An essay on combustion, with a view to a new art of dying and painting: wherein the phlogistic and antiphlogistic hypotheses are proved erroneous / by Mrs. Fulhame.

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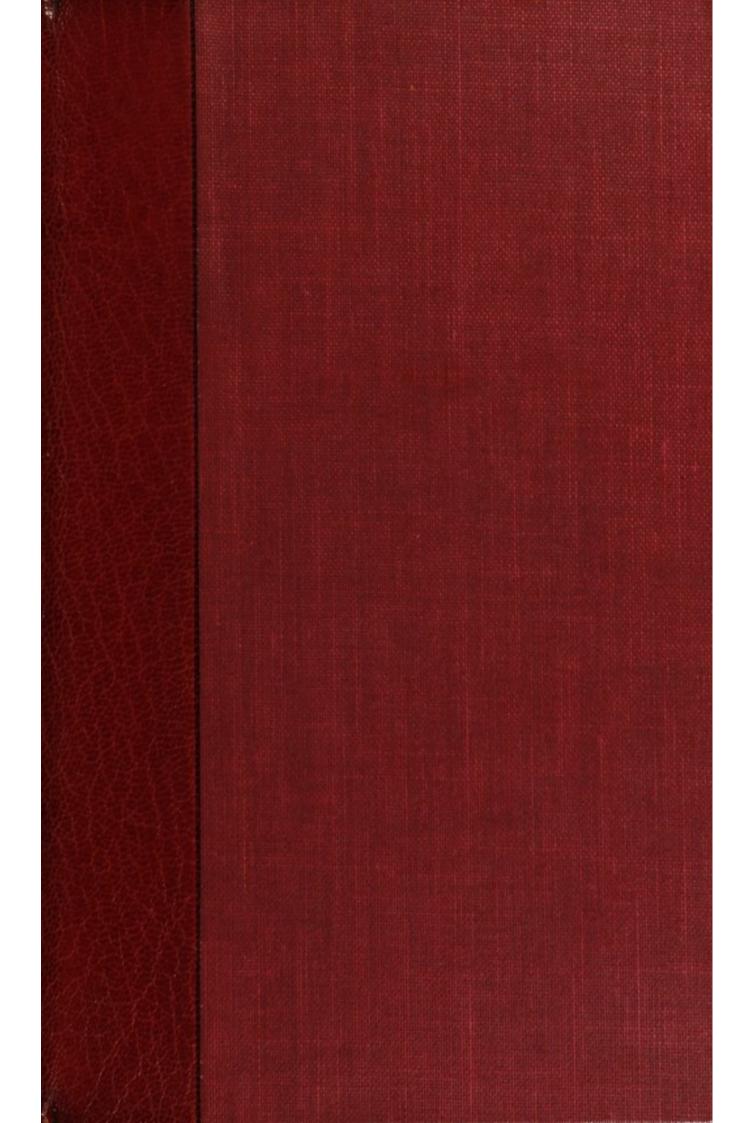
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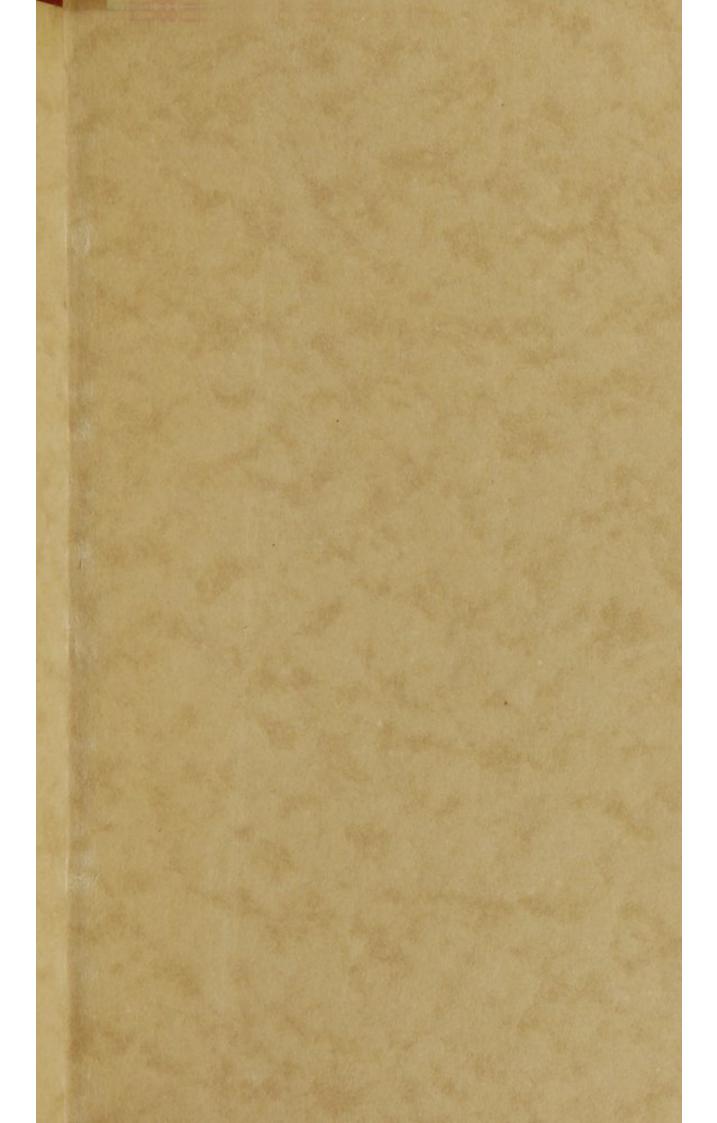
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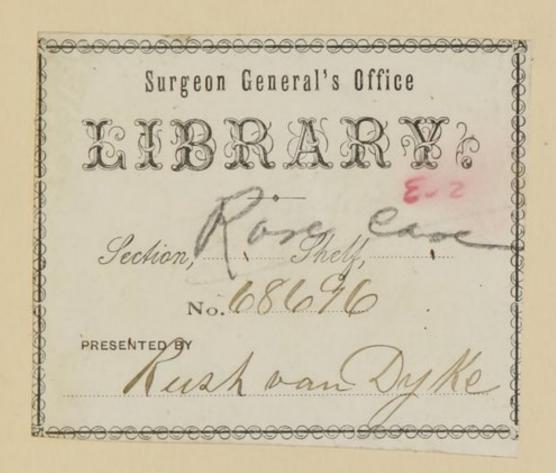
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ON

COMBUSTION,

WITH A VIEW TO

A NEW ART

OF

DYING AND PAINTING.

WHEREIN THE PHLOGISTIC AND ANTIPHLOGISTIC
HYPOTHESES ARE PROVED
ERRONEOUS.

BY MRS. FULHAME.

THE FIRST AMERICAN EDITION.

PHILADELPHIA. 666

PRINTED AND SOLD BY JAMES HUMPHREYS,

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BY THE AMERICAN EDITOR.

THE interesting contents of the subsequent pages, by the very ingenious Mrs. Fulhame, are assuredly deserving of more attention, than they have hitherto received; for although published so far back as the year 1794, little notice has been paid to the numerous experiments, by which she has opposed the doctrines of combustion, &c. advanced by the respective advocates of the phlogistic and antiphlogistic theories. How successfully she has executed this, must be left to the candid inquirer after truth, who, provided the end be attained, does not stop to consider from what source it is derived.

Whether it be that the pride of science, revolted at the idea of being taught by a female, I know not; but assuredly, the accomplished author of this essay, has sufficiently evinced the adequacy of her acquirements, in the promulgation of opinions subversive of a part of the highly esteemed edifice, raised by the efforts of Lavoisier and others.

That the work has hitherto remained unknown in this favoured land, where freedom of inquiry is so sedulously cherished, is matter of surprise; especially when it is known that many years past, the author was elected an honorary member of the then-existing chemical society of Philadelphia, a distinction founded on the merit of this work; yet the doctrines here advanced, appear to have been known to but few individuals, for they have never been comprised in the lectures on chemistry, which are given in various parts of the Union-nor, till lately, has the work been adverted to, in any of the numerous volumes on the science which annually appear from the British press. Truth however, at length appears likely to dissipate those mists, which, from whatever cause arising, have hitherto opposed the merited estimation of the author: in some of the late English treatises, this lady is respectfully mentioned; more particularly by the learned Dr. Thompson, in the third edition of his invaluable System of Chemistry,* when speaking of the reduction of the muriate of gold, whilst liquid, by some of the combustibles, but which decomposition does not happen when dry; he adds "for these very interesting facts we are indebted to the ingenious Mrs. Fulhame:" he then proceeds to mention some of her experiments, and continues "Mrs. Fulhame ascertained, that this reduction of the gold does not happen in any case unless the salt be moistened with water: when perfectly dry, it is not altered. This is not peculiar to the action of combustibles on metallic salts: it holds also, as we shall see afterwards, with respect to the metals. But it is by no means easy to see what makes water so indispensably necessary. It is not, as is commonly supposed, in order to secure the fluidity of the mixture: for Mrs. Fulhame has shewn that ether, though a liquid, has no effect in reducing gold unless water be present. She accounts very ingeniously for the phenomena, by supposing that the water is decomposed. The combustible combines with its oxygen, while its hydrogen combines with the oxygen of the gold, and reproduces water. This theory aecounts very well for the phenomena; but it would require some direct proof to establish it completely."

The concession admitted in the last sentence, from so celebrated a chemist as Dr. Thompson undoubted-

^{*} Vol. III. p. 127, 138.

ly is, although in some degree counteracted by the concluding paragraph, cannot but be esteemed a strong proof of the merit of the opinions here advanced; and as a tacit avowal, of the inadequacy of the usually received explanation, in accounting for the phenomena under consideration.

Convinced by the forcible arguments and experiments of the decomposition of water being essential in all the processes here detailed, and considering the subject much simplified by the exposition given; I cannot but think the same reasoning would apply in many other cases, where some of the most active and energetic agents, are, by the present explanation, altogether thrown into the back ground. Thus, in procuring nitrogen gas from muscular flesh by means of diluted nitric acid, we are told, "that the nitric acid does not furnish the nitrogen gas is obvious, from its saturating after its action as large a quantity of alkali as before; consequently it could not have suffered any decomposition."* That this deduction is not in the true spirit of chemical philosophy, which looks to the action of affinity, by which decomposition, and recomposition may at the same time progress, I have little hesitation in saying; and that the case adverted to is a compound, and not a simple play of affinity must be allowed, or we entirely destroy the agency

^{*} Accum's Syst. of Chemistry, Vol. I. p. 247. 2d Eng. Ed.

of the most powerful body united, whose presence is nevertheless admitted to be essential to the process. If we suppose the nitrogen to be expelled from the flesh, by the action of the acid, which, with the water is also decomposed, we shall have a double portion of oxygen and nitrogen, which may thus combine. The oxygen of the water uniting to the nitrogen of the flesh, will produce a fresh supply of nitric acid, and whilst the nitrogen of the original acid escapes, its oxygen will unite to the liberated hydrogen of the decomposed water, to form an equal quantity. At the conclusion of this process of double affinity then, we shall have a quantity of new formed acid and water equal to the original, but in which the original elements, have changed situations. By this explanation, the acid retains the place of activity it ought to hold; and the necessity of its presence, is hereby maintained.

In like manner it has been said that sulphuric acid is not decomposed in aiding the decomposition of water with iron in procuring hydrogen gas, because it saturates as much alkali as before; but the same objections may be made to the validity of this opinion as to the former; and the process may be more reasonably explained on the principles of compound affinity. When the water is decomposed, its hydrogen escapes, but the acid is also decomposed, and whilst the oxygen of the acid oxydates the iron, the oxy-

gen of the water unites with the sulphur to form a similar quantity of acid, which dissolves the oxydated iron. It would seem incredible, that in any other way, either the nitric or sulphuric acids, should be essential to the processes adverted to; and from these and other circumstances, such as, that a metal placed in dry oxygen gas does not oxydize, which ought to result, if simple affinity only was requisite; and by observing in all the late ingenious experiments of Mr. Davy, the presence of moisture appears to be essential in the decomposition of the alkalies, &c. although he mentions it, as only rendering them conductors, I cannot doubt the justice of the opinions deduced by Mrs. Fulhame from her numerous and well conducted experiments: and although it may be grating to many, to suppose a female capable of successfully opposing the opinions of some of our fathers in science; yet reflection will serve to satisfy the mind devoted to truth, that she has certainly thrown a stumbling block of no small magnitude, in the way of sentiments we have been taught to consider as sacred.

PHILADELPHIA, February 14th, 1810.

PREFACE.

THE possibility of making cloths of gold, silver, and other metals by chymical processes, occurred to me in the year 1780; the project being mentioned to Doctor Fulhame and some friends, was deemed improbable. However, after some time, I had the satisfaction of realizing the idea in some degree by experiment.

Animated by this small success, I have from time to time ever since, prosecuted the subject as far as pecuniary circumstances would permit. I imagined in the beginning, that a few experiments would determine the problem; but experience soon convinced me, that a very great number indeed were necessary, before such an art could be brought to any tolerable degree of perfection.

A narration of the numerous experiments, which I made with this view, would far exceed the bounds I prescribed myself in this essay; I shall therefore present the reader only with a few, selecting such as I judge most interesting, and best adapted to illustrate the subject.

Though I was, after some considerable time, able to make small bits of cloth of gold and silver, yet I did not think them worthy of public attention; but by persevering, I at length succeeded in making pieces of gold cloth, as large as my finances would admit.

Some time after this period, I found the invention was applicable to painting, and would also contribute to facilitate the study of geography; for I have applied it to some maps, the rivers of which I represented in silver, and the cities in gold. The rivers appearing as it were in silver streams, have a most pleasing effect on the sight, and relieve the eye of that painful search for the course and origin of rivers,

the minutest branches of which can be splendidly represented in this way.

Notwithstanding this further success, I was dubious about the propriety of publishing this essay; I therefore shewed some specimens of these metallic stuffs to persons, whom I thought qualified to judge of them; some approved of them very much, and were pleased to say, that the invention would make an era in the arts; others thought it a pretty conceit; and others were of opinion that the stuffs had not that splendour or burnished appearance, which could entitle them to public notice.

The latter opinion had much weight with me; for it must be allowed, that the specimens which I shewed them, had not that lustre and polish necessary for shoulder-knots, lace, spangles, gold muslins, &c. that some of them had a reddish cast, bordering on the colour of copper, some a purple, mixed with gold; and that some of them were unequal in the die and seemed stained; which imperfections were owing to a partial reduction of the metal in the fibres of the silk.

