, when the proportion of acid or alkali is carried beyond a point peculiar to each substance, contraction of the colloid takes place. Such colloids as have been named acquire the power of combining with an increased proportion of water, and of forming superior gelatinous hydrates, in consequence of contact with dilute acid and alkaline reagents. Even parchment-paper is more elongated in an alkaline solution than in pure water. When so



hydrated and dilated, the colloids present an extreme osmotic sensibility. Used as septa, they appear to assume or resign their water of gelatination under influences apparently the most feeble. It is not attempted to explain this varying hydration of colloids with the osmotic effects thence arising. Such phenomena belong to colloidal chemistry, where the prevailing changes in composition appear to be of the kind vaguely described as catalytic. To the future investigation of catalytic affinity, therefore, must we look for the further elucidation of osmose.

## XVI.

### ON THE CAPILLARY TRANSPIRATION OF LIQUIDS IN RELATION TO CHEMICAL COMPOSITION.<sup>1</sup>

From *Phil. Trans.* 1861, pp. 373-386. [*Roy. Soc. Proc.* xi. 1860-62, pp. 381-384; *Chem. Soc. Journ.* xv. 1862, pp. 427-445; *Paris Comptes Rendus*, liii. 1861, pp. 774-777.]

THE passage of liquids under pressure through a capillary tube is here spoken of as liquid transpiration, in accordance with the analogy of gaseous transpiration. The subject owes the development which it has already acquired chiefly to the investigations of the late Dr. Poiseuille.<sup>2</sup> The precision of the results attainable by the mode of experimenting pursued by that physicist has been remarked on by every one who has followed him in the inquiry. The observations on this subject which we owe to M. Poiseuille and other inquirers are very numerous, but have not, so far as I am aware, been connected hitherto with any speculative views of the chemical or molecular constitution of liquids.

The isolated discovery of M. Poiseuille, that diluted alcohol has a point of maximum retardation, coinciding with the degree of dilution at which the greatest condensation of the mixed liquids occurs, appears to offer a starting-point for new inquiries. The same result may be otherwise expressed, by saying that the definite compound of 1 equiv. of alcohol with 6 equivs. of water,  $C_4H_6O_2 + 6HO$ ,\* is more retarded than alcohol containing either a greater or a smaller proportion of water. The rate of transpiration appears here to depend upon chemical composition, and to afford an indication of it. A new physical property may

<sup>1</sup> Received June 20,—Read June 20, 1861.

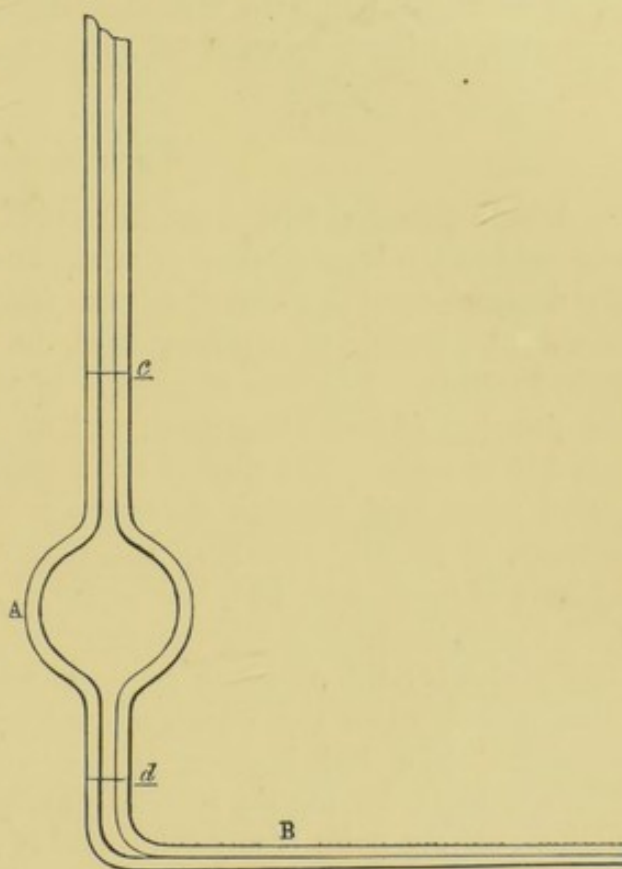
<sup>2</sup> *Mém. Savans étrangers*, tom. ix. p. 433; *Ann. Chim.* 3 sér. tt. 7 et 21.

\* Halving the equivalent of alcohol, the hydrate of greatest retardation becomes  $C_2H_3O + 3HO$ .



thus become available for the determination of the chemical constitution of substances. Methylic alcohol being found to exhibit the same remarkable feature in its transpiration, although the 6-hydrate of that alcohol is not distinguished by extraordinary condensation of volume, the inquiry was extended to the hydrated acids. The results obtained with the latter substances give a certain degree of generality to the relation subsisting between the transpirability and chemical composition of liquids.

The apparatus employed was very similar to that of M. Poiseuille. It consisted of a small but rather stout glass bulb, A (see figure), about two-thirds of an inch in diameter, having a capacity of from 4 to 8 cub. cent., blown upon a thick glass tube, with a bore of about 2 millimetres. A scratch (*c*) was made upon the glass tube above, and another (*d*) below the bulb, to indicate the available capacity of the instrument. The lower tube was bent at a right angle to the upper, and a fine capillary tube, B, from 3 to 4 inches in length, was sealed to the curved extremity of the tube. The bulb and capillary were always held immersed in a vessel of water during the experiment, in order to secure uniformity of temperature. The force



employed to impel the liquid through the capillary was the weight of one atmosphere of 760 millimetres of mercury, and was obtained from compressed air contained in a large reservoir provided with a mercurial gauge, as in Poiseuille's experiments. The time was noted in seconds which the level of the liquid in the bulb took to fall from the mark *c* to the mark *d*. This time varied from about 300 to 900 seconds in different liquids. In successive experiments made upon the same liquid, the variation in the time, or error of observation, did not exceed one or two seconds. The experiment was always repeated two or three times, and a mean taken. The temperature of the liquid transpired was always 20° (68° F.), when not otherwise stated.



The liquid may be introduced into the bulb through the open upper tube by means of a tube-funnel; but it was found more convenient in practice, although requiring a much longer time, to fill the bulb by aspiration through the capillary. With this view the compressed air was shut off by a stop-cock, and the upper tube of the bulb was then allowed to communicate with the receiver of an air-pump, instead, by which exhaustion was produced, while the open end of the capillary was immersed in a portion of the liquid. The liquid which entered the bulb in this manner was sure to be free from any solid matter which could cause obstruction in the capillary during the subsequent passage of the liquid outwards, while the disconnecting of the bulb from the rest of the apparatus, for the purpose of filling the former, was also avoided.

#### *Nitric Acid.*

A bulb provided with a capillary tube, distinguished as capillary C, was used in the transpiration of nitric acid and of several other liquids. The dimensions of this bulb C were as follows:—Capacity of bulb, 8.075 cub. cent.; length of capillary tube, 28 millims.; diameter of bore, 0.0942 millim. The time of passage of water through the tube, under the pressure of one atmosphere and at the fixed temperature of 20°, was 348 seconds. The time of the passage of the most highly concentrated nitric acid through the same capillary was found to be 344.5 seconds, or slightly less than the time of water. This is the protohydrate of nitric acid,  $\text{HO} \cdot \text{NO}_5$  or  $\text{NHO}_6$ . With the addition of water to the acid, the transpiration of equal volumes of liquid becomes gradually slower; till as much as three additional equivalents of water were added, when the transpiration-time rose to its maximum, 732 seconds. The last hydrate is the well-known definite compound  $\text{NHO}_6 + 3\text{HO}$ , having the specific gravity 1.4, and which possesses the highest boiling-point of any compound of nitric acid and water. Diluted beyond this point nitric acid begins to pass more freely, and the transpiration-time approaches again to that of water. With the addition of twice its weight of water, or about 7 equivalents, the acid passed through the capillary in 472 seconds.

The experiments made upon nitric acid are recorded in the following Table. It will be observed that the retardation is considerable for a certain distance on both sides of the maximum point. No unusual retardation appears to occur with the proportions of water corresponding to 2 and 4 equivalents. The specific gravity of the acid liquid is added in the last column of the Table, whenever that property was observed.



TABLE I.—Transpiration of Nitric Acid, at 20° C., by Capillary C.<sup>1</sup>

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid ( $\text{NHO}_6$ ).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
0	0	344.5	0.9899	1.5046
25.47	20.38	692	1.9885	1.4358
28.56 ... 2 eqs. HO	21.43	705	2.0258	
30	23.07	712	2.0459	
40	28.50	725	2.0833	
42.85 ... 3 eqs. HO	29.99	732	2.1034	1.3978
45	31.03	730	2.0977	
50	33.33	728.5	2.0919	1.3816
55	35.48	718	2.0632	
57.12 ... 4 eqs. HO	36.35	712	2.0459	
60	37.50	709.5	2.0387	1.3598
70	41.17	683	1.9626	1.3407
80	44.44	661	1.8994	1.3239
90	47.36	635.5	1.8261	
100	50.00	593	1.7040	1.2943
200	66.66	472	1.3563	

It appears, then, that a certain hydrate of nitric acid is marked out by its low transpirability so distinctly, that nitric acid could be identified by that physical property. Such a property may prove to be typical of a class of acids to which nitric acid belongs. The hydration of nitric acid probably advances by three equivalents at a time,  $\text{NHO}_6 + 3\text{HO}$ , as in the magnesian nitrates,  $\text{NMO}_6 + 3\text{HO} + 3\text{HO}$ . The transpiration of the assumed second hydrate of nitric acid was not made the subject of experiment. A certain steadiness is observed in the transpiration of this acid on either side of the point of maximum retardation.

<sup>1</sup> In the following Tables, the particular capillary employed is in each case designated by a particular letter. Capillary C, which was more employed than any other, became reduced in length during the course of the experiments, the end being ground off on several occasions on account of the choking of the tube. This capillary is then described as C shortened. It did not seem requisite to give in every case the dimensions of the bulb and capillary tube, as all the experiments were conducted on the same plan, and the transpiration of water is in every case given as a standard of comparison. Direct experiments were also made, which proved that the transpiration-times were sensibly inversely proportional to the effective pressure applied to the liquid, as found by Poiseuille; which indicates that the capillaries offered sufficient resistance to the passage of the liquid.



*Sulphuric Acid.*

TABLE II.—Transpiration of Sulphuric Acid, at 20°, by Capillary G.  
(Transpiration-time of water, 109 seconds.)

Water added to 100 acid ( $\text{SHO}_4$ ).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
0	0	2360	21.6514	1.8456
2.5	2.43	2412	22.1284	1.8398
5	4.76	2451	22.4862	1.8346
10	9.09	2516	23.0825	1.8120
12.5	11.11	2548	23.3761	1.7976
15	13.04	2587	23.7340	1.7800
17.5	14.89	2591	23.7706	
18.36 ... 1 eq. HO	15.13	2466	22.6238	1.7590
20	16.66	2398	22.0000	1.7473
30	23.07	1523	13.9724	1.6700
36.73 ... 2 eqs. HO	26.86	1189	10.9090	1.6335
40	28.50	1056	9.6880	1.6146
50	33.33	810	7.4302	1.5600
60	37.50	626	5.7431	1.5118
70	41.17	535	4.9082	
80	44.44	450	4.1284	
100	50.00	382	3.5045	
120	54.54	332	3.0458	
140	58.33	290	2.6605	
160	61.53	260	2.3889	
180	64.28	241	2.2110	
200	66.66	227	2.0825	

The transpiration of sulphuric acid is very slow, being twenty-four times less rapid than that of water, as might be expected from the viscous quality of the acid fluid. It is surprising, however, that the first additions of water do not promote the transpiration, although they lessen in a sensible degree the viscosity of the liquid. The transpiration-time increases from 2360 to 2591 seconds, and then attains the maximum, when 17.5 parts of water have been added to 100 parts of oil of vitriol. The proportion of water named approaches closely to 1 equivalent (18.36 parts). Indeed, it is quite possible that the acid mixture which exhibits the least transpirability might have contained a full equivalent of water, for a portion of aqueous vapour may have been absorbed from the air during the process of filling the bulb. That the crystallizable hydrate of sulphuric acid,  $\text{SHO}_4 + \text{HO}$ , is the liquid of least transpirability is, I believe, the proper inference from these



observations. With increasing proportions of water the transpiration-time rapidly diminishes, till the time is reduced to 227 seconds in a mixture of oil of vitriol with twice its weight of water.

A more minute examination than has been attempted would be required to show whether the existence of other definite hydrates of sulphuric acid may be indicated by a perceptible retardation in the time of transpiration.

*Acetic Acid.*

TABLE III.—Transpiration of Acetic Acid, at 20°, by Capillary C.

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid (C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> ).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
0·8	0·8	445·5	1·2801	
15 ... 1 eq. HO	13·04	890	2·5574	1·0735
20	16·66	921·5	2·6480	1·0742
25	20·00	931	2·6753	
27·5	21·56	933	2·6810	
30 ... 2 eqs. HO	23·07	941	2·7040	1·0752
32·5	24·52	934	2·6839	1·0746
35	25·92	928	2·6666	
40	28·50	912	2·6207	
45	31·04	895	2·5718	
50	33·33	882	2·5344	1·0720
60 ... 4 eqs. HO	37·50	852	2·4482	1·0700
90 ... 6 eqs. HO	47·36	769	2·2098	

The glacial acetic acid made use of in these experiments still retained 0·8 per cent. of water. Its transpiration-time was 445·5 seconds. With the addition of 1 equiv. of water the time rose to 890 seconds; and with 2 eqivs. of water to 941 seconds, when it attained its maximum. This last is the characteristic hydrate of acetic acid, C<sub>4</sub>H<sub>4</sub>O<sub>4</sub> + 2HO. It is marked out with great precision in these transpiration experiments. The times rise very gradually on either side, and appear to culminate exactly at that point. It is also the compound of water and acetic acid of maximum density, as is well known. The transpiration-time of the hydrate referred to is so much as 2·7 times longer than that of pure water. With 6 equivalents of water acetic acid is still transpired 2·2 times more slowly than water.



*Butyric Acid.*TABLE IV.—Transpiration of Butyric Acid,  $C_4H_8O_4$ , at  $20^\circ$ ,  
by Capillary C shortened.

(Transpiration-time of water, 290 seconds.)

Water added to 100 acid ( $C_4H_8O_4$ ).	Water, per cent.	Transpiration-time.		Specific gravity, at $15^\circ$ .
		In seconds.	Water = 1.	
0	0	454	1.565	.9740
10.22 ... 1 eq. HO	9.27	828	2.855	.9901
20.45 ... 2 eqs. HO	16.98	951	3.279	.9975
30.67 ... 3 eqs. HO	23.47	969	3.341	
38.69 ... 4.8 eqs. HO	27.85	863	2.975	

In the transpirability of its hydrates butyric acid presents a considerable analogy to acetic acid, as might be expected from the relation of these acids in composition. The time of the pure acid ( $C_4H_8O_4$ ) is 1.565, referred to that of water as 1, and it rises to 2.855 by the addition of 1 equivalent of water. By a second equivalent of water the time is increased to 3.279. Here, however, the progression does not immediately turn, as with acetic acid, but the time rises to 3.341 with 3 equivalents of water. With 3.8 equivalents of water the time is 2.975, and has accordingly very sensibly receded, the maximum point being passed. It is conceivable that the relation to acetic acid is slightly modified in butyric acid by the interference of some other physical property, such as unctuousity, that is unequally developed in the two acids.

*Valerianic Acid.*

The hydration of this acid cannot be carried beyond 2 equivalents, but up to that point the transpiration is retarded by every addition of water, as in acetic and butyric acids. While the pure basic hydrate ( $C_{10}H_{10}O_4$ ) is transpired in 2.155 times the water period, the time increases to 3.634 with 1 equivalent of water added, and to 3.839 with 2 equivalents.



TABLE V.—Transpiration of Valerianic Acid, at 20° C., by Capillary C shortened.

(Transpiration-time of water, 290 seconds.)

Water added to 100 acid (C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> ).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water=1.	
0	0	625·2	2·155	·9350
8·82 ... 1 eq. HO	8·10	1054	3·634	·9484
17·64 ... 2 eqs. HO	15·84	1113·5	3·839	·9519

*Formic Acid.*

Formic acid appears to diverge considerably from the other members of the acetic acid series in certain physical and chemical characters. While the acetic hydrate is lighter than water, and is increased in density by the addition of water, the formic hydrate has a higher density than water, and has its density uniformly lowered by dilution, as will be seen in the Table which follows. The transpiration-time of formic acid in a concentrated state is also highest, and diminishes with dilution in the same regular manner as the density, showing no evidence of the acetic maximum at the point of 2 equivalents of water. Indeed, formic acid does not appear to affect that particular degree of hydration so characteristic of the acetic acid series. Hence it is, also, that we have no subformiate of lead corresponding with the subacetate of lead, and have occasion to remark a general absence of basic formiates. The physical properties of liquid formic acid are more suggestive of hydrochloric acid than they are of acetic acid.

The most concentrated formic acid that could be prepared still contained 3·6 per cent. of water. The transpiration-time of that liquid, it will be seen, is 1·718 referred to water as 1; and of the 2-hydrate 1·486. There is evidence of retardation between the points of 3 and 4 equivalents of water, but it is difficult to say with which of these two hydrates the retardation should be connected. More numerous and minute observations would be required to settle the point. We can only draw the negative conclusion from the Table, that the maximum retardation does not coincide with the 2-hydrate as in acetic acid.



TABLE VI.—Transpiration of Formic Acid, at 20°, by Capillary C shortened.

(Transpiration-time of water, 293 seconds.)