But all these imperfections, except the want of that burnished lustre so necessary for gold lace, spangles, &c. I knew I could remedy; and therefore the criticism, as far it relates to them, had no great influence with me.

I am in possession of some pieces, one of which is about a yard in length, which have scarce any of these imperfections.

Moreover, that high polish of burnished gold, so necessary in spangles, lace, &c. would in my opinion, be a great imperfection in gold stuffs designed for whole suits; as a person in such a habit would look like a gilded statue.

I saw a piece of gold stuff made for the late king of Spain, which was of a purple colour, with gold wire shining through it, though rather obscurely, and it was much admired; I was so struck with its beauty, that I attempted to imitate it on a small bit of white silk; and succeeded, having produced a beautiful purple colour, with gold beaming through it.

Therefore, the want of that burnished appearance is no objection to this art; for the paler and cooler, to a certain degree, the colour of the gold is, the more lovely do these metallic cloths appear.

I made small bits of gold tiffany, which looked exceedingly beautiful; the fineness of the thread contributing much to that effect; and, in my opinion, such webs are inimitable by mechanical means.

Beside, though I am not able to make cloths like burnished gold, others of greater means and abilities may; for we cannot pretend to prescribe any limits to the perfection, at which chymistry and the arts may arrive.

However, I must acknowledge, that this unfavourable judgment suspended my intention of publishing this little work, until a celebrated philosopher happening, some time in October 1793, to see some of the same pieces, and indeed some of the worst, viewed the performance in a very different light.

This illustrious friend of science, not only approved of the specimens shewn him, but offered to have a memoir on the subject presented to the Royal Society: but different incidents dissuaded me from that mode of publication, and induced me to adopt the present.

I now no longer hesitated about the propriety of publishing; for, every thing considered, I judged, that though this art could never be established, which is by no means my opinion, yet the experiments themselves, upon which I attempted to found it, as they are new, and seem to throw some light on the theory of combustion, are not unworthy the attention of chymists.

Those who viewed my performance with a favourable eye were of opinion, that I should dedicate this essay to some patron of the arts; or apply for his Majesty's royal letters patent, in order to reimburse the expense necessarily incurred in this investigation, an expense so disproportionate to the fortune which supported it, that nothing but a certain fatality and the hope of reward, could induce me to persevere.

As to patrons, I have heard of such beings on the record of fame, but never saw one; on the contrary, it has been my lot to know of many whose malignant breath, as far as its deadly influence can extend, never ceases to blast the unsheltered blossoms of science. And as for a patent, had I even the means I should perhaps never attempt it; for if we may judge of the future by the past, I can safely affirm, that such an application would be vain.

Thus circumstanced, I published this essay in its present imperfect state, in order to prevent the furacious attempts of the prowling plagiary, and the insidious pretender to chymistry, from arrogating to

themselves and assuming my invention in plundering silence; for there are those, who if they cannot by chymical, never fail by stratagem and mechanical means, to deprive industry of the fruits and fame of her labours.

But the British empire should not forget, that she owes her power and greatness to commerce; that she is, as it were, the hive of the arts, and should not, by the sulphureous vapour of oppression and neglect, compel her bees to swarm for protection to foreign climes, but rather permit them to roam in their native soil, and allow them, in the winter of life, to sip a little of the honey of their own industry.

The nation, whose evil genius withholds this protection, only sounds the trumpet of emigration, and must ere long lament her cities deserted, her fields brown with desolation, and herself the easy prey, and vile drudge of surrounding greatness.

I first imagined that the proper title of this performance should be, An Essay on the Art of making Cloths of Gold, Silver, and other Metals, by chymical processes; but reflecting on the imperfect state of the art, and that my experiments related not only to the reduction, but also to the calcination of metals and other combustible bodies, I determined to entitle it, An Essay on Combustion, with a View to a new Art of Dying and Painting, which includes every thing the experiments can extend to.

As to the style, I have endeavoured to relate the experiments in a plain and simple manner, aiming more at perspicuity than elegance.

I have adopted the French Nomenclature, as the terms of it are so framed as to prevent circumlocution, assist the memory, by pointing out the combination and state of the elements existing in each compound, as far they are known; advantages to be found in no other nomenclature.

However, the English reader must regret, that the French chymists have not preferred the terms air, and ammonia, to the less harmonious sounds, gas, and ammoniac. I took the liberty of writing the latter ammonia.

I have not related my experiments in the order in which they were made, sensible that such a narration would be tedious, and that a short extract from them would answer every purpose at present intended.

The experiments related I have endeavoured to arrange in such a manner, as mutually to illustrate each other, by contrasting the successful with those that failed, thus pointing out a general principle, which forms a chain through the whole, connects all the experiments, shews their points of coincidence and disagreement, and by this means furnishes us with data, by which I hope the art may be improved.

This arrangement also facilitates the perusal, and relieves the mind of that fatiguing attention, which must necessarily be given to an indigested mass of insulated experiments, that have no clue to connect them, but has on the other hand its disadvantages; for it throws a sameness on the work, incompatible with that variety which is often so agreeable.

My apparatus consisted chiefly of a few glass vessels for the solution of metals, and the formation of such elastic fluids as I used. The cheapest and the most simple of those described by Dr. Priestley answered my purpose.

Dr. Nooth's machine for combining carbonic acid with water, is very convenient for making small experiments with some kinds of gas, as the base of that machine serves to contain the materials, from which

the gas is obtained; and the middle glass the cloth previously dipped in the metallic solution, on which the experiment is to be made.

The cloth may be suspended in this part of the machine, by means of a thread and a cork.

As this machine is useful only in experiments on a very small scale, I sometimes used tall glass cylinders, in which I suspended the subject of the experiment, by means of a thread, a cork, and a bit are ment.

This cylinder I placed over a vessel containing the materials, which produced the gas.

It is very convenient to have cylinders of different sizes, proportioned to the scale on which the experiments are to be made.

But machinery for confining elastic fluids is not always necessary, as most of the experiments may be performed in the open air.

It may appear presuming to some, that I should engage in pursuits of this nature; but averse from indolence, and having much leisure, my mind led me to this mode of amusement, which I found entertaining, and will I hope be thought inoffensive by the liberal and the learned. But censure is perhaps inevitable; for some are so ignorant, that they grow sullen and silent, and are chilled with horror at the sight of any thing that bears the semblance of learning, in whatever shape it may appear; and should the spectre appear in the shape of woman, the pangs which they suffer are truly dismal.

There are others who suffer the same torture in a still higher degree; but by virtue of an old inspiring tripod, on which ignorance, servility, or chance, has placed them, assume a dictatorship in science, and fancying their rights and prerogatives invaded, swell with rage, and are suddenly seized with a violent and irresistible desire of revenge, manifesting itself by innuendos, nods, whispers, sneers, grins, grimace, satanic smiles, and witticisms uttered sometimes in the acute, and sometimes in the nasal obtuse twang, with an affected hauteur, and contempt of the spectre; shrugs, and a variety of other contortions attending.

Sometimes the goblin, which thus agitates them lurks latent, and nothing is perceived but hollow murmurs, portending storms: sometimes the lurking fiend darts with sidelong fury at the devoted object, which if unarmed falls a victim to the grisly monster.

But happily for human kind, the magic tripod drags none into its dizzy vortex, but those who are radically stupid and malicious, who are the beasts of prey destined to hunt down unprotected genius, to stain the page of biography, or to rot unnoted in the grave of oblivion.

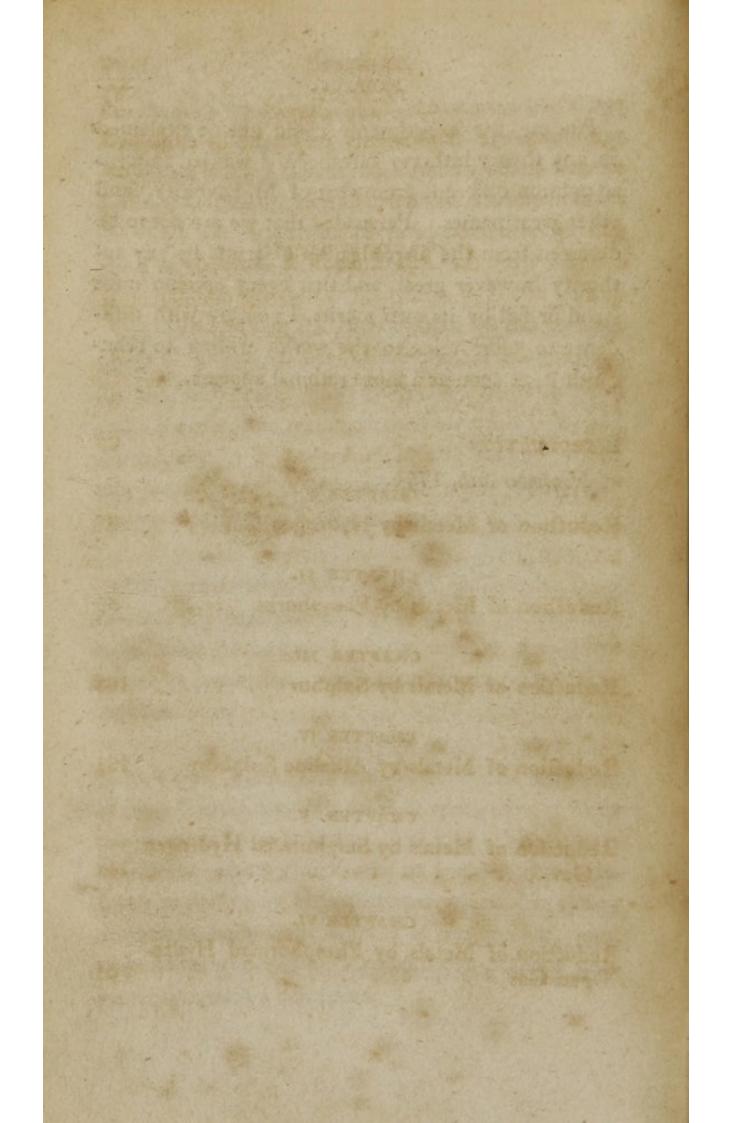
Although the surge of deliberate malice be unavoidable, its force is often spent in froth and bubbles; for this little bark of mine has weathered out full many a storm, and stemmed the boisterous tide; and though the cargo be not rich, the dangers which may hereafter be pourtrayed on votive tablet, may serve as a beacon to future mariners.

But happen what may, I hope I shall never experience such desertion of mind, as not to hold the helm with becoming fortitude against the storm raised by ignorance, petulant arrogance, and privileged dulness.

However, were I not encouraged by the judgment of some friends, and possessed of specimens, to shew the progress made in the art, I should never perhaps venture to publish this Essay; as I am sensible it labours under many imperfections, which inaccuracy of observation and the drapery of imagination, must spread over the whole; imperfections perhaps unavoidable in such a discussion.

Finding, the experiments could not be explained on any theory hitherto advanced, I was led to form an opinion different from that of M. Lavoisier, and other great names. Persuaded that we are not to be deterred from the investigation of truth by any authority however great, and that every opinion must stand or fall by its own merits, I venture with diffidence to offer mine to the world, willing to relinquish it, as soon as a more rational appears.

November 5th, 1794.



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INTRODUCTION.

THOUGH some of the phenomena of combustion were known from the earliest ages, yet no rational attempt to explain them was made till about the middle of the 17th century.

Before that period, it was supposed by alchymists and physicians, that sulphur was the inflammable principle, on which all the phenomena of combustion depended.

But Beccher perceiving, that sulphur did not exist in several combustible bodies, asserted it was not the principle of inflammability; which he maintained, was a different substance, common to sulphur and other combustible bodies: this principle he supposed to be of a dry nature, and called it inflammable earth.

Stahl refined this hypothesis by supposing the inflammable earth of Beccher to be pure fire, fixed incombustible bodies, and constituting an essential part of them.

According to Stahl, a combustible body is a compound, containing fixed fire, or phlogiston; and combustion is the disengagement of this phlogiston from a fixed to a free state, attended sometimes with heat and light: when these phenomena cease, the body becomes incombustible; if this calcined body be now heated with charcoal, or any other inflammable substance, capable of giving it phlogiston, or fixed fire, it returns again to the class of inflammable bodies.

This hypothesis is so simple and plausible, that, since the year 1736, it was received, though differently modified, all over Europe.

The principal objections to it are, that the existence of phlogiston cannot be demonstrated; and that it does not explain, why bodies become heavier after oxygenation, and lighter after reduction. M. Lavoisier discovering, that the increase of weight, which bodies acquire during combustion, is equal to the weight of the combustible substance, and that of the vital air employed, denied the existence of phlogiston, or fixed fire, in combustible bodies; though he grants the existence of combined cauric in them. He seems then to allow the existence of phlogiston, but to have changed its name to that of caloric, and denied it the power of producing combustion.

However, after discovering that the increase of weight, which bodies acquire during combustion, depended on the quantity of the air absorbed, he was led to the following beautiful hypothesis, equally simple as that of Stahl; and if ever any hypothesis deserved the name of theory, surely it is that of M. Lavoisier.

According to M. Lavoisier, "an inflammable body is nothing else but a body which has the property of decomposing vital air, and taking the base from caloric and light; that is to say the oxygene, which was united to them; and that a body ceases to be combustible when its affinity for the oxygene, is satisfied, or when it is saturated with that principle; but that it becomes again combustible, when the oxygene has been taken from it by another body, which has a stronger affinity with that principle "When this decomposition of the air is rapid, and as it were, instantaneous, there is an appearance of flame, heat, and light; when on the contrary, the decomposition is very slow, and quietly made, the heat and light are scarcely perceptible."*

Thus all the phenomena of oxygenation, which Stahl ascribed to the disengagement of phlogiston, M. Lavoisier ascribes to the union of oxygen with combustible bodies.

And on the other hand, all the phenomena of reduction, which Stahl attributed to the union of phlogiston to calcined bodies, M. Lavoisier attributes to the separation of oxygen from the same. Combustion then, according to Stahl, is the transition of phlogiston from one body to another; and according to M. Lavoisier, 'tis nothing but the transition of oxygen from one substance to another.

Stahl supposed, that the heat and light attending combustion proceed from the burning body; but M. Lavoisier supposes, that the heat and light proceed principally, and almost entirely from the vital air.