Water added to 100 acid (C <sub>2</sub> H <sub>3</sub> O <sub>4</sub> ).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
3.73	3.6	503.5	1.718	1.2265
19.56 ... 1 eq.	16.35	484.5	1.653	1.2019
39.13 ... 2 eqs.	20.93	435.5	1.486	1.1765
58.69 ... 3 eqs.	36.98	411	1.402	1.1524
68.47 ... 3.5 eqs.	40.64	401.5	1.368	1.1466
78.26 ... 4 eqs.	43.90	402.5	1.372	1.1408
97.82 ... 5 eqs.	49.44	388.5	1.325	1.1275
117.35 ... 6 eqs.	53.99	376.5	1.284	1.1203
136.95 ... 7 eqs.	57.79	359	1.225	1.1062

*Hydrochloric Acid.*

The most concentrated form of this acid that was dealt with, acid of sp. gr. 1.1553, contained already upwards of 8 equivalents of water. Its transpiration-time was 1.7356, referred to the time of water as 1. With further dilution the time diminished, till at the proportion of 12 equivalents of water the time had fallen to 1.5287. About this point the rate of diminution is reduced, and the transpiration-time even becomes stationary for a short portion of the range of hydration. The retardation observed appears to coincide with the formation of a 12-hydrate of hydrochloric acid. The existence of such a compound is further supported by the fact that solutions of hydrochloric acid tend to the same composition by evaporation at the atmospheric temperature. The degree of hydration of most stability at high temperatures, and having the highest boiling-point, is known to be at or near the proportion of the 16-hydrate. The existence, however, of the latter hydrate, at the ordinary temperature, is not supported by the transpiration experiments now recorded, conducted as these were at a low temperature.



TABLE VII.—Transpiration of Hydrochloric Acid, at 20°, by Capillary C.

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid (H Cl).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
221·8	69·23	604	1·7356	1·1553
250	71·42	569	1·6336	1·1411
280	73·67	536	1·5404	1·1303
290	74·36	532	1·5287	
295·89 ... 12 eqs. HO	74·74	532	1·5287	1·1246
300	75·00	520	1·4942	
310	75·60	516	1·4827	1·1202
380	79·20	486	1·3965	1·1021
394 ... 16 eqs. HO	79·97	479	1·3764	1·0992
410	80·39	469	1·3476	1·0961

*Alcohol.*

The fundamental discovery made by Poiseuille of a point of maximum retardation in the transpiration of diluted alcohol is fully confirmed in the following series of observations. The transpiration-time rises from that of absolute alcohol, 1·1957 (water being 1), to 2·7872, when the alcohol is united with 6 equivalents of water, and then falls off again by further additions of water.

TABLE VIII.—



TABLE VIII.—Transpiration of Alcohol, at 20°, by Capillary D.  
(Transpiration-time of water, 470 seconds.)

Water added to 100 Alcohol.	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
0	0	562	1·1957	
1	0·99	578	1·2297	·7069
3	2·91	615	1·3085	·8030
5	4·76	650	1·3829	·8083
7	6·54	695	1·4787	
10	9·09	734	1·5617	
20	16·66	851	1·8106	·8396
30	23·07	950	2·0212	·8557
40	28·50	1029	2·1893	·8683
50	33·33	1093	2·3253	·8800
60	37·50	1152	2·4510	·8897
70	41·17	1213	2·5808	·8983
72·5	42·02	1230	2·6170	·9003
75	42·85	1231	2·6191	·9021
78·26 ... 4 eqs. HO	43·94	1239	2·6361	·9045
80	44·44	1238	2·6340	·9058
82·5	45·20	1242	2·6425	·9073
85	45·94	1244	2·6468	·9088
90	47·36	1256	2·6723	·9120
100	50·00	1268	2·6978	·9183
110	52·38	1282	2·7276	·9235
112·5	52·94	1287	2·7382	·9249
115	53·49	1298	2·7617	·9255
117·39 ... 6 eqs. HO	54·04	1310	2·7872	·9271
120	54·54	1307	2·7808	·9288
122	55·05	1300	2·7659	·9292
125	55·55	1297	2·7595	·9304
130	56·52	1297	2·7595	·9328
140	58·33	1295	2·7553	·9363
150	60·00	1280	2·7234	·9396
160	61·53	1255	2·6702	·9430
170	62·92	1250	2·6505	·9451
180	64·28	1246	2·6510	·9482
190	65·51	1240	2·6382	·9500
200	66·66	1235	2·6276	·9521
250	71·42	1165	2·4787	·9601
300	75·00	1094	2·3276	·9652
350	77·77	1026	2·1829	·9689
400	80·00	973	2·0702	·9716
450	81·80	934	1·9872	·9738
500	83·33	908	1·9319	·9759

It will be observed that after attaining its maximum the transpiration-time falls off in a very gradual manner, till another equivalent at least of water has been added. With still further dilution the shortening of the transpiration-time is considerably more rapid. The Table appears to indicate a slight retardation at the proportion of four equivalents of water; but this would require confirmation. It is remarkable



that hydrated liquid compounds appear in general to show only one decided transpiration maximum, as with the 1-hydrate in sulphuric acid, the 2-hydrate in acetic acid, the 3-hydrate in nitric acid, the 6-hydrate in alcohol, and the 12-hydrate in hydrochloric acid.

A considerable number of experiments were made upon specimens of *methylic alcohol* prepared at different times, with some discrepancy in the results. Although always derived from crystallized methylic oxalic ether, the liquid varied sensibly in transpirability. As the cause of this variation has not yet been ascertained, I shall confine myself at present to one statement, namely, that a particular specimen of methylic alcohol gave 0.63 as the transpiration-time of the anhydrous substance (water being 1), and 1.8021 as the time of the 6-hydrate,  $C_2H_4O_2 + 6HO$ , and that for a considerable distance on either side of that point of hydration the transpiration was slightly less and nearly constant, as it is in vinic alcohol. It may be inferred, therefore, with some probability, that alcohols have a maximum of retardation at the same stage of dilution.

Three alcohols in a state of purity were transpired through the same capillary, with water for comparison, at  $20^\circ$ . The time of water was 297 seconds.

TABLE IX.—Transpiration of Alcohols, at  $20^\circ$ .

	Transpiration-time.		Specific gravity, at $15^\circ$ .	Boiling point.
	In seconds.	Water = 1.		
Methylic alcohol, . . .	187.25	0.630	.7973	$66^\circ$ C.
Vinic alcohol, . . .	355.1	1.195	.7947	78.5
Amylic alcohol, . . .	1084	3.649	.8204	132

It will be remarked that the transpiration-time of an alcohol increases with the elevation of its temperature of ebullition. A similar observation applies to the transpiration of ethers.

TABLE X.—Transpiration of Ethers, at  $20^\circ$ , by Capillary C shortened.  
(Transpiration-time of water, 290 seconds.)

	Transpiration-time.		Specific gravity, at $15^\circ$ .	Boiling point.
	In seconds.	Water = 1.		
Formiate of ethyl, . . .	148.2	0.511	.9174	$55.5^\circ$
Acetate of ethyl, . . .	160.5	0.553	.8853	74
Butyrate of ethyl, . . .	217.5	0.750	.8490	114
Valerianate of ethyl, . . .	237.5	0.827	.8750	133.5



The transpiration-times of the homologous acids, previously observed, appear also to follow in progression.

Transpiration of Acids, at 20°.

	Acid.	Acid + 2HO.
Acetic acid, . . .	1.2801	2.740
Butyric acid, . . .	1.565	3.279
Valerianic acid, . . .	2.155	3.839

The increase of the transpiration-time of an alcohol, ether, and acid, as each rises in its series, may be connected with the increasing weight of their molecule.

*Acetone.*

The transpiration of this liquid is remarkably rapid. It is also greatly retarded by the addition of water. The time will be found to rise from 0.401, that of anhydrous acetone, to 1.604, the time of the 12-hydrate, taking the equivalent of acetone as  $C_6H_6O_2$ , or of the 6-hydrate with the equivalent  $C_3H_3O$ .

TABLE XI.—Transpiration of Acetone, at 20°, by Capillary C.  
(Transpiration-time of water, 348 seconds.)

Water added to 100 acetone ( $C_6H_6O_2$ ).	Water per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
0	0	139.6	0.401	.7943
15.51 ... 1 eq.	13.42	212.5	0.610	.8384
31.03 ... 2 eqs.	23.68	283.5	0.814	.8604
46.55 ... 3 "	31.76	355.5	1.021	.8850
62.06 ... 4 "	38.29	457	1.313	.8990
77.58 ... 5 "	43.68	464	1.333	.9123
85.34 ... 5.5 "	46.04	469	1.347	.9173
93.10 ... 6 "	48.21	482	1.385	.9219
100	50.00	500	1.436	.9251
108.61 ... 7 "	52.06	515.5	1.479	.9300
124.13 ... 8 "	55.33	531.5	1.527	.9320
139.65 ... 9 "	57.85	537.7	1.543	.9413
155.16 ... 10 "	60.81	552.7	1.586	.9468
170.67 ... 11 "	63.05	555.5	1.594	.9504
186.18 ... 12 "	65.05	558.5	1.604	.9526
201.71 ... 13 "	66.85	556.5	1.599	.9563
217.24 ... 14 "	68.41	557	1.600	.9588
232.75 ... 15 "	69.94	553.5	1.590	.9608
248.27 ... 16 "	71.28	549	1.577	.9632
263.79 ... 17 "	72.23	547	1.571	.9649
279.31 ... 18 "	73.63	546	1.568	.9662
294.82 ... 19 "	74.67	539.5	1.550	.9676
372.24 ... 24 "	78.82	519	1.491	.9736



The transpiration-time of acetone attains a maximum at what is represented in the Table as the compound with 12 equivalents of water. The time is nearly stationary for some distance on either side of that point, the range from 10 to 15 equivalents of water being 1.586 to 1.590, with 1.604 as a maximum for the intermediate twelfth equivalent.

*Glycerine.*

This liquid is too viscid in a state of purity to be transpired by means of the bulb and capillaries employed in these experiments. The observations to be recorded were confined to diluted solutions of glycerine approaching in composition to the 18-hydrate,  $C_6H_8O_6 + 18HO$ . It was imagined that glycerine as a triatomic alcohol might affect combination with water in the proportion named.

TABLE XII.—Transpiration of Glycerine, at 20°, by Capillary C.

(Transpiration-time of water at the same temperature,  
348 seconds.)

Water added to 100 Glycerine ( $C_6H_8O_6$ ).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
170	62.96	1199	3.445	1.1010
176.07...18 eqs.	63.77	1160	3.333	1.0980
180	64.28	1131.5	3.251	1.0960
190	65.51	1068.5	3.070	1.0934
192	65.75	1054	3.031	1.0927
195	66.10	1049	3.014	1.0914
197	66.32	1039	2.977	1.0912
200	66.66	1026	2.948	1.0905

The transpiration-time of 18-hydrate is 3.333, referred to water as 1. There is no indication of a maximum at that point, but the numbers descend according to their place in the Table without any interruption.

The idea having suggested itself that the viscous property of glycerine solutions might overpower or conceal the expected deviation, the transpiration was repeated at a higher temperature, when the solutions possess greater fluidity.



TABLE XIII.—Transpiration of Glycerine, at 60°, by Capillary C.

(Transpiration-time of water at the same temperature,  
186 seconds.)

Water added to 100 Glycerine (C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> ).	Water, per cent.	Transpiration-time.		Specific gravity, at 15°.
		In seconds.	Water = 1.	
170	62.96	435.5	2.341	1.1010
172.5	63.30	432	2.322	1.0999
175	63.63	428	2.301	1.0980
176.08...18 eqs.	63.77	425	2.284	1.0976
177	63.96	422.5	2.271	1.0970
180	64.22	420	2.258	1.0960

Still no retardation appears at the point of 18 equivalents, but the time continues to shorten as the proportion of water is increased, according to a pretty uniform progression. The information respecting the constitution of glycerine which transpiration affords is therefore of a negative character.

The existence of a relation between the transpirability of liquids and their chemical composition appears to be established. It is a relation analogous in character to that subsisting between the boiling-point and composition, so well defined by M. Kopp. Perhaps the most interesting part of the present subject to develop would be the transpiration of homologous series of substances. Judging from the limited observations recorded above on the alcohols, ethers, and acids, the order of succession of individual substances in any series would be indicated by the degree of transpirability of these substances, as clearly as it is by their comparative volatility. In carrying out the inquiry, it would probably be found advantageous to operate at a fixed temperature, which is somewhat elevated. A large number of substances are liquid at 100°, of which the transpiration-time could be easily obtained.

In hydrated substances transpiration also affords a manifestation of definite combination at once striking and precise. I need only refer to the manner in which the "constitutional" hydrate of sulphuric acid  $\text{SHO}_4 + \text{HO}$ , of acetic acid  $\text{C}_4\text{H}_4\text{O}_4 + 2\text{HO}$ , of nitric acid  $\text{NHO}_6 + 3\text{HO}$ , and of alcohol  $\text{C}_4\text{H}_6\text{O}_2 + 6\text{HO}$  is each indicated by its maximum transpiration-time. The indication of the alcohol-hydrate is particularly distinct, although that hydrate must be a comparatively feeble com-



pound. Indeed the extent to which transpiration is affected by the annexation of constitutional water appears to be by no means in proportion to the intensity of combination.

The increased resistance to transpiration observed in these definite hydrates may be connected with their larger molecules. But another speculative view of the retardation can be suggested, in which the phenomenon is referred to a physical agency. When one of these definite hydrates, say the 6-hydrate of alcohol, is being forced through the capillary, it may be imagined that a small portion of the hydrated compound is molecularly decomposed by the friction. A certain portion of the impelling force would thereby be lost, being converted into the latent heat which alcohol and water require to assume when separated from each other, and the transpiration be consequently retarded; for as alcohol and water evolve heat on combining, so they must absorb heat when their union is dissolved by any cause. But the change of temperature representing the lost force appears to be too small to be rendered sensible to observation. It would be capable of raising the temperature of the transpired liquid not more than about one forty-third part of a degree, according to an accurate estimate for which I am indebted to Professor Stokes. In consequence of this circumstance the physical hypothesis now suggested has neither been verified nor disproved.

To this paper are appended two series of observations made on transpiration at different temperatures, the first series being the transpiration of water, and the second that of absolute alcohol. Each series of experiments is repeated with two capillary tubes, one having nearly double the resistance of the other. The numbers from the two capillaries exhibit a fair amount of agreement. The times given are those actually observed, no correction being made for the small variation of the capillary in diameter at different temperatures.

The dimensions of Capillary D were as follows:—Capacity of bulb, 4.135 cub. cent.; length of capillary tube, 37.5 millims.; diameter of bore, 0.10325 millim. Time of passage of water, at 20°, under pressure of one atmosphere, 470 seconds.

The dimensions of Capillary E were as follows:—Capacity of bulb, 3.725 cub. cent.; length of capillary, 53 millims.; diameter of bore, 0.0858 millim. Time of passage of water, at 20°, under pressure of one atmosphere, 913 seconds.



TABLE XIV.—Transpiration of Water at different Temperatures.

By capillary tube D.				By capillary tube E.			
Temperature.	Time in seconds.	Time and velocity of water at 20°=1.		Time in seconds.	Time and velocity of water at 20°=1.		Time and velocity of water at 0°=1.
		Time.	Velocity.		Time.	Velocity.	
0	840	1.7872	0.5593	1629	1.7872	0.5604	1.
1	792	1.6851	0.5934	1568	1.7174	0.5829	1.0389
2	770.5	1.6391	0.6099	1514	1.6582	0.6050	1.
3	749	1.5936	0.6275	1461	1.6002	0.6249	1.1449
4	727	1.5468	0.6465				
5	709	1.5085	0.6629	1382	1.5136	0.6606	1.1787
7	669	1.4234	0.7025	1289	1.4118	0.7083	1.2638
10	618	1.3148	0.7605	1188	1.3012	0.7685	1.3717
14	548	1.1659	0.8576				
15	533	1.1340	0.8818	1037	1.1358	0.8804	1.5709
16	521	1.1085	0.9021				
20	470	1.	1.	913	1.	1.	1.7842
25	414	0.8808	1.1352	823	0.9014	1.0904	1.9793
30	375.5	0.7989	1.2516	743	0.8138	1.2288	2.1924
35	338	0.7191	1.3905	670	0.7338	1.3626	2.4313
40	309.5	0.6508	1.5185	602	0.6593	1.5166	2.7059
45	284.5	0.6053	1.6520	553	0.6056	1.6509	2.9459
50	261	0.5553	1.8007	505	0.5531	1.8079	3.2257
55	243	0.5170	1.9341	475	0.5202	1.9221	3.4294
60	228	0.4851	2.0614	438	0.4797	2.0844	3.7191
65	214	0.4553	2.1967	400	0.4381	2.2825	4.0725
70	200	0.4155	2.3500	378	0.4140	2.4153	4.3122



TABLE XV.—Transpiration of Alcohol at different Temperatures.

Temperature.	Time in seconds.	By capillary tube D.				By capillary tube E.			
		Time and velocity of water at 20°=1.		Time and velocity of water at 0°=1.		Time and velocity of water at 20°=1.		Time and velocity of water at 0°=1.	
		Time.	Velocity.	Time.	Velocity.	Time.	Velocity.	Time.	Velocity.
0° C.	860	1·8297	0·5465	1·0238	0·9767	1·7984	0·5560	1·0079	0·9920
1	840	1·7893	0·5588	1·0012	0·9988	1·7535	0·5702	0·9828	1·0174
3	807	1·7170	0·5824	0·9607	1·0409	1·6834	0·5940	0·9435	1·0598
5	772	1·6425	0·6089	0·9190	1·0880	1·6133	0·6198	0·9042	1·1059
7	738	1·5702	0·6368	0·8785	1·1382	1·5443	0·6475	0·8656	1·1553
10	700	1·4893	0·6714	0·8333	1·2000	1·4786	0·6755	0·8226	1·2066
15	624	1·3276	0·7532	0·7428	1·3461	1·3285	0·7526	0·7446	1·3429
20	562	1·1957	0·8362	0·6690	1·4946	1·1960	0·8360	0·6703	1·4917
25	520	1·1063	0·9038	0·6190	1·6154	1·0963	0·9120	0·6145	1·6273
30	476	1·0127	0·9873	0·5566	1·7646	1·0022	0·9978	0·5617	1·7803
35	428	0·9106	1·0981	0·5095	1·9626	0·9233	1·0830	0·5175	1·9323
40	391	0·8319	1·2020	0·4654	2·1483	0·8455	1·1826	0·4739	2·1101
45	360	0·7659	1·3055	0·4285	2·3333	0·7743	1·2913	0·4340	2·3041
50	331·5	0·7053	1·4177	0·3946	2·5339	0·7064	1·4155	0·3959	2·5100
55	307	0·6531	1·5309	0·3654	2·7301	0·6484	1·5422	0·3634	2·7517
60	285	0·6063	1·6491	0·3392	2·9473	0·6035	1·6569	0·3382	2·9564
65	262	0·5574	1·8005	0·3119	3·2061	0·5585	1·7901	0·3130	3·1941
70	241	0·5127	1·9502	0·2869	3·4854	0·5125	1·9465	0·2873	3·4807



## XVII.

ON THE PROPERTIES OF SILICIC ACID AND OTHER  
ANALOGOUS COLLOIDAL SUBSTANCES.

From the *Journal of the Chemical Society*, 1864.

THE prevalent notions respecting solubility have been derived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal substances. Hydrated silicic acid, for instance, when in the soluble condition, is, properly speaking, a liquid body, like alcohol, miscible with water in all proportions. We have no degrees of solubility to speak of with respect to silicic acid, like the degrees of solubility of a salt, unless it be with reference to silicic acid in the gelatinous condition, in which it is usually looked upon as destitute of solubility. The jelly of silicic acid may be more or less rich in combined water, as it is first prepared, and it appears to be soluble in proportion to the extent of its hydration. A jelly containing 1 per cent. of silicic acid, gives with cold water a solution containing about 1 part of silicic acid in 5000 water; a jelly containing 5 per cent. of silicic acid gives a solution containing about 1 part of acid in 10,000 water. A less hydrated jelly than the last mentioned is still less soluble; and, finally, when the jelly is rendered anhydrous, it forms gummy-looking white masses, which appear to be absolutely insoluble, like the light dusty silicic acid obtained by drying a jelly charged with salts, in the ordinary analysis of a silicate.

The liquidity of silicic acid is only affected by a change, which is permanent (namely, coagulation or pectization), by which the acid is converted into the gelatinous or pectous form, and loses its miscibility with water. This change may be brought about by time alone. The liquidity is permanent in proportion to the degree of dilution of silicic acid, and appears to be favoured by a low temperature. It is opposed, on the contrary, by concentration, and by elevation of temperature. A liquid silicic acid of 10 or 12 per cent. pectizes spontaneously in a few hours at the ordinary temperature, and immediately when heated. A liquid of 5 per cent. may be preserved for five or six days; a liquid of 2 per cent. for two or three months; and a liquid of 1 per cent. has not pectized after two years. Dilute solutions of 0.1 per cent or less are no doubt practically unalterable by time, and hence the possibility of soluble silicic acid existing in nature. I may add, however, that no solution, weak or strong, of silicic acid in water has shown any disposition to deposit *crystals*, but always appears on drying as a colloidal



glassy hyalite. The formation of quartz crystals at a low temperature, of so frequent occurrence in nature, remains still a mystery. I can only imagine that such crystals are formed at an inconceivably slow rate, and from solutions of silicic acid which are extremely dilute. Dilution no doubt weakens the colloidal character of substances, and may therefore allow their crystallizing tendency to gain ground and develop itself, particularly where the crystal once formed is completely insoluble, as with quartz.

The pectization of liquid silicic acid is expedited by contact with solid matter in the form of powder. By contact with pounded graphite, which is chemically inactive, the pectization of a 5 per cent. silicic acid is brought about in an hour or two, and that of a 2 per cent. silicic acid in two days. A rise of temperature of  $1^{\circ}\cdot 1$  C. was observed during the formation of the 5 per cent. jelly.

The ultimate pectization of silicic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid-transpiration tube may be employed as a colloidoscope. With a colloidal liquid alterable in viscosity, such as silicic acid, the increased resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinizing, silicic acid flows like an oil.

A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid, and when it advances, leads to pectization. In the jelly itself, the specific contraction in question, or *synæresis*, still proceeds, causing separation of water, with division into clot and serum, and ending in the production of a hard stony mass of vitreous structure, which may be anhydrous, or nearly so, when the water is allowed to escape by evaporation. The intense *synæresis* of isinglass dried in a glass dish over sulphuric acid *in vacuo*, enables the contracting gelatine to tear up the surface of the glass. Glass itself is a colloid, and the adhesion of colloid to colloid appears to be more powerful than that of colloid to crystalloid. The gelatine, when dried in the manner described upon plates of calspar and mica, did not adhere to the crystalline surface, but detached itself on drying. Polished plates of glass must not be left in contact, as is well known, owing to the risk of permanent adhesion between their surfaces. The adhesion of broken masses of glacial phosphoric acid to each other is an old illustration of colloidal *synæresis*.

Bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but greatly more developed in some sub-



stances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions. These characters appear in the viscosity of liquids, and in the softness and adhesiveness of certain crystalline substances. Metaphosphate of soda, after fusion by heat, is a true glass or colloid; but when this glass is maintained for a few minutes at a temperature some degrees under its point of fusion, the glass assumes a crystalline structure without losing its transparency. Notwithstanding this change, the low diffusibility of the salt is preserved, with other characters of a colloid. Water in the form of ice has already been represented as a similar intermediate form, both colloid and crystalline, and in the first character adhesive and capable of reunion or "regelation."

It is unnecessary to return here to the fact of the ready pectization of liquid silicic acid by alkaline salts, including some of very sparing solubility, such as carbonate of lime, beyond stating that the presence of carbonate of lime in water was observed to be incompatible with the co-existence of soluble silicic acid, till the proportion of the latter was reduced to nearly 1 in 10,000 water.

Certain liquid substances differ from the salts in exercising little or no pectizing influence upon liquid silicic acid. But, on the other hand, none of the liquids now referred to appear to conduce to the preservation of the fluidity of the colloid, at least not more than the addition of water would do. Among these inactive diluents of silicic acid are found hydrochloric, nitric, acetic, and tartaric acids, syrup of sugar, glycerin, and alcohol. But all the liquid substances named, and many others, appear to possess an important relation to silicic acid, of a very different nature from the pectizing action of salts. They are capable of displacing the combined water of the silicic acid hydrate, whether that hydrate is in the liquid or gelatinous condition, and give new substitution-products.

A liquid compound of *alcohol* and silicic acid is obtained by adding alcohol to aqueous silicic acid, and then employing proper means to withdraw the water from the mixture. For that purpose the mixture contained in a cup may be placed over dry carbonate of potash or quicklime, within the receiver of an air-pump. Or a dialysing bag of parchment paper containing the mixed alcohol and silicic acid may be suspended in a jar of alcohol: the water diffuses away, leaving in the bag a liquid composed of alcohol and silicic acid only. A point to be attended to is, that the silicic acid should never be allowed to form more than 1 per cent. of the alcoholic solution, otherwise it may gelatinize during the experiment. If I may be allowed to distinguish the liquid and gelatinous hydrates of silicic acid by the irregularly formed terms of *hydrosol* and *hydrogel* of silicic acid, the two corresponding alcoholic



bodies now introduced may be named the alcosol and alcogel of silicic acid.

The *alcosol* of silicic acid, containing 1 per cent. of the latter, is a colourless liquid, not precipitated by water or salts, nor by contact with insoluble powders, probably from the small proportion of silicic acid present in solution. It may be boiled and evaporated without change, but is gelatinized by a slight concentration. The alcohol is retained less strongly in the alcosol of silicic acid than water is in the hydrosol, but with the same varying force, a small portion of the alcohol being held so strongly as to char when the resulting jelly is rapidly distilled at a high temperature. Not a trace of silicic ether is found in any compound of this class. The jelly burns readily in the air, leaving the whole silicic acid in the form of a white ash.

The *alcogel*, or solid compound, is readily prepared by placing masses of gelatinous silicic acid, containing 8 or 10 per cent. of the dry acid in absolute alcohol, and changing the latter repeatedly till the water of the hydrogel is fully replaced by alcohol. The alcogel is generally slightly opalescent, and is similar in aspect to the hydrogel, preserving very nearly its original bulk. The following is the composition of an alcogel carefully prepared from a hydrogel which contained 9.35 per cent. of silicic acid :—

Alcohol,	. . . . .	88.13
Water,	. . . . .	0.23
Silicic acid,	. . . . .	11.64
		<hr/>
		100.00

Placed in water, the alcogel is gradually decomposed—alcohol diffusing out and water entering instead, so that a hydrogel is reproduced.

Further, the alcogel may be made the starting-point in the formation of a great variety of other substitution jellies of analogous constitution, the only condition required appearing to be that the new liquid and alcohol should be intermiscible, that is, interdiffusible bodies. Compounds of ether, benzole, and bisulphide of carbon have thus been produced. Again, from *etherogel* another series of silicic acid jellies may be derived, containing fluids soluble in ether, such as the fixed oils.

The preparation of the *glycerin-compound* of silicic acid is facilitated by the comparative fixity of that liquid. When hydrated silicic acid is first steeped in glycerin, and then boiled in the same liquid, water distils over, without any change in the appearance of the jelly, except that when formerly opalescent it becomes now entirely colourless, and ceases to be visible when covered by the liquid. But a portion of the silicic acid is dissolved, and a *glycerosol* is produced at the same time as the glycerin jelly. A glycerogel prepared from a hydrate containing



9.35 per cent. of silicic acid, was found by a combustion analysis to be composed of—

Glycerin, . . . . .	87.44
Water, . . . . .	3.78
Silicic acid, . . . . .	8.95
	<hr/>
	100.17

The glycerogel has somewhat less bulk than the original hydrogel. When a glycerine jelly is distilled by heat, it does not fuse, but the whole of the glycerine comes over, with a slight amount of decomposition towards the end of the process.

The compound of sulphuric acid, *sulphagel*, is also interesting from the facility of its formation, and the complete manner in which the water of the original hydrogel is removed. A mass of hydrated silicic acid may be preserved unbroken if it is first placed in sulphuric acid diluted with two or three volumes of water, and then transferred gradually to stronger acids, till at last it is placed in concentrated oil of vitriol. The *sulphagel* sinks in the latter fluid, and may be distilled with an excess of it for hours without losing its transparency or gelatinous character. It is always somewhat less in bulk than the primary hydrogel, but not more, to the eye, than one-fifth or one-sixth part of the original volume. This *sulphagel* is transparent and colourless. When a *sulphagel* is heated strongly in an open vessel, the last portions of the monohydrated sulphuric acid in combination are found to require a higher temperature for their expulsion, than the boiling-point of the acid. The whole silicic acid remains behind, forming a white opaque, porous mass, like pumice. A *sulphagel* placed in water is soon decomposed, and the original hydrogel reproduced. No permanent compound of sulphuric and silicic acids, of the nature of a salt, appears to be formed in any circumstances. A *sulphagel* placed in alcohol gives ultimately a pure *alcogel*. Similar jellies of silicic acid may readily be formed with the monohydrates of nitric, acetic, and formic acids, and are all perfectly transparent.

The production of the compounds of silicic acid now described, indicates the possession of a wider range of affinity by a colloid than could well be anticipated. The organic colloids are no doubt invested with similar wide powers of combination, which may become of interest to the physiologist. The capacity of a mass of gelatinous silicic acid to assume alcohol, or even olein, in the place of water of combination, without disintegration or alteration of form, may perhaps afford a clew to the penetration of the albuminous matter of membrane by fatty and other insoluble bodies, which seems to occur in the digestion of food. Still more remarkable and suggestive are the *fluid* compounds of silicic acid. The fluid alcohol-compound favours the possibility of the exist-



ence of a compound of the colloid albumin with olein, soluble also and capable of circulating with the blood.

The feebleness of the force which holds together two substances belonging to different physical classes, one being a colloid and the other a crystalloid, is a subject deserving notice. When such a compound is placed in a fluid, the superior diffusive energy of the crystalloid may cause its separation from the colloid. Thus, of hydrated silicic acid, the combined water (a crystalloid) leaves the acid (a colloid) to diffuse into alcohol; and if the alcohol be repeatedly changed, the entire water is thus removed, alcohol (another crystalloid) at the same time taking the place of water in combination with the silicic acid. The liquid in excess (here the alcohol) gains entire possession of the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Then alcohol separates from combination, in consequence of the opportunity it possesses to diffuse into water; and water, which is now the liquid present in excess, recovers possession of the silicic acid. Such changes illustrate the predominating influence of mass.

Even the compounds of silicic acid with alkalies, yield to the decomposing force of diffusion. The compound of silicic acid with 1 or 2 per cent. of soda is a colloidal solution, and, when placed in a dialyser over water *in vacuo* to exclude carbonic acid, suffers gradual decomposition. The soda diffuses off slowly in the caustic state, and gives the usual brown oxide of silver when tested with the nitrate of that base.

The pectization of liquid silicic acid and many other liquid colloids, is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may again be liquefied and have its energy restored by contact with a very moderate amount of alkali. The latter change is gradual, 1 part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100° C. Gelatinous stannic acid also is easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyser. The solution of these colloids, in such circumstances, may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid, but alkaline. Liquid silicic acid may be represented as the "peptone" of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali, may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxide of iron, and titanous acid, prepared by dialysis, are assimilated more closely to albumin, being peptized by minute quantities of hydrochloric acid.

*Liquid Stannic and Metastannic Acids.*—Liquid stannic acid is pre-



pared by dialysing the bichloride of tin with an addition of alkali, or by dialysing the stannate of soda with an addition of hydrochloric acid. In both cases a jelly is first formed on the dialyser; but, as the salts diffuse away, the jelly is again peptized by the small proportion of free alkali remaining: the alkali itself may be removed by continued diffusion, a drop or two of the tincture of iodine facilitating the separation. The liquid stannic acid is converted, on heating it, into liquid metastannic acid. Both liquid acids are remarkable for the facility with which they are peptized by a minute addition of hydrochloric acid, as well as by salts.

*Liquid Titanic Acid* is prepared by dissolving gelatinous titanic acid in a small quantity of hydrochloric acid, without heat, and placing the liquid upon a dialyser for several days. The liquid must not contain more than 1 per cent. of titanic acid, otherwise it gelatinizes spontaneously, but it appears more stable when dilute. Both titanic and the two stannic acids afford the same classes of compounds with alcohols, etc., as are obtained with silicic acid.

*Liquid Tungstic Acid*.—The obscurity which has so long hung over tungstic acid is removed by a dialytic examination. It is in fact a remarkable colloid, of which the pectous form alone has hitherto been known. Liquid tungstic acid is prepared by adding dilute hydrochloric acid carefully, and in slight excess to a 5 per cent. solution of tungstate of soda, and then placing the resulting liquid on a dialyser. At intervals of two days, the addition of hydrochloric acid must be repeated two or three times, and the dialysis continued in order to remove the whole alkali. It is remarkable that the *purified* acid is not peptized by acids, salts, or alcohol at the ordinary temperature. Evaporated to dryness, it forms vitreous scales, like gum or gelatin, which sometimes adhere so strongly to the surface of the evaporating dish as to detach portions of it. It may be heated to 200° C. without losing its solubility, or passing into the pectous state, but, at a temperature near redness, it undergoes a molecular change, closing at the same time 2.42 per cent. of water. When water is added to unchanged tungstic acid, the acid becomes pasty and adhesive, like gum; and it forms a liquid with about one-fourth its weight in water, which is so dense as to float glass. The solution effervesces with carbonate of soda. The taste of tungstic acid dissolved in water is not metallic or acid, but rather bitter and astringent. Solutions of tungstic acid containing 5, 20, 50, 66.5, and 79.8 per cent. of dry acid, possess the following densities at 19°: 1.0475, 1.2168, 1.8001, 2.396, and 3.243. Evaporated *in vacuo*, liquid tungstic acid is colourless, but becomes greenish in air, apparently from the deoxidating action of organic matter. Liquid silicic acid is protected from peptizing when mixed with tungstic acid, a circumstance probably connected



with the formation of the double compounds of these two acids which M. Marignac has lately indicated.

*Molybdic Acid* has hitherto been known (like tungstic acid) only in the insoluble form. Crystallized molybdate of soda dissolved in water is decomposed by the gradual addition of hydrochloric acid in excess, without any immediate precipitation. The acid liquid thrown upon a dialyser may gelatinize after a few hours, but again liquefies spontaneously, when the salts diffuse away. After repeated additions of hydrochloric acid, and a diffusion of several days, about 60 per cent. of liquid molybdic acid remains behind in a pure condition. In the dialysis of both tungstic and molybdic acids, the osmose is very great, the acid solutions increasing to two or three times their original volume. The consequent dilution causes the purification to be slow, as compared with that of silicic acid where the osmose is inconsiderable. The solution of pure molybdic acid is yellow, astringent to the taste, acid to test-paper, and possesses much stability. The acid may be dried at  $100^{\circ}$ , without immediately losing its solubility. Dry molybdic acid has the same gummy aspect as tungstic acid. Heated short of the point at which it volatilizes, pure molybdic acid in powder will still dissolve in a solution of carbonate or bicarbonate of potash, with effervescence of carbonic acid gas. Both acids lose their colloidality when combined with soda, and give a variety of crystallizable salts. The pure liquid acids also become insoluble, when heated for some time with hydrochloric or other strong acids.



# UNCLASSIFIED PAPERS.

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## I.

### ON THE HEAT OF FRICTION.

From *Annals of Philosophy*, xii. 1826, pp. 260-262.

EDINBURGH, Sept. 7, 1826.

It is generally allowed, that the heat extricated in friction is inexplicable upon the theory of the materiality of heat, as at present entertained. It would be easy to show that this heat does not arrive at the bodies rubbed together, by the ordinary and admissible methods of conduction or radiation, or, that no reduction of bulk takes place, or diminution of capacity for heat. Yet the materiality of heat is involved in the principal doctrines of chemistry, while the simplicity and easy application of the theory render its establishment exceedingly desirable. In these circumstances, an attempt to reconcile the substantial existence of heat with its appearance in friction, may not be unworthy of attention, even although the suppositions on which it is founded should be altogether novel; elucidating, as they do, other departments of science.