However, this opinion of M. Lavoisier is far from being established; for Doctor Crawford has shewn,

^{*} Essay on Phlogiston, by Mr. Kirwan, new edition, p. 21 and 16.

that inflammable air contains a much greater quantity of heat, than vital air does.

It is evident then, that the great advantage which M. Lavoisier's-hypothesis has over that of Stahl is, that the former seems to account for the increase and decrease of weight, which bodies suffer during calcination and reduction.

Notwithstanding this brilliant discovery, which seems to account, with such ease, for the increase of weight, that bodies acquire during combustion, M. Macquer was of opinion, that M. Lavoisier's hypothesis was insufficient to explode that of Stahl, and endeavoured to remove the objection urged against the non-existence of phlogiston, by supposing it to be light; and that in every case of combustion, light and vital air mutually precipitate each other; so that according to M. Macquer, when a body is oxygenated, vital air unites to it, and disengages light; and on the other hand, when an oxygenated substance is reduced to its inflammable state, light unites to it and disengages vital air.

M. Scheel also modified the hypothesis of Stahl, by supposing that heat, light, and inflammable air, were compounds of empyreal, or vital air, and phlogiston. Light he thought, contained more phlogiston than heat did; and inflammable air more than

either; he farther supposed that these compounds of vital air and phlogiston were convertible into one another, by the addition or subtraction of phlogiston; and that when a metal was reduced by them, they were decomposed; their phlogiston uniting to the substance reduced.

His idea of calcination is, that metals either attract empyreal air by means of their phlogiston, and thus form heat, or that they communicate their phlogiston to the air, and attract heat from the fire: and that, either way, there is empyreal air in the calces, which makes the overplus of their weight.*

The last modification of Stahl's hypothesis is that of M. Kirwan, who supposes that inflammable air exists in a fixed or concrete state in all combustible bodies, and is the true phlogiston of the ancient chymists; and as it can be exhibited in the form of air, its existence is no longer doubtful.

M. Kirwan supposes, that when combustible bodies are calcined, or changed into acids, they combine most commonly with fixed air, formed during the operation, by the union of their phlogiston to vital air; and sometimes to other substances, and water, which is either absorbed in specie, or formed by

^{*} Experiments on Air and Fire. Eng. trans. p. 174.

the union of their phlogiston to vital air, during calcination.

He supposes, that some of these are restored to their combustible state by the decomposition of their fixed air; some partly by the decomposition of their fixed air, and partly by its expulsion, and that of the other foreign bodies they had absorbed; and lastly, that some recover their combustibility by the expulsion of water, and others possibly by its decomposition in high degrees of heat. In all these reductions he supposes a simultaneous reunion of these bodies to phlogiston, or the inflammable principle.*

Though M. Kirwan's hypothesis seems to account for the increase of weight, which bodies acquire during combustion, yet he has not proved the existence of inflammable air in a concrete state, in all combustible bodies; nor has he shewn, that fixed air is a compound of inflammable and vital air; neither has he proved, that fixed air is the acidifying principle.

All these objections have been made, with great justice to his hypothesis, by the Antiphlogistians; who also object, that M. Kirwan's account of calcination and reduction is complex, and repugnant to the simplicity of nature; "for," says M. De Four-

^{*} Essay on Phlogiston, a new edition, p. 38-166.

croy, "as the author had admitted three general species of calcination, it was necessary, that he should likewise admit three kinds of reduction."*

This criticism is very just; but it will appear, that the antiphlogistic account of calcination and reduction is no less complex, erroneous and repugnant to the simplicity of nature; for when we consider the various sources, whence they derive the oxygen, which oxygenates bodies, and the long list of metallic reducers, which they suppose; it must be allowed that if simplicity be a recommendation, their hypothesis is destitute of that advantage.

Thus, according to M. Lavoisier the oxygen which oxygenates combustible bodies, is sometimes derived from vital air, sometimes from atmospheric air, sometimes from acids, sometimes from water, and sometimes from metallic oxids, &c.

On the other hand, the catalogue of substances which reduce bodies to their combustible state, is no less numerous.

"Heat," says M. De Fourcroy, "separates oxygene from some; one metal takes it from another;

^{*} Essay on Phlogiston, p. 207.

hydrogene, or inflammable gas, takes it from most metals, and carbon perhaps from all."*

To this list may be added phosphorus, sulphur, and compounds of these with hydrogen; also light and the electric fluid, &c. as will appear in the sequel.

But I shall endeavour to shew, that the hydrogen of water is the only substance, that restores oxygenated bodies to their combustible state; and that water is the only source of the oxygen, which oxygenates combustible bodies.

Want of simplicity is not the only defect in Mr. Lavoisier's hypothesis: for he supposes, that the increase of weight, which bodies acquire during combustion, depends on the absorption of the oxygenous principle alone.

Thus when a bit of phosphorus, sulphur or charcoal, is burnt in vital air; the increase of weight, which these bodies acquire, he attributes entirely to oxygen, or the base of vital air.

These combustions he explains, by supposing that the phosphorus, sulphur, and charcoal, decompose

^{*} Essay on Phlogiston, p. 205.

oxygen gas, by absorbing its base from caloric and light, which are set free.

"There is," says M. Lavoisier, "a total absorption of vital air, or rather of the oxygene, which forms its base in the combustion of phosphorus, and the weight of the phosphoric acid obtained, is found to be rigorously equal to the weight of the phosphorus, added to that of the vital air employed in its combustion. The same agreement of weights is observed in the combustion of imflammable gas and vital air, in the combustion of charcoal," &c.

His idea of calcination of metals is the same.

wital air combines with metals to form metallic calces, because this manner of enunciating would not be sufficiently accurate: but we say, when a metal is heated to a certain temperature, and when its particles are separated from each other to a certain distance by heat, and their attraction to each other is sufficiently diminished, it becomes capable of decomposing vital air, from which it seizes the base, namely oxygene, and sets the other principle, namely caloric, at liberty.

"This explanation of what passes during the calcination is not an hypothesis, but the result of facts

^{*} Essay on Phlogiston, p. 14.

It is upwards of twelve years, since the proofs have been laid by one of us, before the eyes of the academy, and have been verified by a numerous commission. It was then established, that when the calcination of metals is effected beneath an inverted glass vessel, or in closed vessels containing known quantities of air, the air itself is decomposed, and the weight of the metal becomes augmented by a quantity accurately equal to that of the air absorbed. It has since been found, that when the operation was performed in very pure vital air, the whole might be absorbed.

"No supposition enters into these explanations; the whole is proved by weight and measure."*

Hence it is evident, that M. Lavoisier confounds oxygen with oxygen gas, and considers the latter as a compound of oxygen, light, and caloric.

But since the dryest oxygen gas contains a large proportion of water, as Dr. Priestley and M. Kirwan have shewn; † and since the whole of the gas, except the caloric and light, is absorbed, it necessarily follows that the increase of weight, which bodies acquire during combustion, depends not only on the oxygen, but also on the water, contained in vital air.

^{*} Essay on Plogiston. p. 13-15.

[†] Ibid. p. 25. and Philo. Trans. Vol. 78. p. 314.

Therefore oxids are compounds of combustible bodies united to oxygen, and water.

Another great objection to M. Lavoisier's hypothesis is, that he supposes both oxygenation, and reduction, effected by a single affinity.

Thus according to him, when iron reduces a sulphate of copper, the iron does nothing more than separate the oxygen from the copper, by its superior attraction for that principle.

From this view of combustion, grounded on the most accurate experiments in chymistry, it is manifest that the antiphlogistic hypothesis does not account fully for the increase of weight, which bodies acquire during combustion; and consequently, that it cannot be admitted as a just theory.

COMBUSTION,

&c. &c.

CHAPTER I.

REDUCTION OF METALS

BY

HYDROGEN GAS.

AS Hydrogen, or the base of inflammable air, seems to act an important part in the following experiments, and is, according to some chymists, pure phlogiston itself; I have therefore assigned the first chapter in this essay to hydrogen gas, this being the most simple form, in which hydrogen has hitherto been obtained.

But I had not the means of procuring this gas free of carbon, and other impurities, that it dissolves and elevates during its formation; or of excluding atmospheric air, which circumstances, I am sensible, must, in some measure, influence the result; as it cannot be supposed, that these extraneous bodies would remain inactive during the process of reduction. However, as such exactness is not in the power of every experimenter, I was under a necessity of using hydrogen gas, with the disadvantages here mentioned.

Though most of the experiments in this essay were made on a variety of white and coloured silks, I shall relate only those made on the former, as it exhibits the changes produced more distinctly, and contains less foreign matter to modify the result of experiment; and, for brevity's sake, I shall use the term silk, by which white silk is always designed.

EXPERIMENT I.

GOLD.

I poured a quantity of sulphuric ether on a solution of gold in nitro-muriatic acid, and, by this means, obtained a solution of gold in ether, which I separated from the acid. In this ethereal solution of gold, I dipped a piece of silk; after it was taken out, and the ether evaporated, it was suspended in a tall glass cylinder, placed over a vessel, containing a mixture of diluted sulphuric acid, and iron filings.

The silk thus exposed to a rapid current of hy: drogen gas acquired, after some time, a purple colour, and a large spangle of gold, of an irregular figure, appeared on the upper end of the silk, and looked very brilliant.

The silk was kept exposed to the gas about four months, and frequently observed, but no other remarkable change was perceived, except that the purple colour became more intense: the experiment was now discontinued; and on taking out the silk, and examining it in the light of the sun, particles of reduced gold were observed; but they were very small, and by no means so brilliant, as that, which first appeared.

During the experiment, fresh quantities of materials for supplying hydrogen gas were occasionally added.

From the brilliant spangle of reduced gold observed in this experiment, I concluded, that there was a sufficient quantity of the metal in the fibres of the silk, could it be reduced. This spot of reduced gold was very permanent, and adhered firmly to the silk.

EXPERIMENT II.

GOLD.

In order to determine, whether a solution of gold in ether, or one in water, were best adapted to the object of these experiments; I evaporated to dryness a solution of gold in nitro-muriatic acid, and dissolved the salt in distilled water: in this solution, I immersed a piece of silk, which, after it was dried in the air, was suspended in a glass cylinder, like the former piece, and exposed to the action of hydrogen gas about two months.

The silk after some time assumed a purple colour, and five or six specks of reduced gold, of the size of pin heads, and one much larger, were observed. Examining the silk in the sun-beams, I perceived the whole of it spangled with minute particles of reduced gold.

After many experiments with these two solutions of gold, I was led to conclude, that the solution in water answered best.

EXPERIMENT III.

SILVER.

Having dissolved some pure silver in diluted nitric acid, and evaporated some of the water by a gentle heat, I placed it in the dark to crystallize. The crystals were separated from the solution, and dissolved in distilled water; to one measure of this solution, which was saturated with the nitrate of silver, ten or twelve measures of distilled water were added.

In this diluted solution, a piece of silk was dipped; after it was taken out, it was dried at the fire: the silk dried in this manner, retained its white colour; whereas, were it dried gradually in the air; and especially, were the light considerable, its white colour would be changed to a reddish brown, more or less intense, according to the quantity of light present.

Some kinds of silk, on being immersed in a solution of nitrate of silver, have some of their threads immediately coloured brown; but I often got white silk, which would retain its pure white colour, if dried at the fire, or in the dark.

The piece of silk dried, as above, was suspended in the middle glass of Dr. Nooth's machine; and in-

to the lower glass were introduced a diluted solution of sulphuric acid, and some small iron nails.

The machine was now placed in a dark closet, to exclude the action of light; after some time, the silk, thus exposed to hydrogen gas, put on a light brown colour, which gradually became deeper, until it was changed to a disagreeable black, with some mixture of brown: then very small particles of reduced silver began to appear, which increased by degrees, in number, and brightness.

The experiment was continued four months; after which time, the silk was taken out of the machine: it had a gray metallic appearance, intermixed with a considerable tinge of brown.

This experiment was repeated on another piece of silk, every circumstance being the same, except that a quantity of water was put in the middle glass of the machine, over which the silk was suspended; the intention of interposing the water in this experiment was to purify the gas.

The appearances were much the same, as in the last experiment; except that the silk became black sooner; and that some spangles of the silver were larger, and better reduced.

The specks of reduced silver were permanent, and adhered firmly to the silk.

EXPERIMENT IV.

LEAD.

In a solution of acetite of lead in distilled water I dipped a piece of silk, and dried it in the air; it was then suspended over a quantity of water in Dr. Nooth's machine, and exposed to hydrogen gas about three months.

The appearances were much the same as in the last experiment, except that the silk was not so black: the particles of reduced lead resembled silver.

Similar experiments were made in this machine on bits of silk imbued with a solution of nitro-muriate of gold in water; but the appearances being much the same as those mentioned in the first and second experiments, it is unnecessary to repeat them here.

It is much easier to imagine, than express my anxiety, to discover the cause of the brilliant specks of reduced gold and silver, with which the pieces of silk in these experiments were sometimes spangled; concluding, that were the cause ascertained, it would be a considerable step towards accomplishing the object in view.

But many and diversified were the experiments I made before the circumstance, on which the spangles depended, was perceived.

At length, I found it depended on the presence of moisture; and that the spangles of reduced metal were owing to small drops of water carried up by the elastic fluid, and deposited on the silk.

The experiments, which led to this conclusion, shall be related in their proper places. I shall now proceed to recite the remainder of the experiments in this essay, conformable to the plan laid down in the preface, premising an occurrence observed in the course of them.

I sometimes found, that the production of hydrogen gas from a mixture of acid, water, and iron nails, would unexpectedly stop, which induced me to add more acid; this not succeeding, I added more water; but still no gas was formed: the proportions of acid and water were varied without effect. Thinking the mixture of acid and water unfit for the purpose, I poured it off, and repeatedly washed and agitated the nails with more water, which was also poured off; but happening inadvertently to add some of the mixture of acid and water, which I had before poured off as unfit for use, I was surprised to find the gas produced with great rapidity.

Reflecting on the cause of this odd circumstance, I concluded that it depended on a crust of super-oxygenated iron, formed on the surface of the nails, which defended them from the action of the water and acid, and that this crust was removed by the agitation and washing, which enabled the diluted acid to act again on the iron.

EXPERIMENT V.

GOLD.

I immersed a bit of silk in a solution of nitromuriate of gold in distilled water, and dried it in the air; it was then placed over a cylindrical glass vessel, containing a mixture of diluted sulphuric acid and iron nails, for about half an hour; but no reduction of the metal could be observed.