Heat is observed by us, either radiant in motion, and possessed of great velocity; or in union with matter, and capable of regaining this velocity.

Probably this velocity is necessary to its entering into bodies and uniting with them; at least we never observe heat do so without it. For, when communicated by radiation, this is evident; and in conduction, which in close contact supplies the place of radiation, it is evident that heat is communicated with a force. Indeed, conduction may be reduced with considerable plausibility to an internal radiation.

It appears that this motive power, which is essential to the communication of heat and our perception of it, is really never annihilated. It disappears when heat passes into a body, but it is merely overpowered for a time, and not altogether lost; for upon reduction of temperature, the heat emanates from the body, evincing its pristine velocity. We may compare the state of the heat in union with matter to that of a bent



spring, or a compressed elastic substance, the attraction of the matter for heat being the restraining force. Sensible heat, therefore, we never find destitute of this motive power, nor to lose it—at least heat is never so divested of it as to be incapable of resuming it.

These observations prepare us for the conception of heat in a different state from that in which it is generally supposed to exist. Let us suppose that the calorific principle is capable, likewise, of existing destitute of this motive power; and yet not in combination with matter, which this motive power seems necessary to effect. We may suppose it capable of existing in a state similar to our ordinary conceptions of the electric fluid. As a fluid, powerfully repelling its own particles, and attracting those of other matter, spread equally over the surfaces of all bodies, independently of their composition or temperature, without combining with these bodies, diffused (to borrow an illustration from chemistry) like a drop of oil upon the surface of water, without being in combination with it. To the matter of heat in this quiescent state, we shall, for the sake of convenience, give the name *superficial heat*, from its covering the superficies or surfaces of bodies. It is merely heat to which there has not been imparted that original velocity, upon which the characteristic properties of sensible heat depend. Superficial heat, it is evident, must be insensible. But project it with the necessary velocity, and you render it sensible. This might result from extraordinary accumulation of our idio-repulsive body, or its concentration upon a particular spot. Dissipation, by means of radiation, appears to be a natural effect of the repulsion between the particles of superficial heat, aggravated to a great degree.

Now in friction, circumstances are favourable to the conversion of superficial into sensible heat, in this manner. The surfaces of the bodies rubbed together are brought rapidly into exceedingly close contact, so that as surfaces they virtually cease to exist. From the violent approximation, the idio-repulsive power of the superficial heat investing both the surfaces, is powerfully exerted; so that a portion of the superficial heat is expelled as radiant heat, and impinges upon the rubbing surfaces. But more superficial heat is supplied from the earth; and as long as the friction is continued, superficial heat is converted into sensible, and the bodies become hotter and hotter. Hence the heat attending friction; and the reason why more heat is elicited, when the surfaces are smooth than when they are rough, their approach in the former case being more close, and the investing superficial heat more condensed.

In a course of experiments upon the heat produced in friction, M. Haldat attempted to insulate his apparatus for that purpose, by means of non-conductors of electricity. Upon reference, however, to his paper,<sup>1</sup>

<sup>1</sup> Nicholson's *Journal*, vol. xxvi. p. 30.



it will be found, that notwithstanding the body of the apparatus was electrically insulated with great care, yet the insulation of the machine and contrivance by which motion was conveyed to the rubbing surfaces, was overlooked. The result of this imperfect insulation was a diminution of one-third in the amount of heat evolved. New experiments upon this subject are very desirable.

The theory which we have applied to friction admits of very great extension. We may suggest that the phenomena of electricity are caused by an accumulation, or a deficiency, of our superficial heat. That the electric fluid is really superficial heat, and convertible into sensible heat in the manner explained.

Hence we never perceive anything which we can call the radiation of electricity. We never find that one electrified body communicates any of its electricity to another body at a distance by this means. For it follows from the doctrines illustrated, that should ever electricity (superficial heat) emanate from bodies in this manner, it should be in the shape of radiant heat.

We scarcely need adduce instances, in which heat, in its sensible form, does attend the accumulation of electricity. When a powerful current of the electric fluid is concentrated, by being passed along a thin wire, the wire is heated to a great degree, so as to become strongly radiant. In this way, charcoal, or any other body, may be kept in the voltaic arc in a state of intense ignition. Here, from the great repulsive force that must attend such an accumulation of superficial heat, which will be much enhanced by the retardation of the passage of the fluid, occasioned by the imperfect conducting power of the substance, a large portion is expelled with the necessary velocity, and becomes thereby sensible heat. According to this theory, electrical light and heat are derived from the same source as the heat of friction; and in neither case is there any production or actual generation of these principles.

The simplicity of this theory is its chief recommendation. That heat, possessed of a substantial existence, should be found alone, uncombined with matter, and that this combination, of a most elementary kind, should, at all times, be brought about by the calorific principle impinging with force upon the material body, are not hard postulates. Most material substances, however strong their affinities for each other, require peculiarly favourable circumstances to enable these affinities to act, otherwise the bodies appear to a certain extent repulsive of each other. Moreover, when we attribute to the matter of heat diffused over the surfaces of bodies, an attraction for these substances which yet does not amount to the production of a combination, we are but extending to heat properties, which all other material substances evince, in adhesion, capillary attraction, etc.



It is hoped, likewise, that the theory of superficial heat is not chargeable with that barrenness and want of practical application, which generally characterize premature speculations upon abstract subjects. The knowledge of the existence of such an agent, of its influence in friction and electricity, and of its convertibility into sensible heat, affords a clew of no small importance to guide us in our researches. Its application in galvanism, we shall, perhaps, hereafter, have an opportunity of exhibiting.

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## II.

### ALCOHOL DERIVED FROM THE FERMENTATION OF BREAD.

From *Annals of Philosophy*, xii. 1826, p. 363.

(*To the Editors of the Annals of Philosophy.*)

EDINBURGH, Sept. 25, 1826.

GENTLEMEN,—Two facts of considerable importance in determining the nature of the *panary* fermentation have been made known by your ingenious correspondent upon the art of baking bread. He has shown that the fermentation depends upon the saccharine ingredient of the flour, by renewing it when exhausted by the addition of sugar; and provided for the little alteration in the proportion of sugar existing in the flour, before and after fermentation, by exhibiting the influence of the baking in converting a portion of the starch into sugar. From the known laws of the decomposition of sugar, it is presumed, with considerable reason, that the fermentation is the vinous. The production of alcohol in the course of the fermentation of bread in baking, which we have found to take place, and rendered appreciable, is perhaps a most irrefragable proof of which this theory is susceptible.

To avoid the use of yeast, which might introduce alcohol, a small quantity of flour was kneaded, and allowed to ferment in the usual way, to serve as leaven. By means of the leaven a considerable quantity of flour was fermented; and, when the fermentation had arrived at the proper point, formed into a loaf. The loaf was carefully enclosed in a distillatory apparatus, and subjected for a considerable time to the baking temperature. Upon examining the condensed liquid, the taste and smell of alcohol were quite perceptible, and by repeatedly rectifying it a small quantity of alcohol was obtained of strength sufficient to burn, and to ignite gunpowder by its combustion.



The experiment was frequently repeated, and in different bakings the amount of alcohol obtained, of the above strength, found to vary from 0.3 to 1 per cent. by weight of the flour employed. When the fermented flour was allowed to sour before baking, the amount of alcohol rapidly diminished; and in all cases, the disagreeable empyreuma completely disguised the peculiar smell of the alcohol, when in its first diluted state, and in vapour.—I am, Gentlemen, with great respect, your most obedient servant,

THOMAS GRAHAM.

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### III.

#### EFFECTS OF ANIMAL CHARCOAL ON SOLUTIONS.

From *Quart. Journ. Science*, i. 1830, pp. 120-125. [Dingler, *Polytechn. Journ.* xl. 1831, pp. 443-446; Poggend. *Annal.* xix. 1830, pp. 139-144.]

THE property of withdrawing matters from a state of solution, possessed by the charcoal of bone-black, has been investigated in the case of soluble colouring matters of a vegetable and animal origin. It is known, that the discolouring faculty resides entirely in the charcoal, for the earthy matters and portions of azote combined with it, possess by themselves no such power, and the charcoal discolours without them. This property is also greatly exalted by the state of extreme division and porosity of animal charcoal, arising from the interposition of foreign particles of earthy and saline matter between the particles of carbonaceous matter in bone, which effectually prevents the aggregation of the carbon during calcination. The bright, hard charcoal from the calcination of dried blood has no discolouring power; but the charcoal from the calcination of dried blood, mixed with carbonate of potash, as in the manufacture of prussiate of potash, proves the most efficient discolouring form of charcoal we possess, after the alkaline carbonate is washed out. A very intense heat, however, destroys entirely the discolouring power of bone-black.

The colouring matters are not destroyed or decomposed by the charcoal, but merely withdrawn from a state of solution, in combination with the surface of the charcoal, and may be again dissolved out and made to appear by the action of a more powerful solvent.

M. Lowitz first discovered this property of charcoal in 1791. He



used only charcoal of wood. M. Guilbert observed, that the discolouring power of wood charcoal was improved by exposing it for a considerable time, in a wet state, to the rays of the sun. In 1810, M. Figuier, Professor of Chemistry at Montpellier, discovered that animal charcoal discoloured with much greater power. It has subsequently been used very extensively by the sugar-refiners of France in clarifying their syrups. Of bone or ivory-black, one-sixth of the weight of the raw sugar is boiled with it for ten minutes. The charcoal and impurities are separated by filtering, and the syrup is filtered a second time to separate a little charcoal which comes through the first filter (Payen). In the *Journal de Pharmacie*, tom. iv. pp. 301-7, there is a distinct account of the mode of preparing bone-black, by M. Cadet de Gassicourt; and in the same work, tom. viii. pp. 257-277, an excellent memoir on charcoal, considered as a discolouring substance, by A. Bussy, which was crowned by the Society of Pharmacy of Paris, and contains everything known on the subject. It is followed by another memoir on the same subject by M. Payen, to which a second prize was adjudged. [The substance of the preceding memoir is given in this Journal, vol. xiii. pp. 406-16.]

But the action of animal charcoal on solutions has been considered hitherto only in reference to the removal of colouring matters. More determinate results, however, might be expected in solutions of saline and other chemical bodies, of which the composition is known. The investigation is also interesting, from the light which it may throw upon the state of combination in which bodies exist in cases of ordinary solution, as salt in water, to which the doctrine of definite proportions seems wholly inapplicable. If a solid body, such as carbon, destroy such a combination, and take down the saline matter attached to its surface, we may conclude that there is an analogy between the combination of the salt with the water, and the combination of the salt with the charcoal, and that the former as well as the latter processes have something of a mechanical character.

The same property is possessed by other solid bodies, in a state of minute division, as when newly precipitated, although not in so great a degree. And, in analytic researches, its interference must be guarded against, as it may contribute, in some cases, to increase the weight of precipitates.

The animal charcoal, employed in the following experiments, was prepared from common bone, or ivory-black, by boiling dilute muriatic acid upon it, and afterwards washing it with hot water till the water came off tasteless. No more than 10 or 12 per cent. of charcoal remained after dissolving out the earthy salts. On burning this charcoal, it left a grey ash, amounting to about one-twelfth of the original weight,



insoluble in water and acids, and almost entirely silica. Charcoal prepared in this way, M. Bussy found to go no farther in discolouring than one and a half times its weight of the original ivory-black.

In my first experiments, it was found that the prepared charcoal, in great excess, had no sensible effect in impoverishing a saturated solution of common salt at natural temperatures. The proportion of salt remaining in solution was always as great as water was found capable of retaining, at the same time, at the lowest temperature which had occurred during the experiment.

A solution of nitrate of lead, with the charcoal repeatedly agitated, and occasionally tested with carbonate of soda, gave a distinct precipitate the first day, a much less distinct the second, and the merest trace the third day. But, on heating the water, the charcoal part of the nitrate was re-dissolved, and afforded a copious precipitate, with carbonate of soda and with sulphuretted hydrogen.

The dinitrate of lead, which is soluble, was taken down completely by the charcoal, so that no trace of it was perceived by means of sulphuretted hydrogen. But on heating the water over it to  $200^{\circ}$ , part was re-dissolved, as in the previous case, but again taken down completely by the charcoal on cooling. The action of the charcoal on the cold solution of the dinitrate was immediate, and much more energetic than in the case of the nitrate. The former salt, however, is much less soluble in water than the latter. Other soluble subsalts were tried.

2. Three grains diacetate of lead in one ounce water, with twenty grains common ivory-black; taken down completely, and not re-dissolved in any degree on boiling.

Four grains trisacetate of lead; same results.

Four grains tartar emetic in one ounce water, with twenty grains of the prepared charcoal, in the cold; agitated occasionally for several days; still a copious precipitate, with hydrosulphuret of ammonia. After a second addition of twenty grains of the charcoal, only a trace of antimony, with sulphuretted hydrogen.

Lime-water was deprived entirely of the lime which it contains, in the cold, as Dr. Paris previously observed, so that the liquid remaining did not act on reddened litmus.

Arsenious acid was not taken down entirely in six weeks by great excess of the charcoal, no heat being applied.

No quantity of the charcoal could take down bisulphate of copper.

Ammonia was added in excess to bisulphate of copper, so as to form the deep-blue solution of ammonio-sulphate: the latter was readily taken down by the charcoal, and the liquid became perfectly colourless. Strong ammonia was digested in the cold upon the charcoal containing the salt of copper, and also boiled upon it, without dissolving a trace



of it, as the ammonia did not become blue even when poured off and exposed to the air. In a certain experiment, the deep-blue colour of five grains bisulphate of copper in half an ounce of caustic ammonia, diluted with one and half ounces water, was much impaired by twenty grains of the charcoal. Increasing the charcoal every second day, by five grains at a time, with thirty-five grains, the colour had become very slight, and was entirely destroyed by forty grains; nor did the supernatant ammonia contain any protoxide of copper.

Five grains of nitrate of silver, in the same quantity of ammonia and water, with twenty grains of the charcoal. Next day no trace of silver in solution could be detected: two and a half grains nitrate of silver added; agitated occasionally with the charcoal, but after several days there was still silver in solution. On examining the phial containing the above materials some time afterwards, shining metallic spangles were perceived among the charcoal.

The solution of chloride of silver in ammonia was also taken down completely by the charcoal.

A solution was made of ten grains hydrated protoxide of lead in caustic potash, which was diluted with water till it amounted to three ounces. Twenty grains of the charcoal, added to the above solution, in a phial, which was then corked up, took down so much of the oxide of lead that the white colour of the latter substance was quite discernible among the charcoal. Here we have the colour of the charcoal disguised in the compound. Making successive additions of charcoal, the oxide of lead in solution was reduced to a trace by ninety grains; the last additions of charcoal floated over the heavy portion containing the oxide of lead; the supernatant solution, which had a greenish tinge, was poured off, and the charcoal washed, thrown on a filter, and dried at a heat which did not exceed  $212^{\circ}$ . When dry, innumerable metallic particles were visible in it; so that the oxide of lead is easily reducible by the charcoal attached to it.

The oxide of zinc was withdrawn entirely by the charcoal from solution in caustic ammonia.

A deep-red solution was made of five grains iodine in fifteen grains pure hydriodate of potash, dissolved in two ounces water. Forty grains of the charcoal were added before the colour of the iodine was wholly removed from the solution; the liquid acquired a faint acid reaction: the carbon was washed, and dried in a filter on the sandbath without exhaling any iodine vapours; but on heating it strongly in a flask by a lamp, iodine rose in vapour, and condensed on the sides of the flask with some moisture. The iodine was afterwards re-absorbed by the dry charcoal when cold.

Labarraque's disinfecting fluid (chloride of soda with bicarbonate



of soda) may be boiled without being materially injured; but I was surprised to find that ebullition for a few seconds of a large quantity of that fluid, in contact with a few grains of the charcoal, completely destroyed its bleaching power.

The same effect took place in the cold, on agitating the fluid and the charcoal together for a few minutes. No gas was emitted in either case. On evaporating the saline solution to dryness, it was found to contain no notable quantity of chlorate of soda. Twenty grains of carbon were adequate to destroy the bleaching power of a pint of the disinfecting fluid recently prepared.

A solution of common bleaching powder, chloride of lime, was destroyed by charcoal with nearly equal facility, particularly when hot.

A pound of water, recently impregnated with an equal bulk of chlorine gas, was heated rapidly to the boiling point, in contact with twenty grains of the charcoal, in a glass flask provided with a perforated cork and bent glass tube, for the purpose of collecting any gas which might be given off. Gas was collected, but it was entirely carbonic acid, and most of the charcoal disappeared: muriatic acid was found in the liquid. On collecting the unconsumed charcoal in this and other cases, and washing it several times after being dried on a sandbath, it gave out a few drops of strong muriatic acid, when heated in a glass tube by means of a lamp.

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#### IV.

#### NOTE ON THE PREPARATION OF CHLORATE OF POTASH.

From *Chem. Soc. Mem.* 1841-43, pp. 5-7.

It is well known that the ordinary processes for this important salt are attended with some practical difficulties. When a stream of chlorine gas is passed through a strong solution of carbonate of potash, the absorption of the gas is rapid and complete, till one-half of the alkaline carbonate is decomposed; but the remaining portion, which is in the state of bicarbonate, is not so easily acted upon. To decompose the latter salt completely, chlorine must be applied in excess, and the decomposition is attended by the formation of free hypochlorous acid, as has been proved by Mr. Detmer. The liquid is also at the end highly bleaching, and contains much hypochlorite of potash. The boiling



necessary to convert the latter into chlorate of potash and chloride of potassium occasions, according to M. Morin, a considerable loss of oxygen, and thus lessens the product of chlorate. When a strong solution of caustic potash is substituted in this process for the carbonate, the absorption of chlorine proceeds without interruption; but the liquid when saturated bleaches strongly from hypochlorite formed. A long-continued boiling is required to destroy this property completely, and as oxygen escapes, the chlorate obtained must be deficient in quantity in a corresponding proportion. The process which the author recommends, and which is attended with none of these inconveniences, consists in mixing carbonate of potash intimately with an equivalent quantity of dry hydrate of lime, and exposing the mixture to chlorine gas. This mixture, although quite dry, absorbs the gas with prodigious energy, the temperature rises much above  $212^{\circ}$ , and water is freely evolved. When saturated it may be moderately heated, which destroys a mere trace of hypochlorite it contains. The whole lime is found in the state of carbonate, and the potash as chlorate and chloride of potassium. The solution of the two latter salts is neutral, without any bleaching property, and free from lime. The chlorate of potash may be crystallized from it in the usual way. Carbonate of potash, when moistened and exposed to chlorine, without the hydrate of lime, absorbs the gas with great avidity, and certainly answers better than a strong solution of the same salt; but the absorption becomes slow after the salt is in the state of bicarbonate, and subsequently a large quantity of the bleaching hypochlorite of potash is produced. In the new process described above, there is no reason to believe that the carbonate of potash is decomposed by the dry hydrate of lime till the chlorine is presented to the mixture; then, while the lime attracts the carbonic acid, the chlorine acts simultaneously upon the potash, and the carbonate of potash is thus readily decomposed. The same principle of calling in a secondary agency to promote combination may be taken advantage of in many other cases. One of these, of some interest, is the promotion of the absorption of sulphuretted hydrogen by hydrate of lime, through the influence of other salts. Thus hydrate of lime, dry or slightly damped, ceases to absorb sulphuretted hydrogen long before it is saturated with that gas; but if mixed with an equivalent of hydrated sulphate of soda, the absorption takes place with greatly increased avidity, and goes on till two equivalents of sulphuretted hydrogen are taken up for one equivalent of lime. But here, with the assistance of sulphuretted hydrogen, the hydrate of lime decomposes the sulphate of soda, sulphate of lime being formed, while caustic soda combines with the sulphuretted hydrogen.

The author has found that the last mixture may be applied with



advantage, from its great absorbing power, in purifying coal-gas, where the highest degree of purification is desirable, and where the products, sulphate of lime and hydrosulphuret of sulphuret of sodium, can be economically applied. He recommends it to be introduced into the last of the dry-lime purifiers.

## V.

## LETTRE DE M. GRAHAM À M. DUMAS

SUR QUELQUES CONSIDÉRATIONS QUI DERIVENT DE LA LOI DES  
SUBSTITUTIONS ET SUR UN SYSTÈME DE NOTATION APPLICABLE  
AUX FORMULES DES TYPES.

From *Annal. de Chimie*, iv. 1842, pp. 177-186.

LONDRES, 30 novembre 1841.

“EN vous priant d'accepter la dernière partie de mon ouvrage, je désire en même temps appeler votre attention sur quelques considérations qui dérivent de votre loi des substitutions, et sur un système de notation que je crois particulièrement applicable aux formules des types, de façon à les distinguer de celles que appartiennent à la théorie des radicaux.”

Toute théorie de combinaisons serait incomplète si elle ne tenait compte, dans la constitution assignée aux éléments et aux combinaisons, de la propagation de l'action chimique à une distance qu'on peut apprécier dans une couple voltaïque. Cette considération nous a déjà amenés à conclure que même un élément isolé, tel qu'un métal dans l'état où nous l'employons, possède une structure moléculaire compliquée, ses atomes se groupant réellement de manière à représenter des combinaisons binaires. Ainsi, quand nous combinons deux éléments différents, nous avons réellement à défaire une combinaison préexistante, mais moins stable, avant d'unir les éléments dissemblables. Par suite, même dans les cas où la combinaison paraît la plus directe, elle est réellement due à une double décomposition, ou bien à la substitution d'un élément à un autre dans un cadre de combinaisons préexistantes. De plus, l'aptitude des combinaisons, de toute sorte, à se décomposer sous une action électrique intense, paraît indiquer une simplicité et une identité de composition plus grandes qu'on ne l'admettait généralement.



Nous repoussons l'idée de voir des atomes de même sorte appartenir indifféremment à divers systèmes de combinaison, car la différence de nature paraît la cause déterminante de la combinaison des corps. L'intensité de la combinaison augmente certainement par la différence des éléments, mais cela ne prouve pas que cette différence soit une condition essentielle de la combinaison. L'état de combinaison paraît, en vérité, l'état naturel de la matière, en même temps que la source de sa cohésion et de son agrégation : c'est l'inertie qui lui permet de conserver cette disposition, et, pour la détruire, il faut l'application d'une force telle que celle de la chaleur, pour déterminer la séparation des molécules.

En regardant comme binaire la combinaison fondamentale et élémentaire de chaque composé, l'un des éléments étant négatif et l'autre positif, on peut exprimer cette différence, en séparant par un trait le symbole des deux éléments, mettant l'élément positif au-dessous et l'autre en-dessus : Eau  $\frac{\text{O}}{\text{H}}$  ; acide carbonique  $\frac{\text{O}_2}{\text{C}}$  ; hydrate de potasse

$\frac{\text{OO}}{\text{KH}}$  ; carbonate de potasse  $\frac{\text{O}_2\text{O}}{\text{CK}}$ , gaz oléfiant  $\frac{\text{H}_4}{\text{C}_4}$ , ou  $\frac{\text{H}_2\text{H}_2}{\text{C}_2\text{C}_2}$  ; éther  $\frac{\text{H}_5\text{O}}{\text{C}_4}$  ; alcool  $\frac{\text{H}_5\text{OO}}{\text{C}_4\text{H}}$ .

La plupart de ces formules signifient seulement que certains éléments pris collectivement sont négatifs, et que certains autres, collectivement aussi, sont basiques. Ainsi, dans l'éther, 4 atomes sont basiques  $\text{C}_4$ , et 6 ( $\text{H}_5\text{O}$ ) sont négatifs. Mais on doit supposer que beaucoup de composés admettent une division poussée plus loin : le gaz oléfiant, par exemple, peut se représenter par  $2\text{C}_2\text{H}_2$  ou  $\frac{\text{H}_2\text{H}_2}{\text{C}_2\text{C}_2}$ , ou même  $\frac{\text{HHHH}}{\text{CCCC}}$  ; ce qui peut se résumer ainsi :

1. L'élément basique ou positif est en combinaison immédiate avec l'élément ou les éléments électro-négatifs placés au-dessus dans la formule ;

2. Ces combinaisons binaires s'associent de nouveau pour former la molécule composée, par suite d'une attraction réciproque de tous les éléments basiques et de tous les éléments électro-négatifs. C'est là ce qui maintient réunis les 3 atomes similaires qui forment 1 équivalent d'azote ou de phosphore ; les trois atomes de cyanogène dans l'acide cyanurique ; les différents multiples de  $\text{C}_2\text{H}_2$  groupés ensemble pour former la molécule de gaz oléfiant et des hydrocarbures ses isomères ou bien encore, les multiples de  $\text{C}_5\text{H}_4$  dans la molécule d'essence de térébenthine.

Une molécule organique est donc représentée comme l'association de



deux ou plusieurs combinaisons binaires, d'une constitution simple relativement, souvent susceptibles d'être isolées et douées d'une grande stabilité.

Parmi les corps placés en haut dans les formules, on peut s'attendre à trouver le chlore, l'oxygène, l'azote, l'hydrogène, et en bas le carbone, ou le carbone et l'hydrogène. Les premiers éléments paraissent électro-négatifs dans l'ordre où ils sont placés :

Chlore,  
Oxygène,  
Soufre,  
Azote,  
Hydrogène.

On trouve dans les cas de substitution que les corps placés à la fin du tableau précédent, sont remplacés par ceux qui les précèdent. L'azote paraît plus électro-négatif que l'oxygène, mais seulement dans certaines doubles décompositions où il intervient comme élément de l'ammoniaque, ce qui ne suffit pas pour déterminer son rang ; de même qu'on pourrait aussi placer l'oxygène avant le chlore, d'après la conversion du chloroforme  $\text{FoCl}_3$  en acide formique par la potasse.

*Combinaisons du même type.*—Ce sont des corps qui renferment le même nombre d'atomes élémentaires tant électro-négatifs que basiques.

Type gaz oléfiant  $\frac{\text{H}_4}{\text{C}_4}$  ; chlorure de carbone  $\frac{\text{Cl}_4}{\text{C}_4}$ .

Type éther  $\frac{\text{H}_5\text{O}}{\text{C}_4}$  ; chlorure d'éthyle  $\frac{\text{H}_5\text{Cl}}{\text{C}_4}$  ; éther hydrochlorique chloré  $\frac{\text{H}_4\text{Cl}_2}{\text{C}_4}$ .

Type alcool  $\frac{\text{H}_5\text{OO}}{\text{C}_4\text{H}}$  ; acide acétique  $\frac{\text{H}_3\text{O}_3\text{O}}{\text{C}_4\text{H}_2}$  ; acide chloracétique  $\frac{\text{Cl}_3\text{O}_3\text{O}}{\text{C}_4\text{H}}$ .

Type aldéhyde  $\frac{\text{H}_3\text{OO}}{\text{C}_4\text{H}}$  ; chloral  $\frac{\text{Cl}_3\text{OO}}{\text{C}_4\text{H}}$ .

*Ammoniaque.*—Sa formule paraît être  $\frac{\text{N}}{\text{H}_3}$  et non pas  $\frac{\text{H}_3}{\text{N}}$ . L'hydrogène étant basique, ne serait pas remplacé par le chlore, et l'on n'a pas observé de sels chlorés d'ammoniaque analogues aux éthers chlorés. La connaissance que nous avons de la composition du chlorure d'azote ne suffit pas pour décider la question. On se souvient que dans la formule ci-dessus N équivaut à  $\text{O}_3$  ou  $\text{H}_3$  ; le précipité blanc de mercure de



Wöhler  $\text{HgCl} + \text{NH}_3$ , et le précipité blanc ordinaire  $\text{HgCl} + \text{HgNH}_2$  peuvent être assimilés et représentés respectivement par  $\frac{\text{ClN}}{\text{HgH}_3}$  et  $\frac{\text{ClN}}{\text{HgH}_2\text{Hg}}$ .

Le composé noir produit par l'action de l'ammoniaque liquide sur le calomel est représenté par  $\frac{\text{ClN}}{\text{Hg}_2\text{H}_2\text{Hg}_2}$  ou peut-être par  $\frac{\text{ClHgN}}{\text{Hg}_2\text{H}_2\text{Hg}}$ . Ainsi, la présence de l'amidogène n'est pas nécessaire dans les amides métalliques, mais paraît indispensable à la constitution de l'oxamide et de l'urée. Pour l'oxalate d'ammoniaque et l'oxamide, les formules sont  $\frac{\text{O}_3\text{ON}}{\text{C}_2\text{HH}_3}$  et  $\frac{\text{O}_2\text{N}}{\text{C}_2\text{H}_2}$ .

*Cyanogène et cyanures.*—La formule du cyanogène est  $\frac{\text{N}}{\text{C}_2}$ , car l'acide hydrocyanique est  $\frac{\text{NH}}{\text{C}_2}$ , et non pas  $\frac{\text{N}}{\text{C}_2\text{H}}$ . Que son hydrogène ne soit pas basique, c'est ce que prouve la formation du chlorure de cyanogène par substitution de chlore et production d'acide hydrochlorique. C'est ce qui explique aussi la faible action de la potasse sur l'acide hydrocyanique, son hydrogène étant électro-négatif, tandis que le même hydrogène est promptement remplacé par le mercure, le cyanure de mercure étant  $\frac{\text{NHg}}{\text{C}_2}$ . Ce dernier sel n'est pas décomposé par les acides énergiques, comme cela arriverait si sa composition ressemblait à celle du cyanure de potassium  $\frac{\text{N}}{\text{C}_2\text{K}}$ . Mais le cyanure de mercure est promptement décomposé par le soufre et l'hydrogène sulfuré, ainsi que par l'acide hydrochlorique, le soufre et le chlore formant du sulfure et du chlorure de mercure, tandis que l'hydrogène laissé à la place du mercure employé reproduit l'acide hydrocyanique  $\frac{\text{NH}}{\text{C}_2}$ .\*

Les 2 atomes de cyanure d'hydrogène qui existent dans l'acide ferrocyanique  $\text{FeCy} + 2\text{HCy}$  ont au contraire la constitution d'un hydracide ordinaire, l'hydrogène étant aisément remplacé par les métaux basiques, le potassium, etc. Il contient donc  $\frac{\text{N}_2}{\text{C}_4\text{H}_2}$ . Mais le fer du cyanure de

\* Rien ne prouve mieux la difficulté de concilier les théories anciennes et nouvelles que cette nécessité admise par M. Graham de considérer le cyanure de mercure et celui de potassium comme deux corps renfermant deux radicaux différents.



fer n'étant pas précipité par la potasse, doit être électro-positif, et le cyanure métallique se représente par  $\frac{NFe}{C_2}$ .

Acide ferrocyanique  $\frac{NFe}{C_2} \cdot \frac{N^2}{C_4H_2}$ ;

Ferrocyanure de potassium  $\frac{NFe}{C_2} \cdot \frac{N^2}{C_4K_2}$ .

Les formules de l'acide ferricyanique ( $H_3 + Fe_2Cy_6$ ) et du ferricyanure de potassium ( $K_3 + Fe_2Cy_6$ ) sont  $\frac{NFe_2N_3}{C_6C_6H_3}$  et  $\frac{N_3Fe_2N_3}{C_6C_6K_3}$ .

En donnant au sulfocyanogène  $C_2NS_2$  la formule moléculaire  $\frac{NS_2}{C_2}$ , ses combinaisons seront

Acide hydrosulfocyanique hydraté  $\frac{NS_2}{C_2H}$ ;

Sulfocyanure de potassium  $\frac{NS_2}{C_2K}$ .

L'acide cyanique hydraté et le cyanate de potasse seront représentés par des formules analogues :

Acide cyanique hydraté  $\frac{NO_2}{C_2H}$ ;

Cyanate de potasse  $\frac{NO_2}{C_2K}$ ;

Les deux corps isomères, le cyanate de potasse et l'urée, ont une formule moléculaire différente.

Cyanate d'ammoniaque  $\frac{NO_2N}{C_2HH_3}$ ;

Urée  $\frac{NO_2N}{C_2H_2H_2}$ .

On représente l'urée comme renfermant 1 at. de cyanogène, 2 at. d'eau et 1 at. d'amidogène. D'après l'opinion générale elle contient 2 atomes d'oxyde de carbone et 2 d'amidogène, ce qu'on peut représenter

par la formule  $\frac{O_2NN}{C_2H_2H_2}$ .

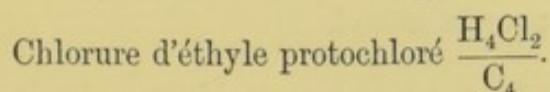
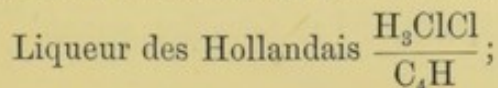
Mais le cyanogène existant probablement dans l'urée, la première formule est préférable. On peut alors comparer l'urée à l'allantoïne, qui contient 2 atomes de cyanogène et 3 atomes d'eau.

Allantoïne  $\frac{N_2O_3}{C_4H_3}$  ou  $\frac{NO_3N}{C_2H_3C_2}$ .



En doublant son atome, cette matière et sa combinaison avec l'oxyde d'argent deviennent  $\frac{N_4O_6}{C_8H_6}$  et  $\frac{N_4O_6}{C_8H_5Ag}$ .

D'après la différence d'action de la potasse sur des corps isomériques, tels que la liqueur des Hollandais et le chlorure d'éthyle protochloré, on ne peut douter de la différence de leur formule moléculaire,



Tandis que les autres composés chlorés de chlorure d'éthyle sont  $\frac{H_3Cl_3}{C_4}$  et  $\frac{H_2Cl_4}{C_4}$ , ceux du gaz oléfiant sont, d'après l'action des alcalis,  $\frac{H_2Cl_2Cl}{C_4H}$  et  $\frac{HCl_3Cl}{C_4H}$ . Car la liqueur des Hollandais et les deux autres corps cèdent à la potasse HCl, et abandonnent trois composés du même type  $\frac{H_3Cl}{C_4}$ ,  $\frac{H_2Cl_2}{C_4}$ , et  $\frac{HCl_3}{C_4}$ .

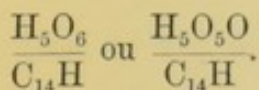
Les éléments qui sont électro-négatifs ou basiques ensemble dans un composé, exercent entre eux une influence réciproque, bien qu'on puisse supposer qu'ils ne sont pas combinés comme ceux dont l'état électrique est opposé, car on trouve une tendance à s'organiser en couples. Ainsi, la combinaison chlorée d'oxyde d'éthyle a pour formule empirique  $C^4H^3Cl^2O$ , et pour formule moléculaire  $\frac{H_3Cl_2O}{C_4}$ , ou mieux

$\frac{H_2Cl_2HO}{C_4}$ , où les 3 atomes d'hydrogène sont associés à 3 autres plus négatifs encore, 2 de chlore et 1 d'oxygène. On ne peut douter que ces trois atomes d'hydrogène ne soient à l'abri de l'action ultérieure du chlore et moins aisément chassés que les deux autres.

La formule moléculaire de l'huile d'amandes amères ou de l'hydrure de benzoïle, paraît être  $\frac{H_6O_2}{C_{14}}$ ; celle de l'acide benzoïque hydraté  $\frac{H_5O_3O}{C_{14}H}$ ;

celle de l'huile de spiræa isomérique avec la dernière  $\frac{H_5O_4}{C_{14}H}$ ; celle de

l'acide chlorosalicylique  $\frac{H_4O_4Cl}{C_{14}H}$ , et celle de l'ac. salicylique hydraté





Dans l'huile de spiræa, le seul atome basique d'hydrogène peut se déplacer, comme dans un hydracide, par la formation d'un sel, tandis que pour l'acide benzoïque hydraté dans la même circonstance, l'hydrogène et l'oxygène disparaissent à la fois.