I dipped another bit of silk in the same solution of gold, and exposed it, while wet to the same current of hydrogen gas, and instantly signs of reduction appeared; for the yellow colour, which the solution imparts to silk, began to change to a green, and very soon a film of reduced gold glittered on the surface opposed to the gas: shortly after, a beautiful blue spot, fringed with orange and purple, was formed on the middle of the silk. During the experiment, which lasted about half an hour, the silk was kept constantly wet with distilled water.

When experiments are made with this preparation of gold, it is necessary to evaporate the solution to dryness, before the salt be dissolved in the water; as an excess of acid prevents the reduction in a great measure. Solutions of gold in these experiments do not admit of being so largely diluted, as solutions of silver, and other metals do.

EXPERIMENT VI.

SILVER.

I immersed a piece of silk in a solution of nitrate of silver, and dried it in a dark place; it was then exposed to a current of hydrogen gas about twenty minutes; but no reduced silver appeared, the only change observable was a brown stain.

I immersed another bit of the same silk in the same solution of silver, and having exposed it, while wet, to a stream of hydrogen gas, I soon observed evident signs of reduction; the white colour of the silk was changed to a brown, which became gradually more intense; and the surface of the silk, opposed to the gas, was coated with reduced silver: various colours, as blue, purple, red, orange, and yellow, attended the reduction. These colours often change, and are succeeded by others in the progress of the reduction. The threads of the silk look like

silver wire, tarnished in some parts, but of great lustre in others.

The silk was kept wet with distilled water during the experiment. When the silk happened to be too much wetted, the under surface opposed to the gas was often covered with scales of a dull blue colour: these, after the silk dries, may be brushed off, and another coat of reduced silver, which adheres firmly, but has no considerable brightness, is left behind.

These experiments on the reduction of gold, and silver, were often repeated with nearly the same result.

EXPERIMENT VII.

SILVER.

Thinking some other preparation of silver might answer better than a nitrate, I precipitated some of the latter with a solution of muriate of soda, and poured the whole on a filter; the precipitate was well washed with distilled water, and dissolved in ammonia. In this solution I immersed a piece of silk, and dried it in the air; and having exposed it to the action of hydrogen gas, I could perceive no signs of reduction, except a faint brown colour.

I dipped another bit of silk in the same solution of silver, and in order to determine if water had the power of promoting the reduction of the silver in this preparation, as it had in the former experiments, I exposed the silk, while wet, to the same current of hydrogen gas; and in a few seconds the metallic lustre was evident on the surface opposed to the current. After some little time, a blue speck and a faint trace of yellow appeared, but soon vanished.

This preparation of silver does not stain white silk so much as a nitrate does; the reduced silver was indeed very brilliant, but soon grew dull, and disappeared; a brown stain only remaining; so that it seems rather inferior to nitrate of silver, which also, after reduction, tarnishes, grows dull, and often disappears; but sometimes part of it remains permanently reduced.

EXPERIMENT VIII.

PLATINA.

With much difficulty I procured a small quantity of the ore of platina, and dissolved it in nitro muriatic acid. The solution was evaporated to dryness, and the salt was then dissolved in distilled water.

A bit of silk was dipped in part of this solution, and dried in the air; it was then exposed to a brisk

current of hydrogen gas about twenty minutes, but no signs of reduction appeared.

Another bit of silk was immersed in the solution of platina, and exposed, while wet, to the same current of hydrogen gas; in five or six minutes the platina was reduced, exhibiting a livid white metallic appearance on the surface of the silk opposed to the current. No colours attended the reduction. This solution imparts a yellowish brown colour to silk.

After some time, the whole of the metallic lustre disappeared, in proportion as the silk became dry.

The solution of platina requires more time, and a stronger current of hydrogen gas for its reduction, than solutions of silver and gold do.

EXPERIMENT IX.

MERCURY.

I immersed a bit of silk in a solution of oxygenated muriate of mercury in distilled water, and dried it in the air: it was then exposed to a stream of hydrogen gas; but underwent no visible change.

I dipped another bit of silk in the same solution of mercury, and exposed it, while wet, to the same current of gas; the metal was soon reduced in a beautiful manner, and resembled silver.

The reduction began suddenly, with scarce any appearance of previous stain; some very faint, but at the same time transparent colours attended it: the most remarkable of these were a light orange, with a fringe of blue, and a yellow verging on a faint green. These colours soon disappeared.

After the silk was turned, I observed, that its texture was, in some parts, concealed by a thin film, which, as the reduction proceeded, was perceived to dart along the threads of the silk, gilding them in a beautiful manner, and exhibiting the texture very distinctly.

After some time, the mercury seemed to disappear, so as to render it doubtful whether any of it remained in the silk; but shaking it in the sun beams, I perceived bright atoms fly off; and rubbing the silk on a bit of blue paper, I observed shining metallic particles, which seemed to have lost their affinity of aggregation, for they did not unite.

One remarkable difference between this preparation of mercury and nitrate of silver, is, that no black or brown stain preceded, attended, or followed, the reduction of the mercury. Mr. Scheele reduced a prussiate of mercury, dissolved in water, by adding iron filings and a smar quantity of sulphuric acid to the solution.*

EXPERIMENT X.

COPPER.

A piece of silk was immersed in a solution of sulphate of copper, then taken out, and dried, and exposed for a considerable time to a brisk current of hydrogen gas; but no signs of reduction could be perceived.

Another bit of silk was dipped in the same solution of copper, and exposed, while wet, to the same rapid current of hydrogen gas; the appearances were the following.

After a minute, or two, the silk assumed a faint brown colour, and, on the surface opposed to the gas, a white metallic pellicle appeared, which vanished in proportion as the silk became dry: wetting the silk again, I perceived a similar pellicle appear, which also vanished, as soon as the silk dried. If the silk be kept constantly wet, the brown colour becomes much more intense, attended with a very slight tinge of

^{*} Scheele, p. 162, French translation. This is the usual process for obtaining the Prussic acid.

red. The margins of the silk projecting beyond the verge of the glass cylinder, and therefore not exposed to the current of the gas, retained the blue colour, which the solution imparts.

In some of these white metallic pellicles there appeared a faint brown inclining to yellow, which reflected the light, though obscurely.

After the silk dried, nothing remained, but a brown stain.

EXPERIMENT XI.

LEAD.

A piece of silk was immersed in a solution of acetite of lead in distilled water; it was then dried, and exposed for some time to a stream of hydrogen gas; but underwent no perceptible change.

Another bit of silk was dipped in the same solution of lead, and exposed, while wet, to the same current of hydrogen gas; in a second, or two, the surface of the silk, opposed to the current, was coated with reduced lead, which looked like silver.

The reduction was accompanied with a brown stain, but by no means so intense as that, which attends the reduction of nitrate of silver.

The other side of the silk was opposed to the current of hydrogen gas, and soon acquired a metallic coat of the same brilliant appearance; exhibiting the texture of the silk, in a very striking manner.

It is remarkable, that lead exhibits no colour, but a light brown, during its reduction; whereas gold, silver, and mercury, display a great variety of colours, especially the two former.

After some time the lead reduced in this manner loses its metallic splendour considerably; and that in proportion as the silk dries.

EXPERIMENT XII.

TIN.

I dissolved some crystals of muriate of tin in distilled water; dipped a bit of silk in the solution; and dried it in the air: it was then exposed to a stream of hydrogen gas a considerable time; but no change or appearance of reduction, could be observed.

Another bit of silk was immersed in the same solution of tin, and exposed, while wet, to the same current of gas; after some little time, the reduction commenced, attended with a great variety of beautiful colours; as red, yellow, orange, green, and blue, variously intermixed.

The reduced tin disappears along with these colours, as the silk dries; nothing remaining but a feuille-morte colour.

The same solution of tin was also reduced by hydrogen gas, obtained from tin, and the muriatic acid.

These experiments do not succeed well with muriate of tin containing an excess of acid.

EXPERIMENT XIII.

ARSENIC.

A muriate of arsenic, which was prepared by digesting white oxid of arsenic in muriatic acid, and continuing the heat, till most of the acid evaporated, and left behind a soft mass of the consistence of tar, was dissolved in distilled water.

In this solution a bit of silk was immersed, and dried in the air: it was exposed to a brisk stream of hydrogen gas, obtained from zinc, and muriatic acid; but no reduction took place.

Another bit of silk was dipped in the same solution, and exposed, while wet, to the same current of hydrogen gas; and instantly, the surface of the silk, opposed to the gas, was covered with a bright coat of reduced arsenic, accompanied with a yellow stain. In a short time the metallic lustre vanished; and nothing remained but the yellow stain.

M. Pelletier restored the acid of arsenic to its metallic state, by passing hydrogen gas through a solution of that acid, in twice its weight of water.*

EXPERIMENT XIV.

BISMUTH.

A bit of silk, which was immersed in a solution of nitrate of Bismuth in distilled water, and exposed dry to hydrogen gas, obtained from zinc, and muriatic acid, underwent no visible change.

Another bit of silk was dipped in the same solution of bismuth, and placed over a languid stream of hydrogen gas; the bismuth was soon restored to its metallic form, on the surface of the silk opposed to the elastic fluid. The reduction was attended with a reddish brown stain, intermixed with a tinge of violet.

^{*} Roz. Journ. Feb. 1782.

EXPERIMENT XV.

ANTIMONY.

A bit of silk was immersed in a solution of tartrite of antimony in distilled water; and dried in the air. It was then exposed to hydrogen gas, obtained from zinc, and muriatic acid; but suffered no visible alteration.

Another bit of silk, which was dipped in the same solution of antimony, was exposed wet to a weak stream of the gas; and, in a short time, the metallic lustre appeared, accompanied by a light yellow colour.

EXPERIMENT XVI.

IRON.

A bit of silk, which was immersed in a largely diluted solution of sulphate of iron, and dried in the air, was exposed to a strong current of hydrogen gas, obtained from iron nails and diluted sulphuric acid; but no visible change was produced on the silk.

Another bit of silk was dipped in the same solution of iron, and placed wet over the same stream of hy-

drogen gas; but no reduced iron could be perceived. The silk was then immersed in a glass of clear water, and transferred a very minute metallic film to the surface of that fluid.

This experiment was repeated, with a rapid current of hydrogen gas, obtained from zinc, and muriatic acid; and, in about a minute, small films of reduced iron were visible on the surface of the silk, opposed to the gas.

The silk was then immersed in water, and transferred to its surface a large metallic pellicle; parts of which were very brilliant; but other parts were dull, and much more imperfectly reduced.

EXPERIMENT XVII.

ZINC.

A bit of silk, which was dipped in a muriate of zinc, largely diluted with water, and dried in the air, was exposed to a rapid current of hydrogen gas, obtained from zinc, and muriatic acid; but suffered no visible alteration.

Another piece of silk was immersed in the same solution of zinc, and exposed, while wet, to the same rapid current of hydrogen gas: in about half a minute, the metal was reduced in a very evident manner, on part of the silk. The silk was then dipped in a glass of clear water, and transferred a bright metallic film to its surface.

As these reductions of iron, and zinc, by hydrogen, are contrary to M. Lavoisier's table of the affinities of the oxygenous principle; I began to suspect, that the films, which were so evident, both on the silk, and the water, might be abraded, or torn from the zinc, by the muriatic acid; and elevated, and deposited on the silk by the gas.

In order to remove this doubt, I dipped a bit of the same silk in distilled water; and exposed it, while wet, to the same current of hydrogen gas, but nothing metallic could be seen on the silk; nor did it when immersed in water transfer a film, or the smallest appearance of a metal, to the surface of that fluid: and therefore, there can be no doubt of the reality of these reductions.

Dr. Priestley restored iron, and lead, to their metallic state, by heating their oxids with a burning glass in hydrogen gas.

These experiments point out an error in M. Bergman's table of elective attractions in the humid way; for he assigned the last place in that table to phlogiston, which he considered as the base of inflammable air; because he was unacquainted with any metallic reductions effected by hydrogen in the humid way.*

Having found, that water promoted, and accelerated these reductions in a very remarkable manner; I was curious to know, if alcohol, and ether, would produce the same effect. With this view, I evaporated a solution of gold in nitro-muriatic acid to dryness; when the vessel cooled, some alcohol was poured on to dissolve the salt; and immediately the vessel containing the salt, became so hot, that it could be scarcely endured by the hand; and diffused a fragrant smell, like that of ether, which, no doubt, was a species of that fluid.

EXPERIMENT XVIII.

GOLD.

In this solution of gold in alcohol, a bit of silk was dipped, and exposed to a stream of hydrogen gas, obtained from diluted sulphuric acid, and iron nails; and kept wet with alcohol: in about two minutes, the silk began to assume a brown colour, and white metallic films appeared on some parts of the surface opposed to the gas; some of these disappeared in a short time; and were succeeded by a few very small spangles of the proper colour of gold. These also

^{*} Elective Attractions, English Translation, p. 87.

soon vanished; and nothing remained but a disagreeable brown stain, intermixed with specks of a dull blue.

I sometimes found, on repeating this experiment, that no yellow films or spangles appeared; and am persuaded, that their appearance, and that of the white pellicles also, depends on the presence of water, contained in the alcohol, or the gas, and deposited on the silk.

EXPERIMENT XIX.

GOLD.

A bit of silk was immersed in a solution of gold in ether, and exposed to a stream of hydrogen gas, and kept wet with ether. The silk underwent no alteration for a few minutes; at length, it began to assume a faint brown colour, but no white, or yellow films appeared.

If this experiment be continued till the silk collects a sufficient quantity of water from the gas, some films will appear.

EXPERIMENT XX.

SILVER.

I procured some nitrate of silver, which had been fused in order to expel as much of its water as possible; and dissolved it in alcohol. I immersed a bit of silk in this solution, and exposed it to a stream of hydrogen gas, and kept it wet with alcohol: in a few seconds, the silk assumed a brown colour, which gradually became more intense: but no reduced silver appeared for several minutes; at length, a few metallic films appeared on part of the surface opposed to the gas.

EXPERIMENT XXI.

MERCURY.

A bit of silk was dipped in a solution of oxygenated muriate of mercury, and dried; it was then exposed to hydrogen gas about ten or fifteen minutes, and kept constantly wet with alcohol. The silk, during the first minutes, suffered no perceptible alteration: at length, a few small films were visible on the side of the silk opposed to the current.

EXPERIMENT XXII.

LEAD.