L'acide bromobenzoïque hydraté et bibasique est une association de deux acides, dont l'un perd 1 at. d'hydrogène remplacé par le brome  $O + C_{14}H_5O_4$  et  $H + C_{14}H_4BrO_4$ . Les formules seront  $\frac{H_5O_4O}{C_{14}H}$  pour le premier, et  $\frac{H_4O_4BrO}{C_{14}H}$  pour le second.

Pour la benzamide  $Bz + Ad$  ou bien  $C_{14}H_5O_2 + NH_2$ , la formule peut être  $\frac{H_5NO_2}{C_{14}H_2}$ , où N remplace les 3 O de l'acide benzoïque hydraté.

L'hydrobenzamide  $C_{14}H_6N\frac{2}{3}$  provient de l'action de l'ammoniaque sur l'hydrure de benzoïle. La formule moléculaire est  $\frac{H_6N\frac{2}{3}}{C_{14}}$ , ou bien celle de l'huile dans laquelle  $N\frac{2}{3}$  remplace 2 O.

La salicylimide  $HO + C_{14}H_5ON\frac{2}{3}$  provient de l'action de l'ammoniaque sur l'acide salicylique. Sa formule est  $\frac{H_5O_2N\frac{2}{3}}{C_{14}H}$  ou  $\frac{H_5N\frac{2}{3}OO}{C_{14}H}$ , c'est-à-dire celle de l'acide salicyleux où  $N\frac{2}{3}$  remplace 2 O.

La chlorosalicylimide  $C_{14}H_3Cl_3O_2N\frac{2}{3}$ , serait  $\frac{H_2Cl_3N\frac{2}{3}O_2}{C_{14}H}$  ou  $\frac{Cl_3H_2O_2N\frac{2}{3}}{C_{14}H}$ , le chlore remplaçant 3 atomes d'hydrogène électro-négatif.

*Formation des acides.*—La formule de la benzine est  $\frac{H}{C_{12}}$ , celle de la sulfobenzide  $\frac{H_5SO_2}{C_{12}}$  ou  $\frac{H_5O_2}{C_{12}S}$ ; l'acide sulfobenzique se forme avec fixation d'acide sulfurique  $\frac{H_5O_2O_3O}{C_{12}SSH}$  ou  $\frac{H_5SO_2O_3O}{C_{12}SH}$ .

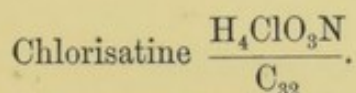
L'acide sulfureux est un corps analogue à la sulfobenzide; l'acide hyposulfurique renferme un hydrate d'acide sulfurique. L'acide sulfureux est  $\frac{O_2}{S}$ . L'acide hyposulfurique hydraté est  $\frac{O_2O_3O}{SSH}$ .

La benzile neutre  $C_{14}H_5O_2$  ou  $C_{28}H_{10}O_4$  devient du benzilate de potasse en fixant les éléments de l'hydrate de potasse. Benzile  $\frac{H_{10}O_4}{C_{28}}$ ; benzilate de potasse  $\frac{H_{10}O_4OO}{C_{28}HK}$ . En saturant la potasse par un acide



énergique, on forme l'acide benzilique hydraté  $\frac{H_{10}O_4OO}{C_{23}HH}$ . Neutralisé par les bases, cet acide perd 1 atome d'eau et le remplace par 1 atome d'oxyde métallique.

*Chlorisatine*.—Dissoute dans la potasse, elle se convertit en chlorisatinate.



Chlorisatinate de potasse  $\frac{H_4ClO_3OON}{C_{16}HK}$ ; avec un acide énergique on obtient l'acide chlorisatinique  $\frac{H_4ClO_3NOO}{C_{16}HH}$ .

Les acides concentrés lui enlèvent son eau et reproduisent la chlorisatine neutre. Il est clair que les acides anhydres tels que  $SO_3$ ,  $PO_5$ , appartiennent à la classe de la sulfobenzide et de la chlorisatine, et doivent à la présence d'un atome d'eau le pouvoir de se combiner aux bases.

Hydrate d'acide sulfurique  $\frac{O_3O}{SH}$ ; hydrates d'acide phosphorique  $\frac{O_4O}{PH}$ ,  $\frac{O_5O_2}{PH_2}$ ,  $\frac{O_5O_3}{PH_3}$ .

Nous avons d'autres séries de combinaisons dont les termes diffèrent par les proportions d'eau ou de ses éléments, comme l'amidon, la gomme et le sucre d'amidon; la gomme étant l'amidon plus 1 atome d'eau, et le sucre représentant l'amidon plus 2 atomes d'eau. On ne peut cependant aujourd'hui assigner une formule moléculaire probable au radical de l'amidon et de bien d'autres séries de combinaisons, faute de savoir le rôle que joue l'hydrogène dans leur constitution; là, en effet, il n'est point remplacé par un autre élément plus décidément basique ou négatif.

## VI.

### NOTE ON THE USEFUL APPLICATIONS OF THE REFUSE-LIME OF GAS-WORKS.

From *Chem. Soc. Mem.* ii. 1843-45, pp. 358, 359. [*Erdm. Journ. Prak. Chem.* xxxvi. 1845, pp. 48, 49; *Franklin Inst. Journal*, xi. 1846, pp. 281, 282.]

I HAD lately occasion to examine the lime as removed from a dry lime purifier. The gas before reaching the latter had been washed with



dilute sulphuric acid, which accounts for the absence of ammonia and cyanogen compounds. The lime had not been exposed more than a few hours to the air before it was operated upon. Still, to my surprise, it did not blacken an acid salt of lead, and contained no sulphuret of calcium. It was not dried, but analysed in a damp state, exactly as it is sent out of the works to be used as manure.

*Composition of Gas-Lime.*

Hyposulphite of lime, . . .	12.30
Sulphite of lime, . . .	14.57
Sulphate of lime, . . .	2.80
Carbonate of lime, . . .	14.48
Hydrate of lime, . . .	17.72
Sulphur, . . .	5.14
Sand, . . .	.71
Water combined, . . .	8.49
Water (free), . . .	23.79
	100.

With no more than a trace of ammonia and cyanogen.

The lime in the porous condition in which it is taken from the dry-lime purifiers, absorbs oxygen so rapidly from the air as to heat, and hence the state of oxidation in which the sulphur is found. If the lime be very damp, or diffused through a quantity of water, as it comes from the wet-lime purifiers, then the absorption of oxygen is much slower. The fluid portion then contains in solution the bisulphuret of calcium of Herschel, which may be crystallized from it; and at first very little else.

After the first rapid absorption of oxygen, the further oxidation of the gas-lime is decidedly slow. A specimen kept in an open vessel, and repeatedly moistened and rubbed to powder when it dried, was found after three months' exposure to retain 7 per cent. of sulphurous acid, besides all the free sulphur originally present. The hyposulphurous acid had entirely disappeared. Hence, if added to soil as manure, gas-lime must be powerfully deoxidising, a property which will generally impair its utility.

It appears advisable, where the refuse-lime does not possess any value from ammonia, to dry it strongly, or roast it. It would thereafter consist of nearly equal weights of sulphate and carbonate of lime, and be in the condition most valuable as a manure.

Refuse-lime, such as was examined, may be recommended as a convenient and most economical source of the hyposulphites. The lime, after being taken from the purifiers, should be exposed to air for two or three days, till it loses all smell of sulphuretted hydrogen. The highly



soluble hyposulphite of lime may then be dissolved out by little more than an equal weight of cold water. The solution may be evaporated at  $120^{\circ}$ , and the hyposulphite of lime crystallized out; or, the solution, by adding carbonate of soda, converted into hyposulphite of soda, which is a more stable salt, may be evaporated at a higher temperature, and crystallizes more easily.

From the refuse-lime, one-sixth of its weight of crystallized hyposulphite of lime has been obtained in a state of purity by a single crystallization. When the gas is washed with sulphuric acid to remove ammonia, before being conducted into the lime-purifier, it yields the refuse-lime more suitable for this purpose. The preparation of the hyposulphites in quantity is becoming the more important, as besides their use in electro-plating and photography, they are likely to be applied largely to the extraction of chloride and bromide of silver from silver ores.

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## VII.

### NOTE ON THE EXISTENCE OF PHOSPHORIC ACID IN THE DEEP-WELL WATER OF THE LONDON BASIN.

From *Chem. Soc. Mem.* ii. 1843-45, pp. 392, 393. [*Bibl. Univ.* lx. 1845, pp. 385, 386.]

THIS water is obtained on piercing the London clay, which forms an impervious bed, generally exceeding 200 feet in thickness, and flows from fissures in the subjacent chalk. It is always highly soft and alkaline, and remarkable for the predominance of soda salts over earthy salts among its solid constituents. I have never found it to contain a sensible quantity of potash, although salts of the vegetable alkali appear among the constituents of the water of the deep Artesian well of Grenelle.

When evaporated considerably, a small deposit takes place in the London deep-well water, which consists chiefly of carbonate and phosphate of lime. The remaining liquid gives with nitrate of silver a precipitate of chloride and carbonate of silver, which is white without any shade of yellow; but if a portion of the water, amounting to an ounce or two, be evaporated to dryness in a platinum capsule, without removing the precipitate, and the heat afterwards continued so as to raise the temperature of the resulting dry saline matter to low redness, then, on redissolving by distilled water, and adding nitrate of silver, a precipitate is obtained, in which the yellow colour of the phosphate of silver is very



perceptible. The earthy phosphate is decomposed by ignition with the alkaline belonging to the water, and the soluble phosphate of soda is produced.

The following are the results of the analysis of the water from the deep well in the brewery of Messrs. Combe and Delafield, Long Acre. An imperial gallon of the water contained 56·45 grains of solid matter, 100 parts of which gave—

Carbonate of soda, . . . .	20·70
Sulphate of soda, . . . .	42·94
Chloride of sodium, . . . .	22·58
Carbonate of lime, . . . .	10·96
Carbonate of magnesia, . . . .	1·92
Phosphate of lime, . . . .	0·34
Phosphate of iron, . . . .	0·43
Silica, . . . .	0·79
	<hr/>
	100·66

The growth of green confervæ in this water is extremely rapid, and occasions inconvenience when the water is kept in open tanks. It is a subject perhaps worthy of inquiry, whether the value of some waters for irrigation may not depend upon their containing phosphoric acid, this constituent having hitherto been generally overlooked in waters.

## VIII.

### OBSERVATIONS ON ETHERIFICATION.

From *Chem. Soc. Journ.* iii. 1851, pp. 24-28. [*Journ. de Pharm.* xviii. 1850, pp. 124-130; Liebig, *Annal.* lxxv. 1850, pp. 108-116.]

IN the ordinary process of etherizing alcohol by distilling that liquid with sulphuric acid, two distinct chemical changes are usually recognised; namely, first, the formation of sulphovinic acid, the double sulphate of ether and water; and secondly, the decomposition of the compound named, and liberation of ether. The last step, or actual separation of the ether, is referred to its evaporation, in the circumstances of the experiment, into an atmosphere of steam and alcohol vapour, assisted by the substitution of water as a base to the sulphuric acid, in the place of ether. The observation, however, of M. Liebig, that ether is not brought off by a current of air passing through the heated mixture of



sulphuric acid and alcohol, is subversive of the last explanation, as it demonstrates that the physical agency of evaporation is insufficient to separate ether. Induced to try whether ether could not be formed without distillation, I obtained results which appear to modify considerably the views which can be taken of the nature of the etherizing process.

The spirits of wine or alcohol always employed in the following experiments, was of density 0.841, or contained 83 per cent. of absolute alcohol.

*Expt. 1.*—One volume of oil of vitriol was added to four volumes of alcohol, in a gradual manner, so as to prevent any considerable rise of temperature. The mixture was sealed up in a glass tube, 1 inch in diameter and 6.6 inches in length, of which the liquid occupied 5.2 inches, a space of 1.4 inch being left vacant, to provide for expansion of the liquid by heat. The tube was placed in a stout digester containing water, and safely exposed to a temperature ranging from  $284^{\circ}$  to  $352^{\circ}$  ( $140^{\circ}$  to  $178^{\circ}$  C.) for one hour.

No charring occurred, but the liquid measured on cooling, 5.25 inches in the tube, and divided into two columns, the upper occupying 1.75 inches, and the lower 3.5 inches of the tube. The former was perfectly transparent and colourless, and on opening the tube, was found to be ether, so entirely free from sulphurous acid, that it did not affect the yellow colour of a drop of the solution of bichromate of potash. The lower fluid had a slight yellow tint, but was transparent. It contained some ether, but was principally a mixture of alcohol, water, and sulphuric acid. The salt formed by neutralizing this acid fluid with carbonate of soda, did not blacken when heated, from which we may infer that little or no sulphovinic acid was present.

The principal points to be observed in this experiment, are its entire success as an etherizing process, without distillation, without sensible formation of sulphovinic acid, and with a large proportion of alcohol in contact with the acid, namely, two equivalents of the former nearly, to one of the latter. When the proportion of the alcohol was diminished, the results were not so favourable.

*Expt. 2.*—A mixture of one volume of oil of vitriol and two volumes of alcohol, sealed up in a glass tube, was heated in the same manner as the last. The liquid afterwards appeared of an earthy-brown colour by reflected light, and was transparent and red by transmitted light. Only a film of ether was sensible after twenty-four hours, floating upon the surface of the dark fluid.

*Expt. 3.*—With a still smaller proportion of alcohol, namely one volume of oil of vitriol with one volume of alcohol, which approaches the proportions of the ordinary etherizing process, a black, opaque liquid



was formed at the high temperature, thick and gummy, without a perceptible stratum of ether, after standing in a cool state.

Crystals of bisulphate of soda, containing a slight excess of acid, were found to etherize about twice their volume of alcohol, in a sealed tube, quite as effectually as the first proportion of oil of vitriol, when heated to the same temperature. The two liquids found in the tube were colourless, no sulphurous acid appeared, and only a minute quantity of sulphovinic acid. Crystals of bisulphate of soda, which were formed in an aqueous solution and without an excess of acid, had still a sensible but much inferior etherizing power.

*Expt. 4.*—A mixture was made of oil of vitriol with a still larger proportion of alcohol, namely, 1 volume of the former and 8 of the latter, or nearly 1 equivalent of acid to 4 equivalents of alcohol. This mixture was sealed up in a tube and heated for an hour between  $284^{\circ}$  and  $317^{\circ}$  ( $140^{\circ}$  and  $158^{\circ}$  C.), which appeared sufficient for etherizing it. A second exposure for another hour to the same temperature did not sensibly increase the ether product. The column of ether measured 1.25 in the tube, and the acid fluid below 2.5 inches. Both fluids were perfectly colourless.

It thus appears to be unnecessary to exceed the temperature of  $317^{\circ}$  ( $158^{\circ}$  C.) in this mode of etherizing, and that the proportion of alcohol may be increased to eight times the volume of the oil of vitriol without disadvantage.

*Expt. 5.*—The proportions of the first experiment were again used, namely, 1 volume of oil of vitriol with 4 volumes of alcohol, and the mixture heated as in the last experiment to  $317^{\circ}$  ( $158^{\circ}$  C.). The upper fluid, or ether, measured 1.1 inch in the tube, the lower fluid 2.65 inches. The latter had a slight yellow tint, like nitrous ether, but only just perceptible. It gave, when neutralized by chalk :—

Sulphate of lime, . . . .	83.11 grains.
Sulphovinate of lime, . . . .	4.91 „

The last salt was soluble in alcohol, and crystallized in thin plates.

Here again the formation of sulphovinic acid in a successful etherizing process is quite insignificant.

New results at  $317^{\circ}$ , from the other proportions of 1 volume of oil of vitriol with 1 and 2 volumes of alcohol, were quite similar to those obtained in experiments 2 and 3, at the higher temperature of  $352^{\circ}$ . In none of these experiments did there appear to be any formation of olefiant gas, and the tubes could always be opened, when cool, without danger.

Neither glacial phosphoric acid nor crystallized biphosphate of soda etherized alcohol to the slightest degree, when heated with that sub-



stance in a sealed tube, to  $360^{\circ}$  ( $182^{\circ}$  C.). Even chloride of zinc produced no more, at the same temperature, than a trace of ether, perceptible to the sense of smell.

*Expt. 6.*—To illustrate the ordinary process of ether-making, a mixture was prepared, as usually directed, of—

100 parts of oil of vitriol,  
48 „ of alcohol (0.841),  
18.5 „ of water.

This liquid was sealed up in a glass tube, and heated to  $290^{\circ}$  ( $143^{\circ}$  C.) for one hour. It became of a dark greenish-brown colour, and opalescent, with a gummy-looking matter in small quantity. No stratum of ether formed upon the surface of the fluid.

The tube was opened and the fluid divided into two equal portions. One of the portions was mixed with half its volume of water, and the other with half its volume of alcohol, and both sealed up in glass tubes and exposed again to  $290^{\circ}$  for one hour.

It would be expected, on the ordinary view of water setting free ether from sulphovinic acid, that much ether would be liberated in the mixture above, to which water was added. The ether which separated, however, amounted only to a thin film, after the liquid had stood for several days. In the other liquid, on the contrary, to which alcohol was added, the formation of ether was considerable, a column of that liquid appearing, which somewhat exceeded half the original volume of the alcohol added. In fact, the sulphovinic acid was nearly incapable of itself of yielding ether, even when treated with water. But it was capable of etherizing alcohol added to it, in the second mixture, like bisulphate of soda or any other acid salt of sulphuric acid.

The conclusions which I would venture to draw from these experiments are the following:—

The most direct and normal process for preparing ether appears to be, to expose a mixture of oil of vitriol with from four to eight times its volume of alcohol of 83 per cent. to a temperature of  $320^{\circ}$  ( $160^{\circ}$  C.), for a short time. Owing to the volatility of the alcohol, this must be done under pressure, as in the sealed glass tube. The sulphuric acid then appears to exert an action upon the alcohol, to be compared with that which the same acid exhibits when mixed in a small proportion with the essential oils. Oil of turpentine, mixed with one-twentieth of its volume of sulphuric acid, undergoes an entire change, being chiefly converted into a mixture of two other hydrocarbons, terebene and colophene, one of which has a much higher boiling point and greater vapour-density than the oils of turpentine. This hydrocarbon does not combine with the acid, but is merely increased in atomic weight and gaseous



density without any further derangement of composition, by a remarkable polymerizing action (as it may be termed) of the sulphuric acid. So of the hydrocarbon of alcohol; its density is doubled in ether, by the same polymerizing action. Chloride of zinc effects, with alcohol, at an elevated temperature, a polymeric catalysis of the latter, of the same character, but in which hydrocarbons are formed, of even greater density, and free from oxygen.