A bit of silk which was immersed in a solution of acetite of lead, and dried, was exposed about fifteen minutes to a stream of the gas; and kept constantly wet with alcohol; but suffered no visible change; except that a very minute film was reduced on one of its margins, which did not project beyond the verge of the glass vessel on which it was placed.

When we compare these experiments with those, in which water was used, to wet the silk, 'tis evident, that alcohol, and ether, do not promote the reduction of metals, as water does; and that the few films, which appear, when the silk is kept wet with ether or alcohol, depend entirely on water collected from the gas, or deposited by them on the silk during their evaporation.*

In order to compare the effects of hydrogen gas, obtained from water, iron nails, and muriatic acid, with that, procured from the same materials, by means of the sulphuric; I made some experiments on gold, silver, mercury, and lead, in the same man-

^{*} Or, which is most probable, from water contained in the alcohol, owing to the great difficulty of procuring it perfectly rectified. Am. Ed.

ner, as the preceding; and the principal difference was, that the colours produced in all the pieces of silk, except that, which was dipped in acetite of lead, were much brighter, and more beautiful, than any produced, when the sulphuric acid was used.

The reduction of the lead was accompanied with its usual brown colour.

On the upper surface of a bit of silk, which was dipped in a solution of gold, a green colour instantly appeared; and soon changed to a deep olive, in proportion as the reduction advanced: now examining the under surface, I saw it coated with a bright film of reduced gold, in the middle of which a blue spangle, mixed with purple, soon began to appear: I then moistened the upper surface of the silk with water; and in a few seconds, it also was coated with reduced gold.

The blue on the other side of the silk became much more intense: the piece was now turned; and on each colour I let fall a drop of water: the drop on the blue had a blue film, the drop on the purple, had a purple film, and the drop on the yellow, a film of reduced gold.

After some time, these drops of water evaporated, and the films came again in contact with the silk: some parts of which were left bare, as generally happens, when too much water is applied.

On the under surface of a bit of silk, which was immersed in a solution of nitrate of silver in water, a coat of reduced metal was formed, with various colours, as green, blue, orange, and yellow, the beauty and brightness of which were remarkable.

In some time a muriate of silver is formed in the fibres of the silk, which on exposure to light becomes of a bluish black colour; but the whole of the silver does not undergo this change, for part of it remains in its metallic state. The colours remain a considerable time, if the silk be removed from the gas before this muriate is formed.

Hence it appears, that hydrogen gas should not be prepared with an acid, which forms an insoluble compound with the metal to be reduced.

I also found, that hydrogen gas produces different effects not only according to the difference of the acid, but also according to the difference of the metal employed to obtain it; for this gas procured from zinc or tin, and muriatic acid, did not restore gold to its proper metallic lustre; but formed on the silk, a white metalline coat like silver.

The experiments related in this chapter indicate the following conclusions.

- 1. Hydrogen is capable of reducing the metals in the ordinary temperature of the atmosphere.
- 2. Water promotes and accelerates these reductions, in a very remarkable manner.
- 3. Ether and alcohol do not promote these reductions, without the aid of water.
- 4. A variety of colours accompanies these reductions, similar to what appears, during the calcination of metals by heat and air; and depends on the same cause; viz. the quantity of oxygen combined with the metal.

These colours have not been observed hitherto; nor indeed could they, as the metals were reduced in close vessels, and in high degrees of heat.

5. These reductions often disappear.

This is commonly owing to an imperfect and partial reduction of the metal; for the acid and water remaining in that part of the metallic solution, not reduced, re-calcines these delicate films; sometimes the disappearance of the metallic lustre depends on the nature of the metal itself; thus arsenic, lead, silver, &c. suffer some degree of calcination by water and atmospheric air. Messrs. Bergman and Keir relate instances, in which silver after being precipitated in its metallic state, was re-calcined, and disappeared.

I first imagined, that water promoted these reductions by minutely dividing the particles of the metallic salt, and by condensing the gas, and bringing its hydrogen, and the metallic oxide, within the sphere of attraction; the hydrogen either uniting to the metallic earth and reducing it, as the Phlogistians suppose; or uniting with, and separating the oxygen of the metal, and thus restoring it to the metallic form, as the Antiphlogistians maintain.

But it is evident from the experiments related, that water does not promote these reductions solely, by minutely dividing the particles of the metallic salt; for were this the case, ether and alcohol should promote the reduction of the metallic salts, which they dissolve, since they divide their particles as minutely as water can.

Since then metallic solutions in ether, and alcohol, cannot be reduced by hydrogen gas; it follows that the above supposition concerning the mode of agency of water does not account for the reduction of metals in this way.

And indeed were it true that hydrogen condensed by water reduced metals in the manner above mentioned, it would follow, that the reduction was effected by a single affinity, which cannot be admitted; 1st. because the existence of a single affinity in such cases has not been proved; 2dly, because a double affinity always takes place in preference to a single affinity, which is demonstrated by the following facts, transcribed from the works of Mr. Kirwan.

"If a solution of silver in the nitrous acid be thrown into a mixed solution of fixed alkali and common salt, the silver will be precipitated by the marine acid of the common salt, and not by the free alkali, contained in the liquor: for a luna cormea is found."*

"I repeated the experiment with a solution of lead, and also of mercury in the nitrous acid, and the result was similar; horn lead and marine salt of mercury were formed."

In these experiments of Messrs. Monnet and Kirwan, 'tis evident that a double affinity takes place in preference to a single one: for the nitrous acid of these different nitrates unites with the alkali of the common salt, while the muriatic acid of the latter seizes the silver, mercury, and lead, of the nitrates, and forms muriates of silver, mercury and lead: the free alkali remaining passive in the mixture.

^{*} M. Monnet Dissolution de Metaux, p. 159. † Phil. Trans. Vol. 73. An. 1783.

M. Lavoisier says, "There exists only in nature, as far as we can observe them, cases of double affinity, often triple, and others perhaps still more complicated."

complicated."

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Now as water does not promote these reductions merely by dissolving, and minutely dividing, the particles of the metallic salts, and condensing the hydrogen gas; and since a double affinity takes place in preference to a single affinity; it is obvious that the water must be decomposed in these reductions in the following manner.

The hydrogen of the gas unites to the oxygen of the water, while the hydrogen of the latter unites in its nascent state to the oxygen of the metal, reduces it, and forms water.

Thus what could never be effected by a single, is readily performed by a double affinity.

Hence it follows, that the hydrogen of the gas is oxygenated by the oxygen of the water, while the metal is, at the same time, restored to its combustible state. It also follows, that the quantity of water formed is double that decomposed.

I Essay on Phlogiston, a new Edit. by M. Kirwan, p. 46.

CHAPTER II.

REDUCTION OF METALS

BY

PHOSPHORUS.

THE next substance, of whose effects in reducing metals in the fibres of silk, I shall treat, is phosphorus, one of the most inflammable substances we are acquainted with.

I was for some time at a loss, how to apply it to this purpose; but learning from a note of Mr. Lewis, that it is soluble in ether, I dissolved a small quantity of it in that fluid, which can be easily effected, if the ether be good. The solution is considerably promo-

made in a small phial, which should be nearly filled with the ether, and accurately corked; a common cork is preferable for this purpose, to a glass stopper; and a single-grain of phosphorus is sufficient for a great number of experiments.

I sometimes applied a much greater degree of heat than the above, by placing the phial in hot sand, pressing on the cork at the same time with my finger, to prevent its being forced out by the expansion of the ether, part of which is converted into an elastic fluid, and holds some phosphorus in solution: the ether soon begins to boil; the phosphorus melts, and a strong solution is obtained in a few minutes by shaking the phial. If the solution be removed to a cool place, it frequently deposits crystals.

This manner of preparing the solution is attended with some danger, for should the phial burst or the cork be extruded, the contents will be thrown out with considerable force, and that part of the phosphorus not dissolved by the ether burn with great violence.

The only objection to this preparation of phosphorus is the ether, which must necessarily modify the result, and prevent that simplicity so desirable in experiment.

But, after some observation, it was perceived, that the ether flies off and leaves the phosphorus pure, and minutely divided in the fibres of the silk; the ether, from its great volatility, first evaporates, and at the same time, produces a very considerable degree of cold, which effectually prevents the evaporation, and combustion, of the phosphorus.

After the ether evaporates, the cold ceases, and the combustion of the phosphorus commences, attended with white fumes, which continue till the whole is consumed, if no other power intervene.

Hence it is evident, that this preparation of phosphorus has a simplicity and elegance not always to be obtained.

It has also another great advantage in experiments of this kind; for it does not change in the smallest degree, the white colour of silk, during its slow combustion, which is not attended with heat sufficient to affect the most delicate colour. This property of not affecting the colour of the silk renders observation and experiment more accurate; as whatever change supervenes, must depend either on the metallic solution itself, or on the action of the phosphorus on the same. But this advantage is confined to a certain range of the thermometer; for if the heat be increased to about 86° of Fahrenheit, and the silk be dry, the phosphorus is apt to set fire to it.

EXPERIMENT I.

GOLD.

I immersed a bit of silk in a solution of gold in ether, and after the ether evaporated, dropped on it some of the solution of phosphorus, which diffused itself through the silk like a drop of oil, and formed a circumscribed spot, whose limits, as the ether evaporated, assumed a brown colour, which soon diffused itself equally over every part to which the solution of phosphorus was applied; but the parts of the silk, to which the latter did not reach, retained the yellow colour, which the solution of gold gave them.

The silk viewed by transmitted light presented the same colours, except that the limits of the brown appeared more intense, and seemed to border on a faint purple.

Examining the silk next day, I found that the whole of the brown stain acquired a faint shade of purple, which was most evident on the margins of the stain.

EXPERIMENT II.

GOLD.

I dipped a bit of silk in the solution of gold in ether, and after it was well dried, half of it was wetted with distilled water; the other half remaining dry: the solution of phosphorus was applied to both the moist and dry parts of the silk; instantly the part wetted with the water began to acquire a purple colour; and soon after the metallic splendour of the gold appeared; but that part which was kept dry acquired only a brown stain, similar to that described in the preceding experiment.

I repeated these experiments many times, and always found, that the gold was reduced only in proportion to the water applied.

Finding water promoted the reduction of gold by phosphorus, I began to form various conjectures about its mode of action; I first supposed it acted by holding the particles of the salt minutely divided, thus diminishing their attraction of cohesion, and consequently increasing their chymical attraction.

The truth of this supposition might, I thought, be decided by using ether and alcohol, instead of water,

to wet the silk, avoiding aqueous moisture, as much as possible; accordingly I made the following experiments, which were frequently repeated with nearly the same result.

EXPERIMENT III.

GOLD.

A piece of silk was immersed in the solution of phosphorus; as soon as the ether evaporated, and the phosphorus began to fume, an ethereal solution of gold was dropped on the silk, which immediately got a brown colour; the piece was kept constantly wet with ether, in some time a purple tinge appeared on parts of the silk, and shortly after small films of reduced gold appeared; the silk was now remarkably wet, and seemed to have a great power of collecting water; this I supposed was partly attracted from the air by the salt, and phosphorous acid formed during the combustion, which has a powerful attraction for water, and partly deposited in the silk by the ether during its evaporation.

In order to determine if the ether during its evaporation deposited water in the silk, I kept a bit of silk wet with ether for a few minutes, and found, that after the evaporation ceased, the silk was moist; but this humidity was not so great, as that observed in the silk, to which the ethereal solutions of phosphorus and gold were applied.

Another bit of silk was dipped in the ethereal solution of gold, and after the ether evaporated, the solution of phosphorus was applied; a brown colour was produced; the silk was kept wet with ether, and in a short time, a purple tinge appeared on parts of it; but chiefly at the margin of the stain, which gradually diffused itself over the whole.

The only difference between this and the preceding experiment on gold is the order, in which the solution of gold and phosphorus were applied to the silk, but there is a considerable difference in the result, for in this the brown and purple colours were formed much more slowly, and no particles of reduced gold appeared till after a much longer time.

EXPERIMENT IV.

GOLD.

A piece of silk was immersed in the solution of phosphorus, and when the white fumes began to rise, a solution of gold in alcohol was applied to the silk, which was kept wet with alcohol, a brown tinge which soon changed to a purple, appeared on different parts, and in a little time after, a very small film of reduced gold was visible on a part of the margin.

In another experiment, conducted in the same manner, the reduction was more evident.

The solution of gold used in this experiment was very rich, and had a great attraction for water, for bits of silk tinged with it, could not be dried without difficulty, and after they were removed to a cool place, they very soon became moist again. This is more or less the case with solutions of gold in general.

EXPERIMENT V.

GOLD.

A bit of silk was dipped in a solution of gold in alcohol and dried, then some of the solution of phosphorus was poured on the silk, a brown and then a purple colour appeared, and in some parts a small portion of the gold was reduced, the reduction was very obscure, but became gradually more evident, in proportion as it attracted water from the air. The silk was occasionally wetted with alcohol.

This experiment was repeated, with this difference, that the silk was not kept wet with alcohol, and no reduced gold could be perceived.

EXPERIMENT VI.

GOLD.

In order to exclude water more effectually, a small phial was carefully dried by placing it in hot sand, and then corked, to prevent the access of moisture from the air; when the phial cooled, it was nearly filled with ether, and a small bit of phosphorus dropped into it, it was then corked and replaced on the hot sand, the phosphorus soon melted, and a strong solution was obtained by shaking the phial.

Into this solution a small bit of silk, which was dipped in a rich solution of gold, and carefully dried, was introduced; the silk immediately got a brown tinge, but not a particle of reduced gold could be perceived. The solution in a short time became turbid, and deposited a brown powder. The colour of the precipitate was exactly the same, as that which the silk acquired. The experiment was continued about three months, and carefully observed, but no other change could be perceived; at the end of this time the silk was taken out of the phial, and the solution of phosphorus was found capable of reducing gold and silver by the aid of water.

EXPERIMENT VII.

GOLD.

In order to contrast the effects of water with those of ether, and alcohol, more fully, a piece of silk was immersed in a solution of nitro-muriate of gold in water, and dried in the air about twelve hours; during which time the yellow tinge, the solution of gold gave the silk, remained unchanged: the solution of phosphorus was then applied; a brown stain appeared; the ether soon evaporated; the phosphorus began to fume; and the silk acquired a purple colour; but not a particle of reduced gold could be perceived. The purple tinge in this bit of silk was much more intense, and more equal, than in the pieces, in which ether and alcohol were used.

EXPERIMENT VIII.

GOLD.

I dipped a piece of silk in the solution of phosphorus, when the ether evaporated, and the phosphorus began to fume, a solution of gold in water was applied; instantly the silk was covered with a splendid coat of reduced gold. Nothing can be more striking than this experiment, which was repeated times without number, or demonstrates the necessity of water in these reductions in a more convincing manner.

This piece, viewed by transmitted light, had a purple colour with a considerable tinge of blue; and the margin of the reduced gold was fringed with purple.

EXPERIMENT IX.

GOLD.

Thinking the phosphorus applied in the form of vapour through the medium of water might be more effectual than a solution of it in ether, I immersed a small bit of silk in an aqueous solution of gold, and suffered it to dry a little; it was then suspended in a phial over a little water, into which a small bit of phosphorus was previously introduced: the phial was then corked, and placed on hot sand: the phosphorus began to melt, and ascend in white vapours, which, as soon as they reached the lower end of the silk, gave it a brown tinge, succeeded by a purple; and the gold began to assume its metallic splendour: in a short time these appearances were evident over the whole silk.

The following propositions are deducible from these experiments.

- 1. Water does not promote the reduction of gold merely by dissolving, and minutely dividing, the particles of the salt, and thus diminishing their attraction of cohesion, and consequently increasing their chymical attraction, as I first supposed; for were this the case, ether and alcohol, which equally dissolve and divide the salt, should produce the same effect.
- 2. Ether and alcohol do not promote these reductions without the aid of water; for it is evident from the experiments related, that the few particles of reduced gold which appear when they are employed, depend entirely on the quantity of water which they leave in the silk during their evaporation, and that attracted from the air by the solution of gold, and by the phosphorus during its combustion, both of which have a strong attraction for water.
- 3. Phosphorus does not reduce gold by giving the metallic earth phlogiston, as the Phlogistians suppose; for were this opinion true, a solution of gold in ether, or alcohol, should be reduced by the phosphorus as effectually as a solution of gold in water is.
- 4. Phosphorus does not reduce gold, by combining with, and separating, the oxygen of the gold, as the

Antiphlogistians assert; for were this the case, the particles of the phosphorus so attenuated by the ether, should reduce a solution of gold in ether, or alcohol, as well as a solution of gold in water, since the impediment opposed by the attraction of cohesion is equally removed in both cases.

I shall conclude these remarks on the reduction of gold with the following experiment, which often amused me.

EXPERIMENT X.

GOLD.

A small bit of silk was immersed in a solution of gold in ether, and dried; then the solution of phosphorus was applied, which changed the yellow colour of the silk to a brown: when the phosphorus began to fume, I placed the silk on the palm of my hand, and breathed on it a considerable time; a purple tinge gradually succeeded the brown, and in some little time after, the metallic lustre of the gold began to appear.

The same experiment succeeds with a solution of gold in alcohol.

Another bit of silk, treated in the same manner, was placed over the vapour of warm water for some time; the same appearances took place, and particles of reduced gold were evident in the silk.

If the water, whence the vapour arises, be too hot, the heat retards, and sometimes prevents, the reduction, by volatilizing the phosphorus.

EXPERIMENT XI.

SILVER.

I dipped a bit of silk in a solution of fused nitrate of silver in alcohol, and dried it in the air: then some of the solution of phosphorus was applied, which produced a brown stain, whose margin, after a few minutes exposure to the air, acquired a livid white appearance, caused by a partial and imperfect reduction of the silver.

This, however, would not be taken by a person unacquainted with experiments of this kind for reduced silver.

EXPERIMENT XII.

SILVER.

A bit of silk was immersed in the solution of phosphorus; as soon as the ether evaporated, and the phosphorus began to fume; a few drops of the solution of silver in alcohol were applied: immediately a black stain, intermixed with some brown, appeared; and, after some time, obscure films of reduced silver presented themselves; these appeared on different parts of the stain, but were so minute as to be scarcely visible. The only difference between this and the preceding experiment is the order, in which the solutions were applied; but even this modifies the result in some measure.

That these imperfect reductions depended on water, deposited in the silk by the alcohol, during its evaporation, or attracted from the air by the phosphorus during its combustion, will appear from the following experiment.

EXPERIMENT XIII.

SILVER.

A small phial was well dried in hot sand, then corked, and removed to a cool place: after the phial

cooled, it was nearly filled with ether, and a small bit of phosphorus which was repeatedly washed in alcohol to free it from any aqueous moisture, that might adhere to it, was introduced; the phial was then corked and placed in hot sand; when the phosphorus melted, I shook the phial and obtained a strong solution.

Into this solution a small bit of silk, which was dipped in a solution of silver in alcohol, and dried, was introduced; the phial was corked, the silk instantly assumed a brown colour, but not a particle of reduced silver could be seen, though the experiment was continued about three months, nor did the solution of phosphorus become turbid, or deposit any precipitate, as happened in similar experiments on gold.

At the end of this period the silk was taken out of the phial wetted with water, and suspended in a window, and after a considerable time, reduced silver was manifest on different parts of the silk.

With the solution of phosphorus, in which the silk stood during that time, I reduced gold and silver with the assistance of water.

In order to compare the effects of water with those of ether and alcohol, I made the following experiments.

EXPERIMENT XIV.

SILVER.

I dipped a bit of silk in a solution of nitrate of silver in water, and dried it at the fire; the silk thus dried retained its white colour, the solution of phosphorus was then applied, and immediately produced a brown colour, which soon, in proportion as the phosphorus fumed acquired a deeper tinge verging on black, and slight signs of reduction appeared after a little time on the margin of the stain.

Another bit of silk, treated in the same manner, but dried much better, exhibited still fainter signs of reduction, for the brown stain did not appear on this piece as soon as on the former, nor was it so intense; however, after some minutes exposure to the air, the stain became deeper, and its margin acquired a livid white appearance, owing to a partial reduction of the silver.

It has been often remarked, that the reduction commences first on the margin of the stain, which the solution of phosphorus and that of the metal produce in the silk; I was a long time at a loss to account for this appearance, but the cause was accidentally discovered; for happening to spill a few drops of the solution of phosphorus on a table, I observed, that as they evaporated, watery circles were formed round the spaces on which the drops fell, and that all the parts within the circles were dry.

This explains why the reduction begins on the margin of the stain.

I observed the same of alcohol, for if it be dropped on a level surface, it leaves a watery ring behind,
though not near so soon as a solution of phosphorus
in ether does; this is the reason why alcohol seems
to promote the reduction of some metals; I say seems,
for it does not promote it, but in proportion to the
quantity of water it contains, or attracts from the
air, and deposits in the silk during its evaporation.

How essential water is to the reduction of metals will appear from the following experiment.

EXPERIMENT XV.

SILVER.

I immersed a piece of silk in the solution of phosphorus, and after the ether evaporated, and the phosphorus began to fume, a solution of nitrate of silver in water was applied; instantly the silver was restored to its metallic splendour.

This experiment is very amusing, and well calculated to strike the beholder with surprise.

The reduction is sometimes attended with spangles of a beautiful blue, which appear chiefly where the solution of silver is most abundant.

The solution of silver is commodiously applied by a camel's hair pencil.

I also tried the effects of the vapour of phosphorus on bits of silk dipped in a solution of nitrate of silver in water, and exposed to the vapour, in the same manner as in experiment the 9th, and the silver was always reduced; but a solution of phosphorus in ether seems preferable to the vapour.

A small glass tube, resembling a thermometer, with its bulb terminating in a smaller and nearly capillary tube, I found useful, and economic, especially in experiments on gold: by immersing the smaller end in the metallic solution, and inspiring through the tube at the same time, the bulb may be filled: by this means a single drop, or more if necessary, may be applied to the silk; and thus a great number of experiments can be made on a single grain, or a much less quantity of gold, or any other metal.

This little instrument may be used also to apply the solution of phosphorus to the silk; and it was by using it for this purpose, I discovered, that phosphorus has not the power of reducing silver without the aid of water; for blowing the solution of phosphorus from the tube on bits of silk, which had been dipped in a solution of silver and dried, I was surprised to find films of reduced silver frequently appear; whereas none appeared, when I applied the solution of phosphorus in a different manner: this unexpected event often occurred, before I learned the cause; at length I suspected it might depend on the moisture of the breath; and I was soon convinced by moistening the silk with water, that the suspicion was well founded.

It is evident from these experiments on silver, that water is essential to the reduction of this metal by phosphorus; and that ether and alcohol do not promote it.

It is also evident that these experiments, and those made on the reduction of gold, mutually illustrate each other; and confirm the conclusions drawn from them.

EXPERIMENT XVI.

PLATINA.

I immersed a bit of silk in a solution of nitro-muriate of platina in distilled water and dried it in the air; the solution of phosphorus was then applied to the silk but no appearance of reduction could be perceived.

Another bit of silk was dipped in the solution of phosphorus; when the ether evaporated and the phosphorus began to fume, the solution of platina was applied to the silk, and in some time, delicate films of reduced platina were visible where the water was most abundant. These films of platina commonly disappear, and nothing remains but a brown tinge which, however, is more intense than what the solution of platina alone gives the silk.

To succeed in this experiment the silk should be replete with phosphorus, which is easily done by applying the solution twice or thrice, and waiting after each application till the fumes begin to appear. It is also necessary to keep the silk constantly wet with wate. Sometimes it requires from ten to twenty minutes to reduce platina in this manner.

EXPERIMENT XVII.

MERCURY.

I dipped a bit of silk in a solution of oxygenated muriate of mercury and dried it in the air; then the solution of phosphorus was applied; when the ether evaporated and the phosphorus began to fume, a yellow stain commenced on the margin and gradually appeared over the whole.

To compare the effects of different degrees of moisture, I immersed a bit of silk in the same solution of mercury, and dried it carefully at the fire; the solution of phosphorus was then applied; the silk began to fume, but no change except a very slight ring of a yellow hue appeared. The rest of the silk retained its white colour.

Another bit of silk was immersed in the solution of phosphorus; when the ether evaporated and the phosphorus began to fume, the same solution of mercury in distilled water was applied, and in a few seconds a bright film of reduced mercury was visible on the margin of the part to which the metallic solution was applied, and after some time appeared on the whole. The reduction was attended with the colours of the rainbow.

After a little time these colours vanish and the metallic film becomes much more obscure, according as the silk dries, and is succeeded by a yellow stain.

EXPERIMENT XVIII.

MERCURY.

A bit of silk was dipped in a solution of nitrate of mercury in distilled water, and dried at the fire; then the solution of phosphorus was applied; and when it began to fume, a brown stain commenced at the margin, which soon diffused itself over the whole and gradually acquired a faint tinge of black.

Another piece of silk, treated in the same manner, but dried in the air, exhibited the same appearances; except that the brown tinge verged more on black.

Another bit of silk was immersed in the solution of phosphorus, and when it began to fume, the solution of nitrate of mercury was applied; a brown colour instantly appeared, accompanied with a film of reduced mercury, which was most evident where the metallic solution was most abundant. This film soon disappeared and was succeeded by a black stain, in which, however, reduced mercury was visible. No

colours but black and brown appeared in this experiment.

It appears from these experiments on mercury, that the reduction kept pace with the quantity of water present.

EXPERIMENT XIX.

COPPER.

A piece of silk was immersed in a solution of sulphate of copper and dried in the air: then a strong solution of phosphorus was applied; the silk acquired a brown colour, but no other visible alteration occurred.

Another piece of silk was dipped in the same solution of copper and dried at the fire much better than the preceding; the solution of phosphorus was applied; when the ether evaporated and the phosphorus began to fume, a brown tinge commenced on the margin of the silk, and gradually diffused itself over the whole; but the stain was by no means so intense as that produced in the preceding piece; so that there can be no doubt that the difference was owing to the different degrees of moisture in the silk. After this piece remained in the air for some time, the brown tinge became more intense, a proof that it attracted water from the air. This difference in the appearances of pieces dried in the air and at the fire, I frequently remarked.

EXPERIMENT XX.

COPPER.

A strong solution of phosphorus was applied to a piece of silk, when the ether evaporated and the phosphorus began to fume, a solution of sulphate of copper was applied; a brown stain was instantly produced, and its margins were soon covered with a white metallic film, parts of which, after some time, verged on the colour of copper, intermixed with purple, green and blue. If the solution of phosphorus be weak, which is always the case when the ether is bad, nothing appears on the silk but the brown stain and the white metallic film. As the silk dries most of these appearances vanish; but some of the blue tinge survives, and the silk looks very unseemly.

A bit of silk was immersed in the same solution of copper, and exposed to the vapour of phosphorus, as in experiment the 9th, but no change was produced on the silk, except a few brown spots, though the heat was such that the vapour filled the phial, and circulated through it: the vapour corroded a brass pin which was used to suspend the silk in the phial. This induced me to try its effects on copper, which was corroded by it in a remarkable manner, and changed into a black substance resembling a mixture of charcoal and oil. It appears then that phosphorus is ill adapted to the reduction of this metal.

EXPERIMENT XXI.

TIN.

A bit of silk was immersed in a solution of muriate of tin in distilled water, and dried in the air, the solution of phosphorus was then applied to the silk, and though it fumed considerably, no change whatever could be perceived in the colour of the silk, nor was there the smallest appearance of reduction.

I poured some of the solution of phosphorus on a bit of silk, and when it began to fume the solution of tin was applied; after a few seconds, white metallic films appeared, first on the margin, and were gradually diffused over that part of the silk to which the muriate of tin was applied, a yellow colour intermixed with red sometimes attends the reduction. After some little time these films of reduced tin vanish, and scarcely leave a stain behind.

I did not succeed in reducing acetite of lead, muriate of arsenic, or sulphates of iron, and zinc, in this way.

These experiments on tin shew that water is essential to its reduction by phosphorus, and give additional force to the preceding conclusions.

M. Sage discovered that gold, silver, &c. are precipitated from their solutions in the metallic form, by pieces of phosphorus, which are covered at the same time with bright coats of gold, silver, &c.

To determine if water were essential to these reductions performed by M. Sage, I made the following experiments.

EXPERIMENT XXIL

GOLD.

Some solution of phosphorus in ether was poured into a china cup, and a few drops of the ethereal solution of gold were added, instantly a brown powder was precipitated similar to what appeared in experiment the 6th, but no gold in its metallic form could be perceived.

EXPERIMENT XXIII.

GOLD.