This view of etherification is only to be considered as an expression of the contact-theory of that process which has long been so ably advocated by M. Mitscherlich.

The formation of sulphovinic acid appears not to be a necessary step in the production of ether; for we have found that the etherizing proceeded most advantageously with bisulphate of soda, or with sulphuric acid mixed with a large proportion of alcohol and water, which would greatly impede the production of sulphovinic acid. It appears, indeed, that the combination of alcohol with sulphuric acid, in the form of sulphovinic acid, greatly diminishes the chance of the former being afterwards etherized; for, when the proportion of oil of vitriol was increased in the preceding experiments, which would give much sulphovinic acid, the formation of ether rapidly diminished. The previous conversion of alcohol into sulphovinic acid, appears, therefore, to be actually prejudicial, and to stand in the way of its subsequent transformation into ether.

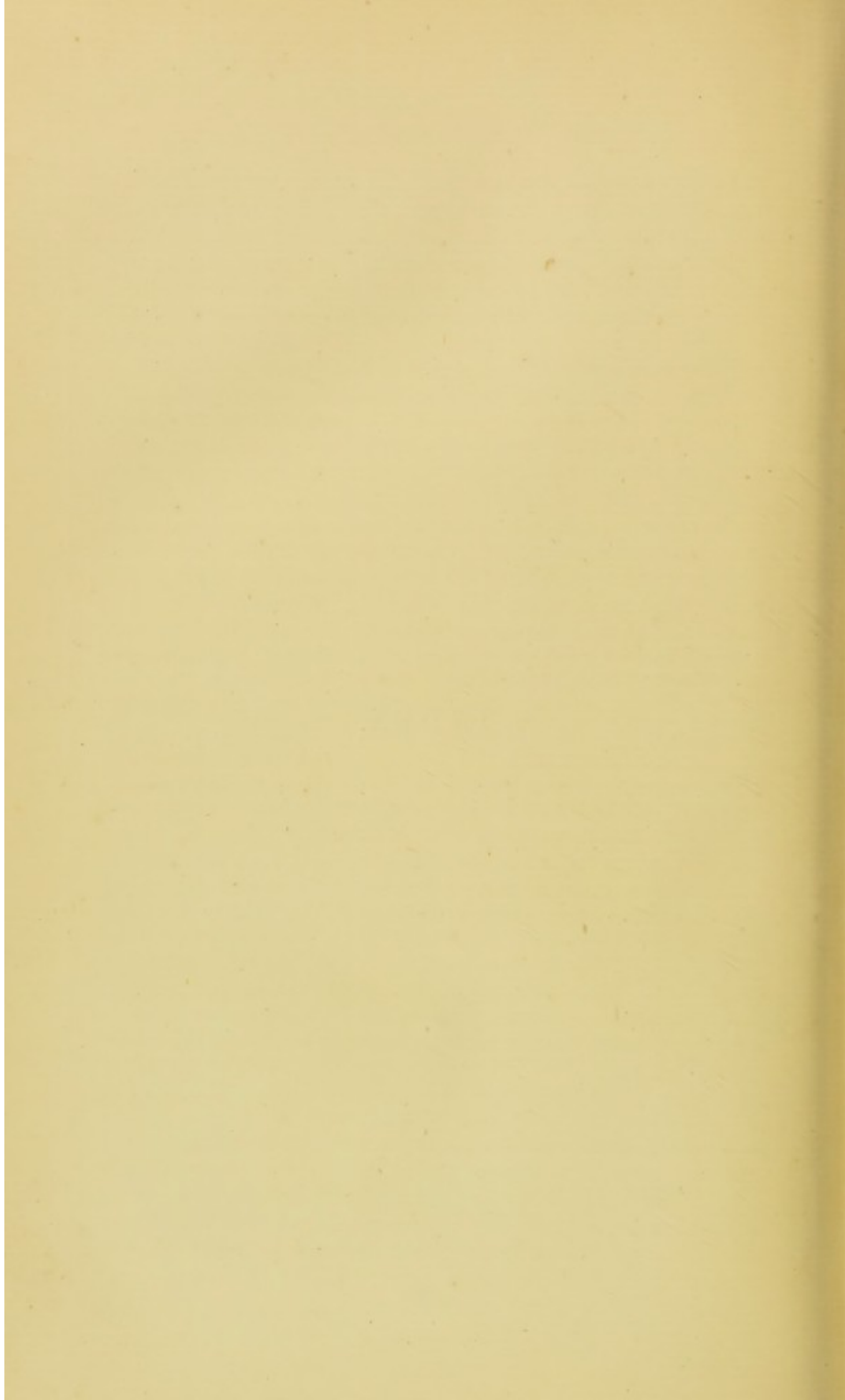
The operation of etherizing has attained a kind of technical perfection in the beautiful continuous process now followed. The first mixture of alcohol and sulphuric acid is converted into sulphovinic acid, the sulphate of ether and water, which acid salt appears to be the agent which polymerizes all the alcohol afterwards introduced into fluid. Bisulphate of soda, with a slight excess of acid, acts upon alcohol in the same manner, and its substitution for the acid sulphate of ether would have a certain interest, in a theoretical point of view, although a change of no practical importance in the preparation of ether.

Sulphuric acid does not appear to be adapted for the etherizing of amylic alcohol. M. Balard, by distilling these substances together, obtained a variety of hydrocarbons, some of them of great density, but no ether. The polymerizing action of the sulphuric acid appears to advance beyond the ether stage. I have varied the experiment by heating amylic alcohol, in a close tube, to  $350^{\circ}$  ( $176^{\circ}$  C.) with oil of vitriol, to which 1, 2, 3, 4, and even 6 equivalents of water had been added, without obtaining anything but the hydrocarbons of Balard. The formation of these was abundant, even with the most highly hydrated acid, and with a very moderate colouration of the fluid.



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# GRAHAM'S

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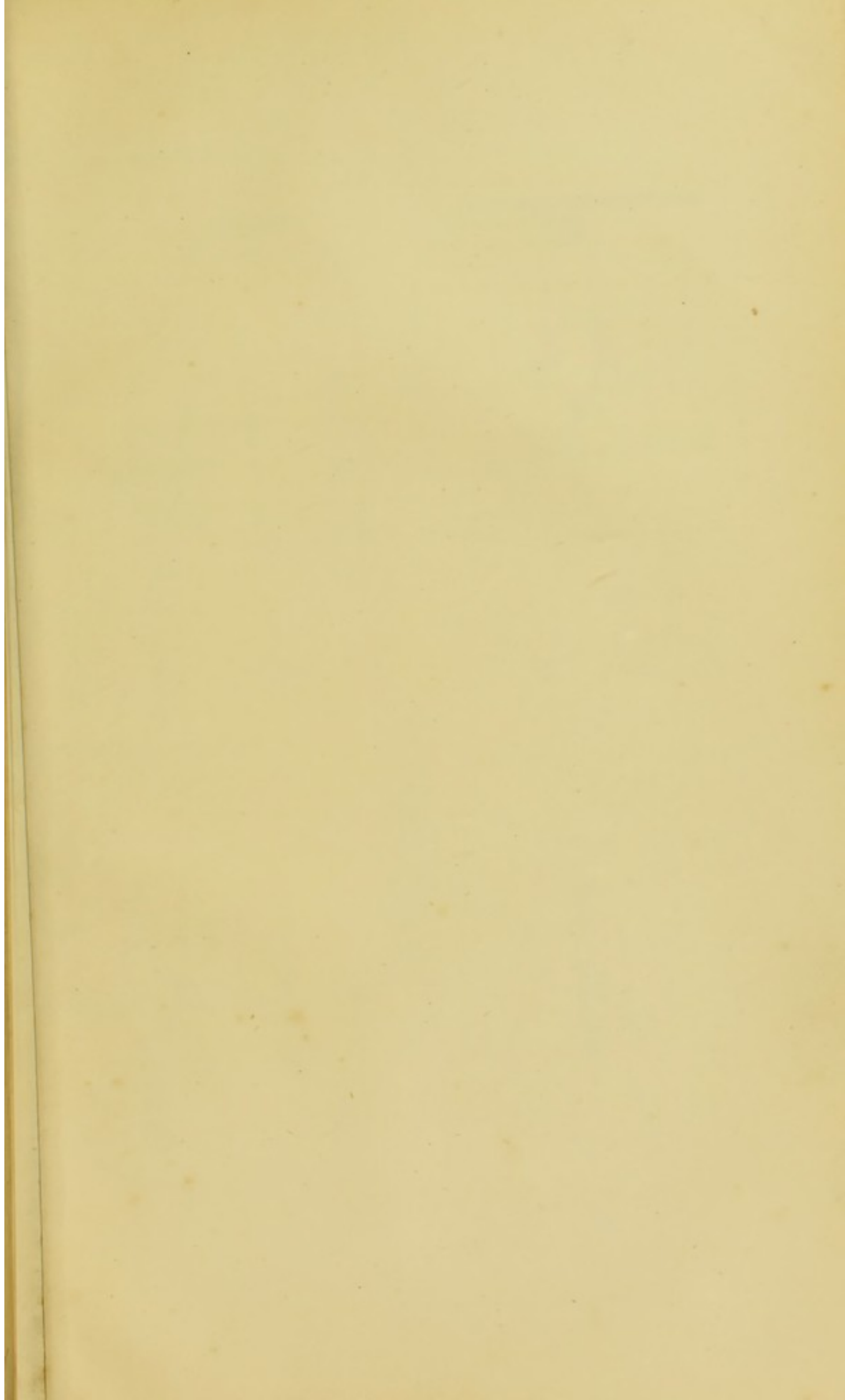




Fig. 1.

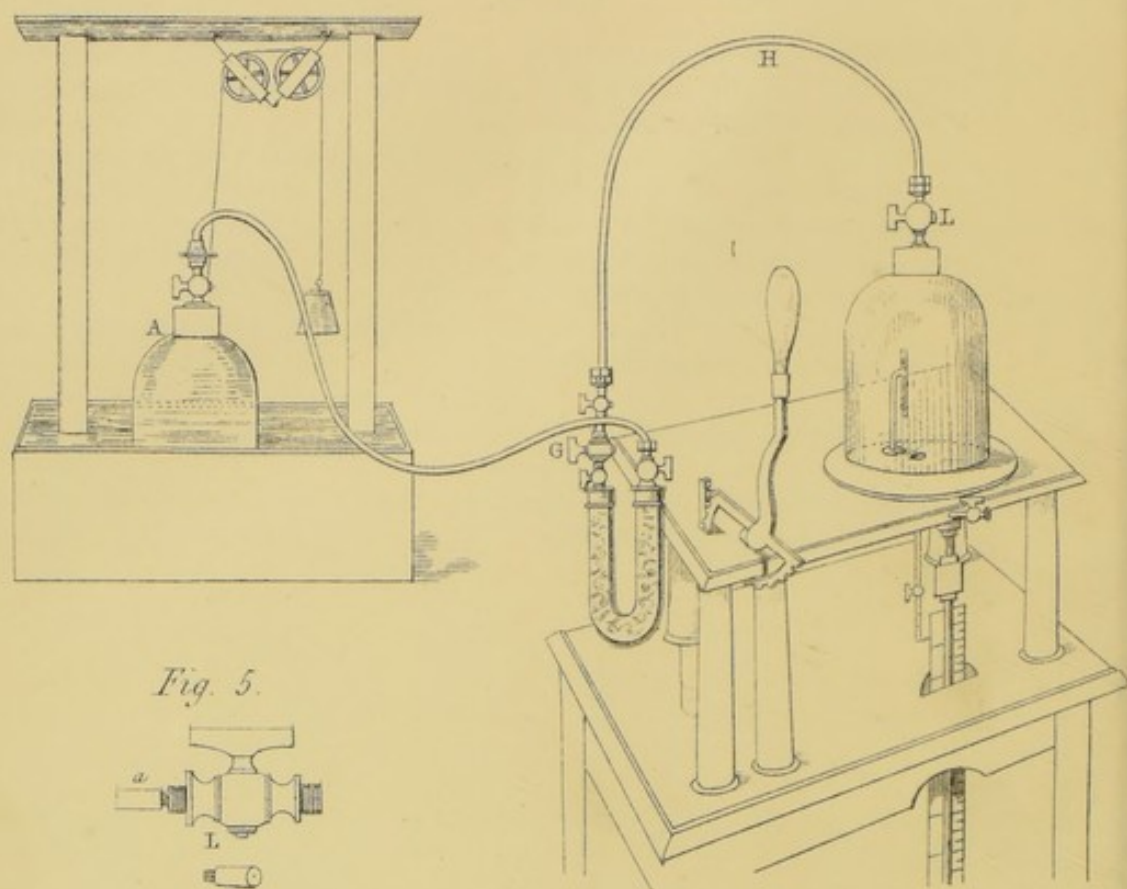


Fig. 5.

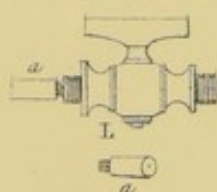


Fig. 3.

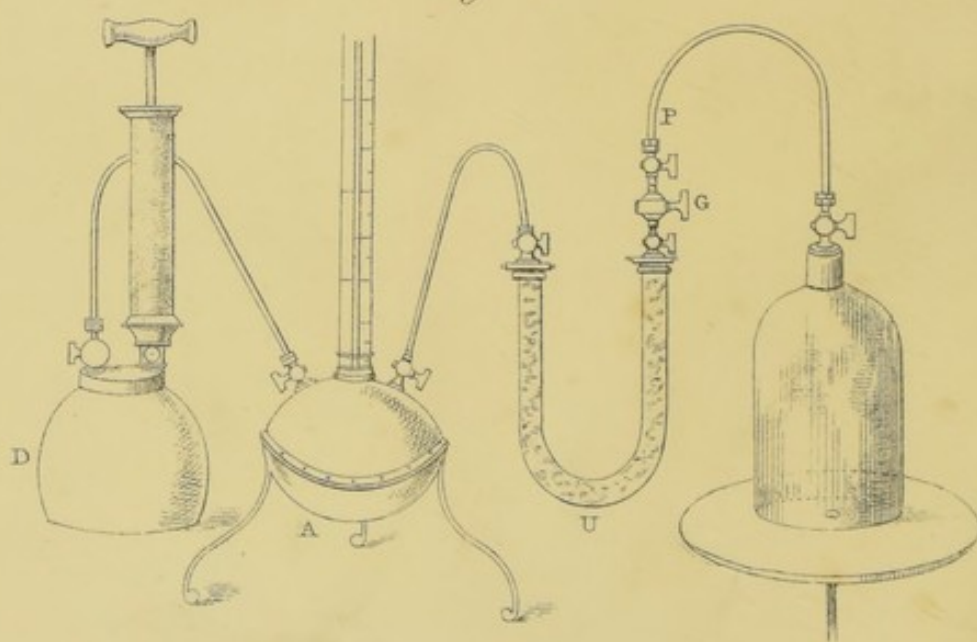




Fig. 2.