A solution of nitro-muriate of gold in water was poured into a china cup, containing a solution of phosphorus in ether, instantly the gold began to assume its metallic splendour, attended with a variety of colours, as purple, blue, and red, the beauty of which cannot be described; the quantity of the blue was gradually diminished, and what remained, was dispersed over the surface in small films, intermixed with spangles of reduced gold. Most of the blue films were of a circular figure, some had a central speck of ruby red, and were fringed with purple; some had a round central speck of a darker blue than the surrounding parts, and some were of an irregular figure, fringed with purple or ruby red. I often observed these blue films assume the real colour of gold without suffering any intermediate change of colour, and I think, I observed the same of one of the largest specks of ruby red, that appeared in this experiment. All these colours disappeared, when the reduction was completed.

The variety of colours, which these films assume, depends on the different degrees of reduction; that is to say, on the quantity of oxygen combined with the metal, in proportion as the metal is deprived of the oxygen, it assumes various colours, which often succeed each other in a regular order, shewing the different stages of the reduction; thus when gold is reduced, the first perceptible change is a green which soon becomes olive, this is succeeded by blue and purple, and sometimes by a ruby red; the purple tinge is a mixture of blue and red.

The various colours which metals and their calces communicate to glass and other substances, are explicable on these principles, and the difficulty of obtaining a ruby-coloured glass by gold is readily understood from the facility with which that metal parts with oxygen.

EXPERIMENT XXIV.

GOLD.

A thread was passed by means of a needle through a small bit of phosphorus which was freed from any moisture that might adhere to it, by immersing it for some time in alcohol, it was then suspended by means of the thread in a solution of gold in ether, contained in a phial, which was carefully dried in hot sand; in a few minutes the solution became turbid, an effervescence commenced, and a brown precipitate was

formed; according as the precipitate fell the solution became clear, lost its yellow colour, and the whole of the gold seemed to have been precipitated, but not a particle of reduced gold could be seen.

Another bit of phosphorus was suspended in the same manner in a solution of nitro-muriate of gold in water, and in a few minutes got a splendid coat of reduced gold.

EXPERIMENT XXV.

SILVER.

A few drops of a solution of fused nitrate of silver in alcohol were poured into a china cup containing a solution of phosphorus in ether; instantly a black precipitate with a tinge of brown was formed, but no silver in its metallic state could be perceived.

After some time the precipitate attracted moisture from the air, and some films of reduced silver appeared.

The same experiment was made in a phial, which was corked to exclude the moisture of the air, and nothing but the black precipitate appeared.

Some of the same solution of silver was diluted with water, and dropped on a solution of phosphorus in ether, and instantly films of reduced silver floated on the surface.

EXPERIMENT XXVI.

SILVER.

A bit of phosphorus was suspended by a thread in some of the same solution of silver in alcohol, contained in a phial carefully dried, a black precipitate with a tinge of brown soon appeared, but no silver in its metallic state could be observed; part of the precipitate adhered to the phosphorus, and part fell to the bottom of the phial.

In another experiment made in a phial not sufficiently dried, a few small films of reduced silver were observed on the sides of the phial, but not a particle of silver in its metallic form could be seen on the phosphorus.

Another bit of phosphorus was suspended in a diluted solution of nitrate of silver in water, and in some hours, the phosphorus was covered with redueed silver. The case of silver, which covered the phosphorus prevented its spontaneous combustion in the air; the same was observed of the bit of phosphorus coated with gold.

Hence it appears, that M. Sage's success in reducing metals by phosphorus, depended on the water of the metallic solution.

These experiments were often repeated with nearly the same result, but some variety often occurs, depending on various circumstances, as the strength of the metallic solution, and that of the phosphorus, the quantity of water present, and the purity of the materials employed.

It is difficult to obtain ether, or alcohol, with the least possible quantity of water, and equally difficult to expel all moisture from the surface of glass; for this reason the bits of phosphorus in the experiments made with alcohol and ether, were suspended by threads, so as not to touch the sides of the glass.

I shall conclude this chapter with a general view of the inferences, which seem naturally to flow from these experiments with phosphorus.

1. Water is essential to the reduction of metals by phosphorus, for these experiments shew that the re-

duction is effected only in proportion to the quantity of water present.

- 2. Phosphorus does not reduce the metals by giving them phlogiston.
- 3. Phosphorus does not reduce the metals by uniting with, and separating their oxygen.

How then is the reduction effected? are we not to conclude, that it is effected by the decomposition of the water, in the following manner?

The phosphorus attracts the oxygen of the water, while the hydrogen of the latter unites in its nascent state with the oxygen of the metal, and effects the reduction.

Hence it follows, that the phosphorus is oxygenated by the oxygen of the water, while the metal is restored to its combustible state.

Thus what could never be affected by a single, is readily performed by a double affinity, which always takes place in preference to a single affinity, as the experiments of Messrs. Monnet and Kirwan, mentioned in the preceding chapter, shew.

It is well known, that phosphorus kept in water acquires an oxygenated crust, which could not happen without a decomposition of the water; this fact serves to confirm the explanation here offered.

And indeed the decomposition of water in these experiments must be granted, or it must be supposed, that water itself reduces the metals by uniting with their earths, and constituting their phlogiston; or by uniting with, and separating their oxygen; suppositions repugnant to our present knowledge of chymistry.

CHAPTER III.

REDUCTION OF METALS

BY

SULPHUR.

THOUGH Sulphur, as far as my reading extends, has seldom been considered as a reducer of the metals, yet as it holds a distinguished rank among combustible bodies, analogy led me to examine its powers in reducing and fixing the metals in the fibres of silk.

The vapour of sulphur appeared to be the most simple form in which it could be applied to this pur-

pose, and may be obtained by placing a phial containing flowers of sulphur in hot sand; as the sulphur melts, it assumes the form of vapour, which soon fills the phial, expels the atmospheric air, and bears a considerable heat before it inflames; a bit of silk prepared for the experiment may be held over the vapour as it issues from the phial, or immersed in it. The neck of the phial should be of a convenient size for this purpose.

But these experiments are more conveniently made by means of a sulphurous match, and a glass funnel, in which the silk imbued with the metallic solution may be suspended by a thread passed through it, and made fast with a cork, which also serves to confine the vapour.

The glass is then placed on a table, and by moving it a little beyond the verge of the same, a lighted match is readily introduced, which, as soon as the glass is filled with vapour, may be withdrawn; the vapour is confined by making the glass glide back on the table; and thus the phenomena of the experiment can be easily observed.

Though the vapour obtained in this manner be chiefly sulphurous acid gas; yet its effects are not less interesting on that account.

EXPERIMENT I.

GOLD.

A bit of silk was dipped in a solution of gold in ether and dried, it was then suspended in the glass funnel, and exposed for some time to the vapour obtained from a burning match; but no change could be perceived, except that the silk became a little brown.

Another bit of silk prepared in the same manner was immersed in the vapour of sulphur, formed in a phial placed in hot sand, with the same result.

EXPERIMENT II.

GOLD.

A piece of silk was immersed in a solution of nitro-muriate of gold in water, suspended in the glass funnel, and exposed while wet to vapour of sulphur, formed by a burning match; no sooner did the vapour touch the silk than the reduction commenced, and in a few seconds the whole piece was covered with a splendid coat of reduced gold, permanent and retentive of its lustre, but had a few specks of a dull violet hue.

The silk viewed by transmitted light appeared of a beautiful blue colour; and being removed from the vapour, and suspended in the air, began in about ten minutes to exhale a vapour which continued about two hours, and smelled acid and pungent.

Another bit of silk, dipped in the same solution of gold and dried, was wetted with alcohol and exposed to the same vapour: the silk acquired a brownish hue, and a small white metallic film appeared on its lower end, where the alcohol most abounded: the silk was then wetted with water and replaced in the vapour; instantly a lively purple with a bright pellicle of reduced gold appeared.

EXPERIMENT III.

SILVER.

A piece of silk was immersed in a solution of nitrate of silver in water, and suspended in the air of a dark closet to dry; the silk retained its white colour, though it remained in the air twenty four hours; it was then exposed fourteen hours to the vapour obtained from a burning match; but suffered no change, except that it acquired a brown tinge: it was now wetted with alcohol, and replaced in the vapour for some time; no signs of reduction appearing, it was wetted again with the alcohol and exposed to the vapour: but still no signs of reduction could be perceived: I then wetted the silk with distilled water, replaced it in the sulphureous vapour; and in about a minute reduced silver appeared.

EXPERIMENT IV.

SILVER.

I dipped a bit of silk in a solution of nitrate of silver in distilled water, and exposed it, while wet, to the vapour of sulphur, as in the preceding experiment; in a few seconds the silver appeared in its metallic form, attended with a variety of lively colours: the most remarkable of these were a pleasant blue, orange, purple and yellow, which soon disappeared: the reduced silver also disappeared in a great measure, some faint traces only remaining. The silk was removed from the vapour into the air, but exhaled no vapour, as happened in experiment the second.

A small bit of sulphur was suspended in a phial containing a solution of nitrate of silver in water; and

after some weeks the sulphur was coated with reduced silver of no great lustre.

EXPERIMENT V.

PLATINA.

A bit of silk was immersed in a solution of nitromuriate of the ore of platina in distilled water, and dried in the air; it was then suspended in the glass funnel, and exposed to the vapour of a burning match: but no signs of reduction could be observed; the silk retained the colour the solution gave it.

Another bit of silk was dipped in the same solution of platina, and exposed, while wet, to the sulphureous vapour; in a few seconds the reduction was very evident. The silk was immerged in a glass of clear water, and transferred bright films of reduced platina to the surface of that fluid; most of them were of the same colour as the spangles in the ore of platina; and some were distinguished by lively blue and purple colours.

Another bit of silk, dipped in the same solution of platina, was immersed, while wet, in the vapour of sulphur, formed in a phial placed in hot sand; the reduction soon commenced, and was much more per-

feet and permanent than in pieces exposed to the vapour obtained from ignited matches.

It is remarkable that sulphur reduced this metal much better than phosphorus or hydrogen gas did, but the reduced platina disappears after some time, and leaves nothing behind but a brown stain.

If the films be transferred from the silk to water, they may be preserved in their metallic form.

EXPERIMENT VI.

MERCURY.

A bit of silk was immersed in a solution of nitrate of mercury in distilled water, and dried; parts of the silk immediately acquired a slate colour; the silk was then exposed to the vapour of sulphur, obtained from a burning match, but it suffered no change, except that the colour became a little more intense.

Another bit of silk was dipped in the same solution of mercury, and exposed while wet to the same vapour; the reduction instantly commenced in a very evident manner, accompanied with several colours, as blue, purple and yellow. The silk was removed from the vapour and soon lost most of its lustre, which was succeeded by a slate colour, through which some particles of reduced mercury were observed to shine.

EXPERIMENT VII.

MERCURY.

A bit of silk was immersed in a solution of oxygenated muriate of mercury in water and dried in the air; it was then exposed to the sulphureous vapour obtained from a burning match; but the silk underwent no visible change. This solution of mercury does not change the white colour of silk, as that of nitrate does.

Another bit of silk was dipped in the same solution of oxygenated muriate of mercury, and exposed, while wet, to the vapour; in a few seconds reduced mercury appeared, unattended by any colour, except a slight tinge of citron yellow on part of the silk. After some time the whole of the reduced mercury vanished.

EXPERIMENT VIII.

COPPER.

A piece of silk was immersed in a solution of sulphate of copper and dried; It was then suspended in the glass funnel and exposed to the vapour obtained from a burning match; but the silk suffered no change, retaining the colour, which the solution gave it.

Another bit of silk was dipped in the same solution of copper and exposed, while wet, to the vapour of an ignited match; in a short time a white metallic film appeared, accompanied with a brown tinge: the silk becoming dry was wetted with water and exposed to a brisk vapour from another match; the film became more evident and parts of it verged on yellow, bordering on a copper colour. After some time this white metallic film disappears, and nothing remains but a light brown stain.

EXPERIMENT IX.

LEAD.

A bit of silk was immersed in a solution of acetite of lead in distilled water, and dried in the air; it was then exposed to the sulphureous vapour of a burning match; but underwent no visible change whatever.

Another bit of silk was dipped in the same solution of lead, and exposed, while wet, to the vapour; reduced lead soon appeared all over the silk; but after some time this reduced lead disappears, unless it be transferred to the surface of water.

EXPERIMENT X.

TIN.

A bit of silk was immersed in a solution of muriate of tin in distilled water, and dried in the air: it was then exposed to the vapour obtained from a burning match, which soon filled the glass; but produced no visible change on the silk.

Another bit of silk was dipped in the same solution of tin, and exposed, while wet, to the sulphureous vapour; and in a few seconds reduced tin appeared all over the silk; but the tin soon disappears, if not transferred to water.

EXPERIMENT XI.

ARSENIC.

A bit of silk was immersed in a solution of muriate of arsenic in distilled water, and dried in the air; it was then exposed to the vapour of sulphur, obtained from a burning match; but the silk suffered no apparent alteration.

Another bit of silk was dipped in the same solution of arsenic, and exposed, while wet, to the vapour: in a few seconds the arsenic was reduced, but not in a very evident manner; the silk was immerged in water, and several bright films of reduced arsenic floated on the surface of that fluid.

EXPERIMENT XII.

BISMUTH.

A bit of silk was immersed in a solution of nitrate of bismuth in distilled water, and dried in the air; it was then exposed to the vapour of sulphur obtained from a burning match; but no signs of reduction appeared.

Another bit of silk was dipped in the same solution of bismuth, and exposed, while wet, to the sulphureous vapour; the bismuth was soon reduced, accompanied with a brown stain; but the metallic lustre soon disappeared.

EXPERIMENT XIII.

ANTIMONY.

A piece of silk was immersed in a solution of tartrite of antimony in water, and dried; it was then exposed to the vapour of a burning match; but no change could be observed; nor did the silk immerged in water deposit any films on its surface.

Another piece of silk was dipped in the same solution of antimony, and exposed, while wet, to the vapour: the silk, in a few seconds, acquired a yellow colour, and a bright bluish film of reduced antimony appeared on the lower end of the silk, where the water was most abundant: the silk was then immerged in a glass of water, and transferred a large pellicle of reduced antimony to the surface of that fluid.

EXPERIMENT XIV.

IRON.

A bit of silk was immersed in a largely diluted solution of sulphate of iron in distilled water, and dried in the air, it was then exposed to the vapour of sulphur obtained from a burning match; after some time the colour of the silk became a little brown, but no reduced iron could be seen, nor did the silk immerged in a glass of clear water transfer any thing metallic to its surface.