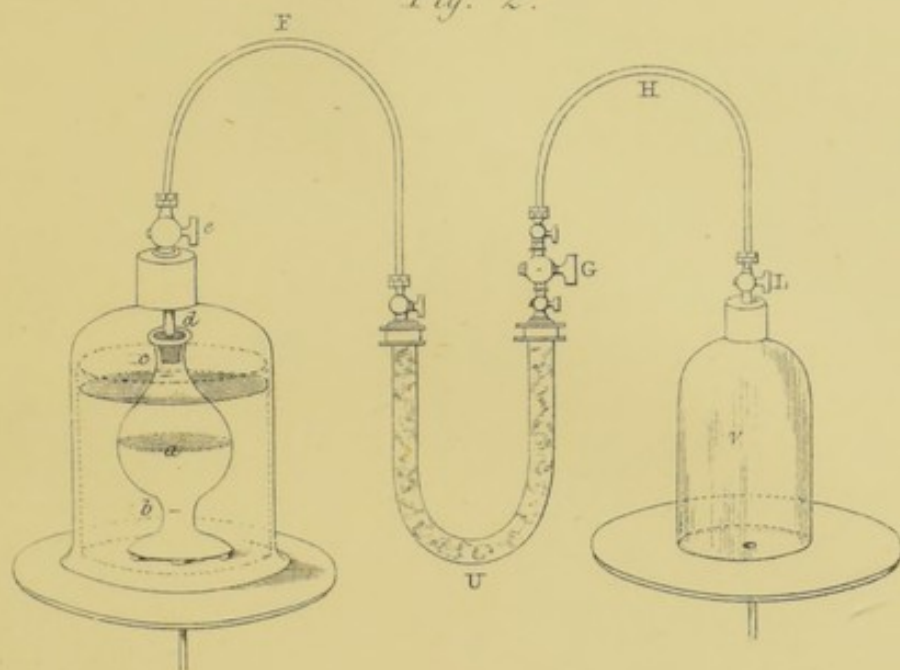
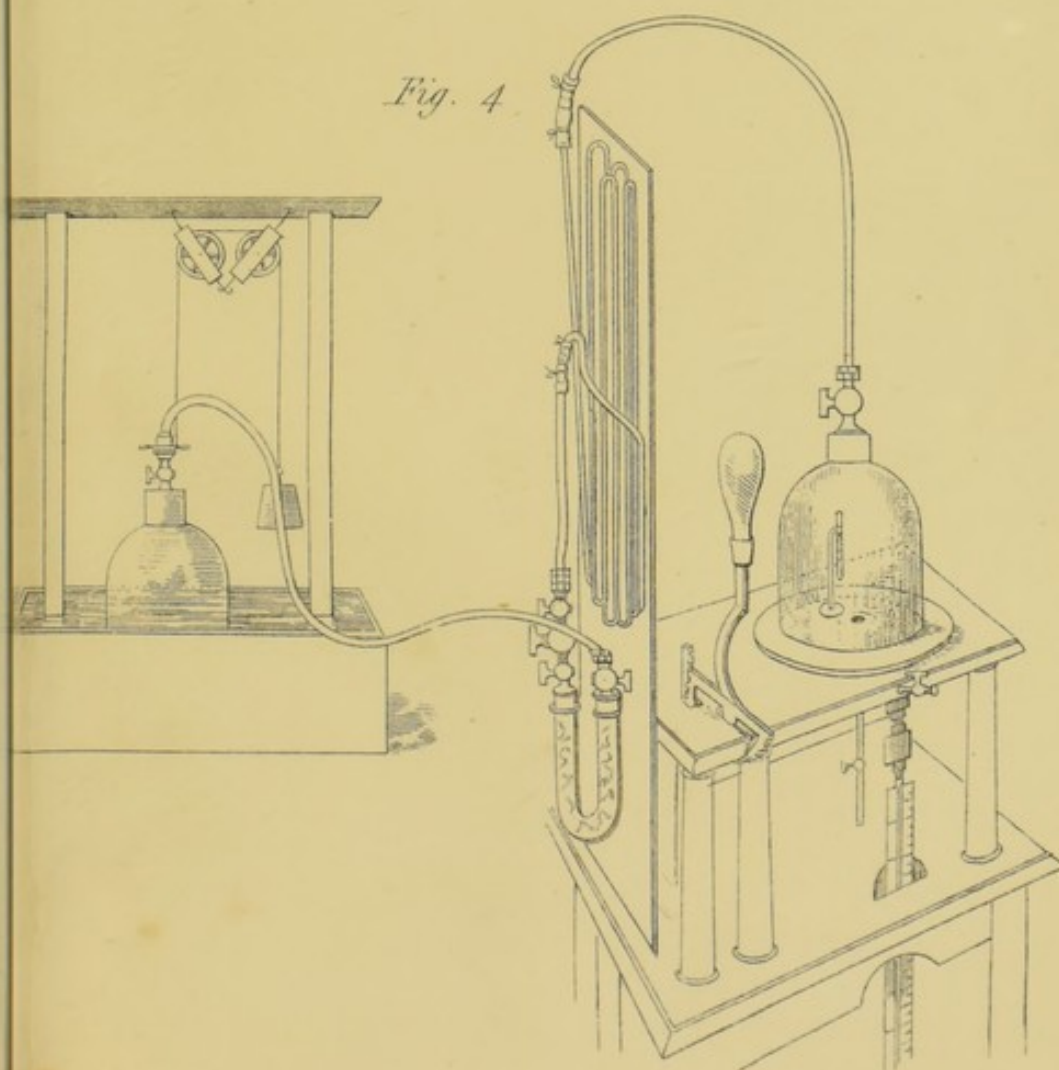
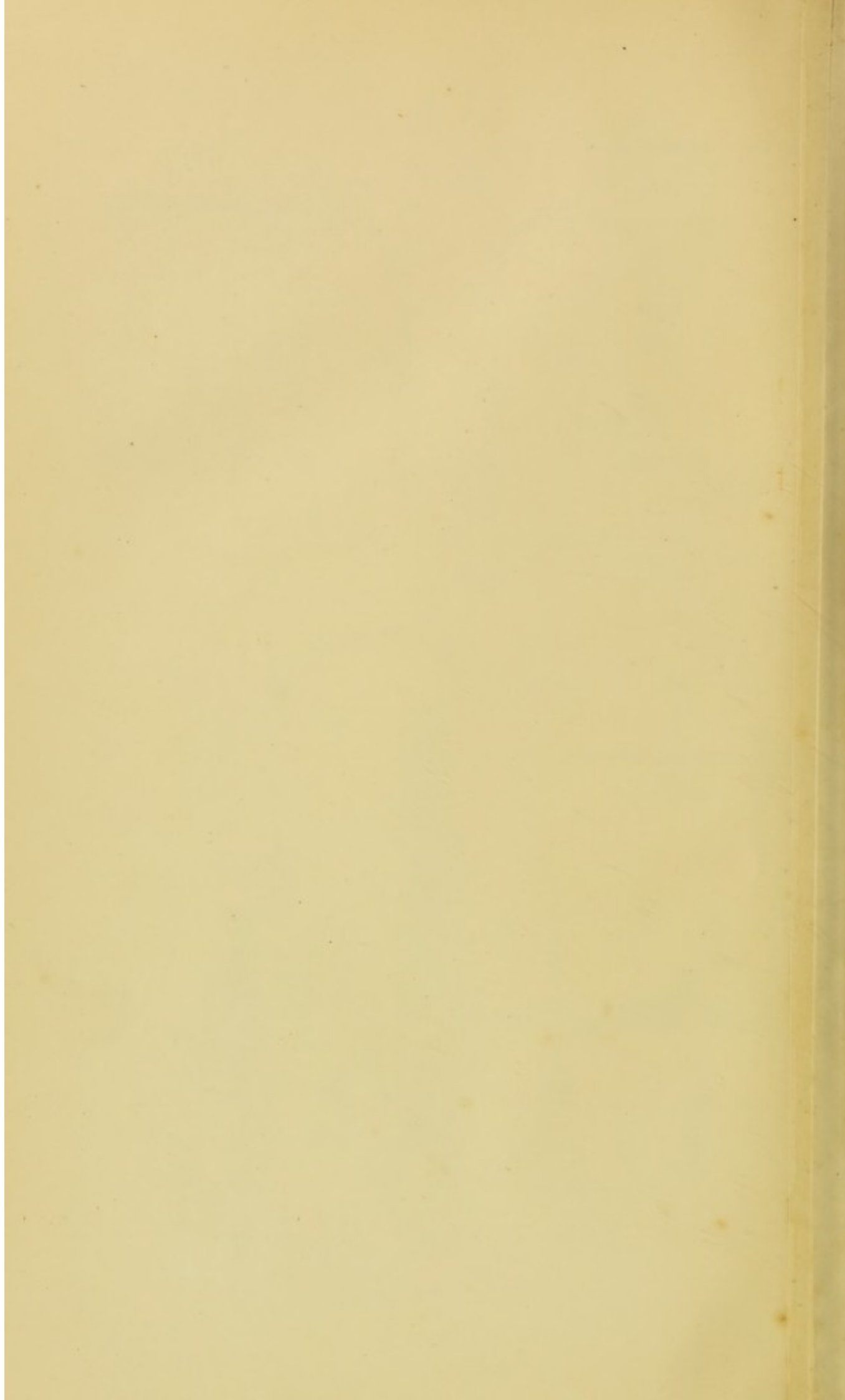


Fig. 4.





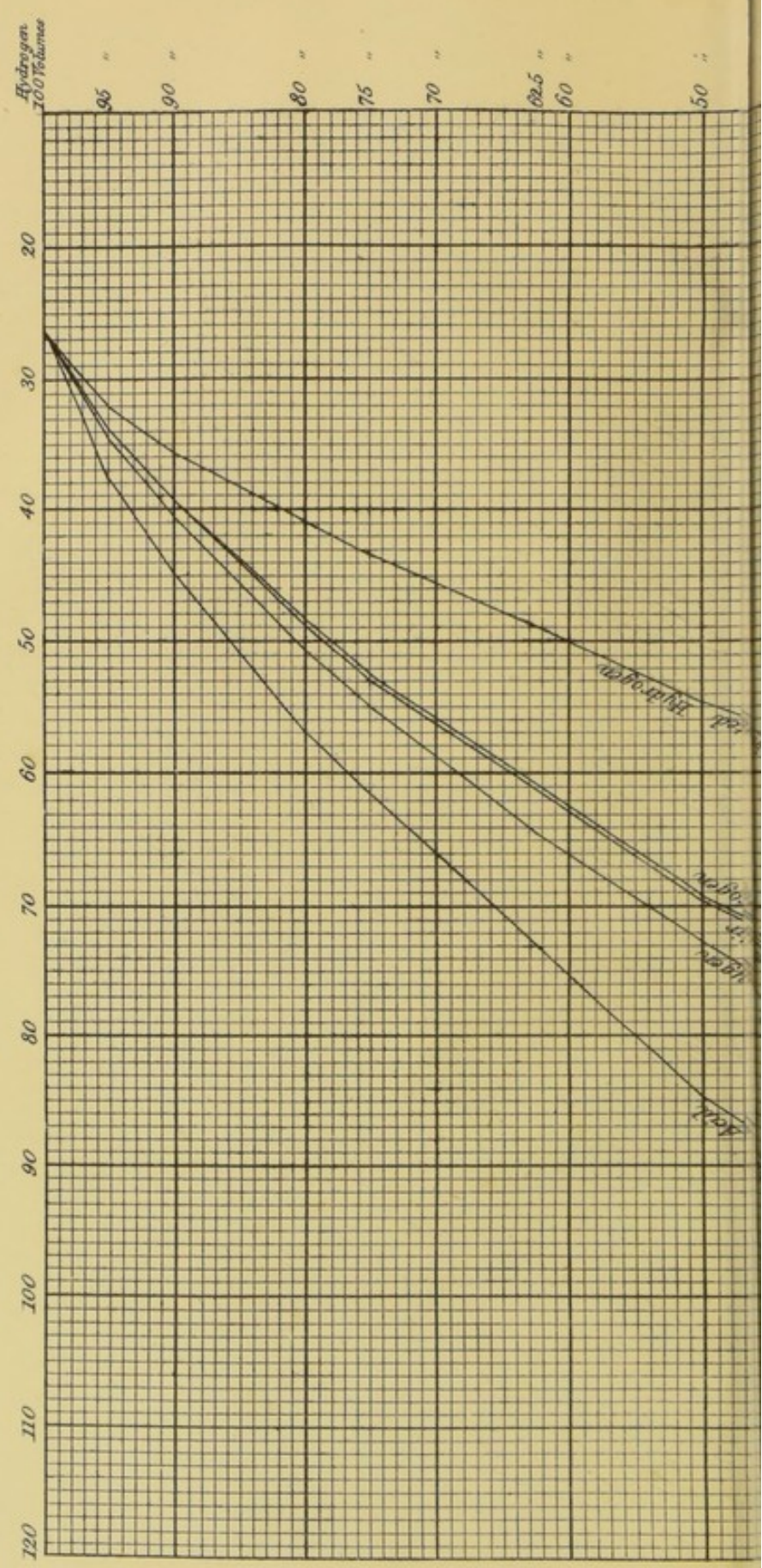




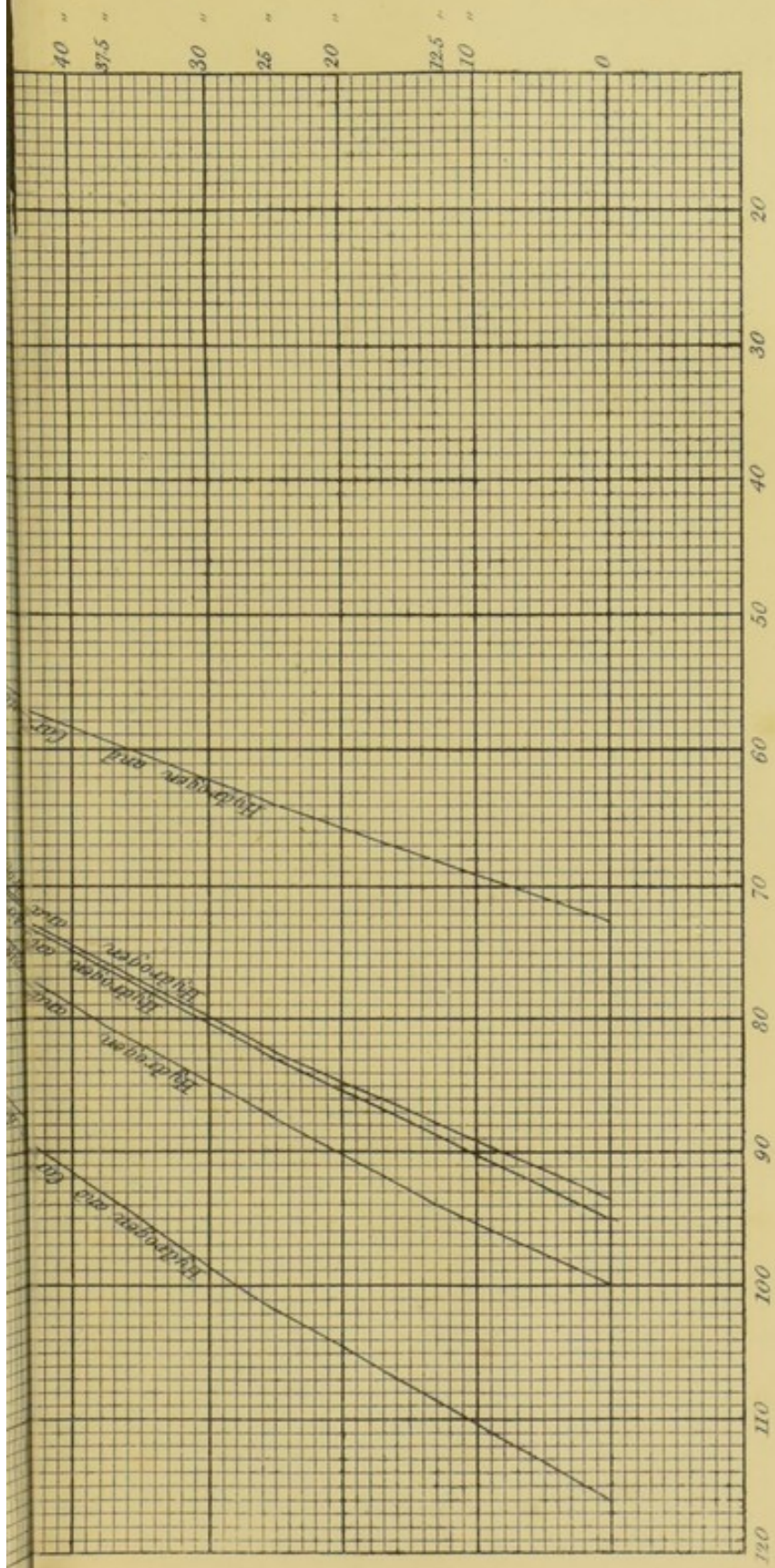




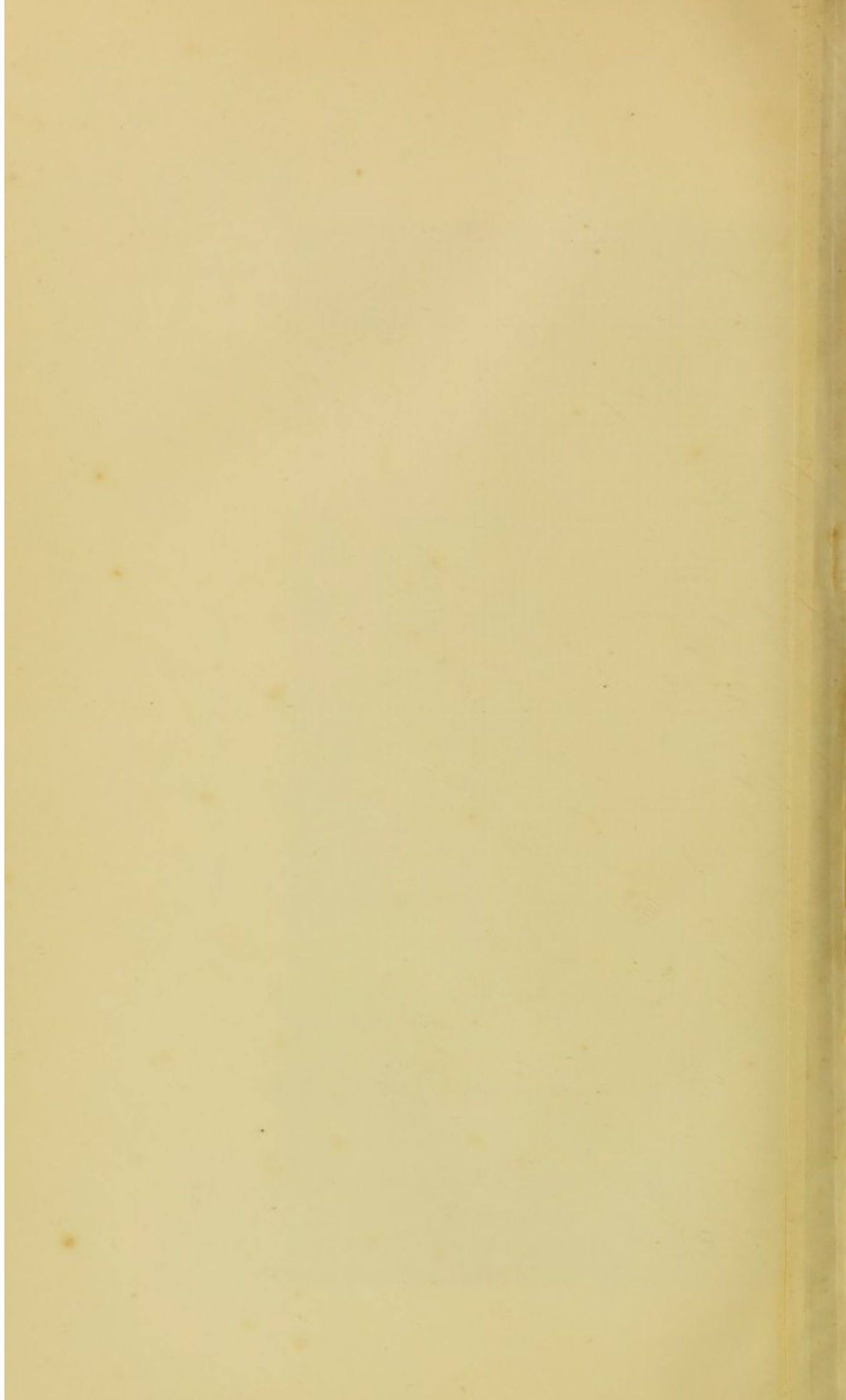
*Effusion of mixed Gases.*

















*Transpiration of mixed Gases.*