Another bit of silk was dipped in the same solution of iron, and exposed while wet to the sulphureous vapour; in a short time the sil! was withdrawn, and a minute shining film of a livid white colour, was visible on its lower margin, where the water most abounded; the silk was then immerged in a glass of water, and transferred a large film of reduced iron to its surface.

This experiment succeeded also with the vapour of sulphur formed in a phial placed on hot sand. The films of reduced iron were seldom visible on the silk, but were soon rendered visible by transferring them to water.

EXPERIMENT XV.

ZINC.

A piece of silk was dipped in a diluted solution of sulphate of zinc and dried, it was then exposed to the vapour obtained from a burning match, no change whatever could be perceived; the silk was immerged in a glass of water, but deposited no film on its surface.

Another piece of silk was dipped in the same solution of zinc, and immersed while wet in the vapour of sulphur formed in a phial placed on hot sand; in about half a minute the silk was withdrawn from the vapour, and some parts of it had a shining livid appearance, which I took for reduced zinc; in order to determine if the reduction were real, the silk was immerged in a glass of clear water, and transferred to its surface a bright film of reduced zinc.

If the silk be kept too long in the vapour, some sulphur will be condensed on its surface, and give it a yellow colour; if it be then dipped in a glass of water, it will deposit both the sulphur and the metallic films on its surface, but the appearance of the sulphur is so different from that of the reduced metal, that they are easily distinguished.

Another bit of silk was immersed in a largely diluted solution of muriate of zinc, and exposed while wet, to the vapour obtained from a burning match; the silk being withdrawn exhibited a few minute shining films on its lower end, and on immersion in water left bright films of reduced zinc floating on the surface of that fluid.

Very often these films cannot be seen, until they are transferred to water, which I found a very useful test in doubtful cases; they are better seen in the gray light than in sunshine.

These experiments on the reduction of metals by sulphur were often repeated with nearly the same result; but some variety occurs depending on the quantity of water present, the strength of the metallic solution, and sulphureous vapour, and also on the time the silk is exposed to the vapour.

When the experiments are made in a phial placed in hot sand, part of the metallic solution frequently drops from the silk, and falling on the bottom, or sides of the phial is reduced, covering these parts with a metallic crust, on which the sulphur soon reacts, and changes the greater part into a sulphure. The phial commonly cracks.

The following conclusions are deducible from the experiments related in this chapter.

- 1. Water is essential to the reduction of metals by sulphur, for this effect is always in proportion to the quantity of water present.
- 2. Alcohol does not promote these reductions without the aid of water.
- 3. Sulphur does not reduce the metals by giving them phlogiston, nor by uniting with and separating their oxygen, for were either of these opinions just, the sulphur so minutely divided by heat, should reduce metallic solutions in alcohol as effectually as it does metallic solutions in water.

When we compare these reductions by sulphur, with those effected by phosphorus, and consider that, water is essential to both, we must conclude, that the reduction is effected in the same manner, viz. by the decomposition of water, which may be thus explained.

The sulphur attracts the oxygen of the water, while the hydrogen of the latter unites in its nascent state to the oxygen of the metal, and restores it to the metallic form.

Hence it follows, that the sulphur is oxygenated by the oxygen of the water, while the metal is restored to its combustible state. It also follows, that a quantity of water equal to that consumed is formed by the hydrogen of the water, and the oxygen of the metal.

This explanation is supported by a fine experiment of Dr. Priestley, who obtained inflammable air by passing the vapour of water through sulphur heated in an earthen tube;* and farther confirmed by the experience of some judicious makers of oil of vitriol, who always sprinkle the sulphur with a certain proportion of water, before they inflame it.

The decomposition of water in these reductions must be granted, or it must be supposed that a single takes place in preference to a double affinity; which cannot be admitted.

These experiments point out several errors in M. Lavoisier's Table of the Affinities of the Oxygenous Principle; for he has placed sulphur at a much greater distance from that principle than any of the metals treated of in this chapter except gold, and even in this instance his table is erroneous, unless it be proved that sulphur reduces metals by directly uniting with, and separating their oxygen; a supposition which implies, that the reduction is effected by a single affinity, and therefore inadmissible.

^{*} Priestley, Vol. VI. p. 150.

I shall close this chapter with a short extract from the Chymical Essays of Bishop Watson, as it seems to have some relation to the experiments related here.

His lordship says, that his experiments on "the "Derbyshire lead ore instruct us to believe, that the "lead in this kind of ore is in its metallic state; as "the ore was changed into lead without the addition of any substance containing the inflammable principle."*

But the reduction of lead by sulphur and water, related in this chapter, points out an evident source of the inflammable principle; for the ore itself must contain some water, a constituent part of which is hydrogen, or the base of inflammable air; beside his lordship thinks no appearance of lead would have taken place, had there been no communication with the external air; but as air always holds water in solution, an ample source of the inflammable principle is evident.

^{*} Chem. Essays, Vol. III. p. 219.

CHAPTER IV.

REDUCTION OF METALS

BY

ALKALINE SULPHURE.

THE Sulphure I made use of, was prepared by fusing equal parts of carbonate of potash and flowers of sulphur, till the effervescence ceased.

M. Gengembre has made a very important observation on alkaline sulphure, prepared in this way, which is, that this substance has no smell, and that it exhales no gas while it continues dry, but that when it is dissolved in water, or attracts humidity from the air, it diffuses an offensive smell.

From this circumstance M. Gengembre inferred, that the disengagement of this gas depended on the decomposition of water; for he discovered both by analysis and synthesis, that this air consists of hydrogen, one of the principles of water, combined with sulphur and caloric.

There can then be no doubt, but alkaline sulphure has the power of decomposing water; and may therefore be happily employed to illustrate the mode of action of sulphur, and other combustible substances, treated of in this essay.

When diluted acids are poured on solid alkaline sulphure, the decomposition of the water is promoted and accelerated, sulphurated hydrogen gas being formed in great abundance.

I made two solutions of this alkaline sulphure, one in water, and the other in alcohol.

EXPERIMENT I.

GOLD.

A bit of silk was immersed in the solution of sulphure in alcohol, and then a solution of gold in ether was applied; a brown matter was formed in the silk, but no reduced gold could be perceived. Another bit of silk was dipped in the same solution of sulphure in alcohol, and a solution of nitro-muriate of gold in water was applied; a white metallic film was slowly formed, but no other signs of reduction were visible.

This experiment was repeated on another bit of silk with this difference, that the solutions of the gold and sulphure were both in water, and the white metallic film was instantly formed, accompanied by a considerable precipitate of a brown matter.

It is obvious then, that water accelerates, and is necessary to the appearance of this film: for when both solutions were in water, it appeared much sooner.

EXPERIMENT II.

GOLD.

A piece of silk was immersed in an aqueous solution of gold, in which the acid predominated, then a few drops of the aqueous solution of sulphure were applied; a white pellicle which looked like silver was immediately formed, and the silk got a deep brown colour. To another piece of silk dipped in the same solution of gold, the solution of sulphure in alcohol was applied, a white metallic film appeared, but not so evident or so soon as in the preceding experiment, wherein the solution of sulphure in water was used; beside the film produced by the aqueous solution of sulphure was more permanent, and the stain, which the silk acquired, was more intense, than those produced by the solution of sulphure in alcohol.

EXPERIMENT III.

SILVER.

I immersed a piece of silk in a solution of the sulphure in alcohol, and after most of the spirit evaporated, a solution of nitrate of silver in alcohol was applied; nothing appeared on the silk but a brown stain. The nitrate of silver used in this experiment was fused, to expel as much water as possible.

Another piece of silk was dipped in the same solution of sulphure; when most of the alcohol evaporated, a solution of crystallized nitrate of silver in water was applied to the silk, and instantly the metallic lustre of the silver appeared, attended with a brown stain.

EXPERIMENT IV.

SILVER.

A piece of silk was dipped in the solution of alkaline sulphure in water, and an aqueous solution of crystallized nitrate of silver was applied; the silver was immediately reduced in greater quantity than in the preceding experiment, in which the alkaline sulphure employed was dissolved in alcohol. The stain produced in the silk was also more intense.

EXPERIMENT V.

SILVER.

A bit of silk was immersed in a solution of the sulphure in water, and then a solution of nitrate of silver in alcohol was applied, but nothing appeared on the silk, except a brown stain. The nitrate of silver used in this experiment, was fused, which deprived it of a great part of its acid. That this was the circumstance which prevented the reduction of the silver, appears from the following experiment.

A bit of silk was immersed in the same solution of silver in alcohol, then some diluted nitric acid

was applied, lastly the aqueous solution of sulphure was dropped on the silk, and instantly the silver was restored to its metallic splendour. It is evident then, that acids contribute to the reduction of silver by alkaline sulphure, which they effect by promoting the decomposition of water.

In some time the reduced silver disappears for the most part, and indeed the white metallic films which were produced in the experiments on gold, totally disappeared.

EXPERIMENT VI.

PLATINA.

A bit of silk was immersed in a solution of nitromuriate of the ore of platina in distilled water and dried, then the solution of sulphure in alcohol was dropped on the silk; nothing appeared but a brown stain.

Another bit of silk was dipped in the aqueous solution of sulphure, and a little of the solution of platina applied; in a short time, a film of reduced platina appeared. To another bit of silk which was dipped in the solution of platina, a few drops of distilled vinegar were applied, and then the solution of sulphure in water was added; a brown stain was immediately produced, and more platina reduced than in the preceding experiment.

EXPERIMENT VII.

MERCURY.

To a bit of silk, which was immersed in a solution of oxygenated muriate of mercury in water, and dried in the air, some of the solution of sulphure in alcohol was applied, but no change, except a light yellowish brown, was produced.

After the silk was some time exposed to the air, some very faint shades of black were visible on parts of it.

To a piece of silk which was immersed in the solution of sulphure in water, some of the same solution of mercury was applied, immediately the metal was restored to its metallic lustre in a very striking manner, and it was remarkable, that the precipitate on the silk was very small. This experiment was repeated with this difference, that the silk was first wetted with distilled vinegar, and more of the mercury was reduced than in the preceding experiment, attended with an olive precipitate, which gradually turned blackish; the quantity of precipitated matter in this was much greater than in the former experiment, but the reduced metal was not so bright.

EXPERIMENT VIII.

MERCURY.

A bit of silk which was dipped in a solution of nitrate of mercury and dried in the air, had no change produced on it by a solution of sulphure in alcohol, except a stain compounded of the slate colour, which the nitrate imparts, and the yellow of the sulphure.

To another bit of silk which was immersed in the aqueous solution of sulphure, some of the same solution of mercury was applied; the metal was immediately reduced, and a very black stain attended the reduction.

EXPERIMENT IX.

COPPER.

A piece of silk was dipped in a solution of sulphate of copper and dried in the air, a solution of the sulphure in alcohol was applied to it, but no change except a brown stain was produced.

To another bit of silk immersed in the aqueous solution of sulphure, some of the same solution of copper was applied, a white metallic film was slowlyformed, attended with a brown colour.

On another bit of silk, which was dipped in the same solution of copper, and placed on a saucer, some distilled vinegar was dropped, and then a few drops of the aqueous solution of sulphure were added: immediately a white metallic film appeared in greater quantity than in the preceding experiment.

EXPERIMENT X.

LEAD.

A piece of silk was immersed in a solution of acetite of lead in distilled water, and dried in the air, then the solution of sulphure in alcohol was applied, but nothing appeared on the silk except a brown stain.

A bit of the same silk was dipped in the same solution of lead, then the solution of sulphure in water was applied; the lead was soon reduced to its metallic state; a brown stain and precipitate of the same eolour attending the reduction.

The same experiment was repeated with this difference, that the silk was first wetted with distilled vinegar, and instantly the lead was reduced of greater lustre, and in greater quantity, than in the preceding experiment.

This experiment was tried on a bit of white calico dipped in distilled vinegar, and placed on the palm of my hand, and instantly the metallic lustre of the lead, which was reduced in great quantity, appeared in a very remarkable manner, attended with a brown stain.

EXPERIMENT XI.

TIN.

To a bit of silk dipped in a solution of muriate of tin in distilled water and dried in the air, the solution of sulphure in alcohol was applied, nothing appeared but a brown stain.

Another bit of silk was immersed in the solution of sulphure in water, then the same solution of muriate of tin was applied, in a short time some reduced tin appeared on the silk. Vinegar promoted the reduction of this metal also in a remarkable manner.

EXPERIMENT XII.

ARSENIC.

A bit of silk was immersed in a solution of muriate of arsenic in distilled water and dried in the air, the solution of sulphure in alcohol was then applied, the silk first looked yellow, in a short time the yellow colour almost entirely disappeared, leaving behind a whitish precipitate, but no other change was produced.

Another bit of silk was dipped in the solution of sulphure in water, then some of the same solution of arsenic was applied, a yellow precipitate was formed, and shortly after this precipitate was surrounded by a violet margin, but no other change could be observed.

I immersed another bit of the same silk in the same solution of arsenic, some distilled vinegar was then dropped on it, and lastly the aqueous solution of sulphure was applied; after some time a few minute films of reduced arsenic bright as silver were visible.

Some attention is necessary to discover the reduced arsenic, as the particles reduced are few, and minute, and sometimes none can be seen.

EXPERIMENT XIII.

BISMUTH.

To a bit of silk which was dipped in a solution of hitrate of bismuth in distilled water and dried in the air, the solution of sulphure in alcohol was applied, the silk appeared first yellow, then brown, but no farther change could be observed.

Another bit of silk was immersed in the solution of sulphure in water, some of the same solution of bismuth was then applied to it, the metal was immediately reduced, and a brown precipitate was formed. Vinegar seems neither to promote nor retard the reduction.

Two bits of white calico were dipped in the same solution of bismuth, to one of these placed on a saucer some distilled vinegar was added, then a single drop of the solution of sulphure in water was applied, and the whole of the calico except that part on which the drop fell was covered with reduced bismuth, which looked exceedingly bright; the same appearance was observed on the other bit, to which no vinegar was added.

EXPERIMENT XIV.

ANTIMONY.

To a bit of silk which was dipped in a solution of tartrite of antimony in distilled water and dried in the air, the solution of sulphure in alcohol was applied; the silk got a yellow colour, whose margins some time after, acquired an orange hue, but no other change was perceived.

Another bit of the same silk was immersed in the aqueous solution of sulphure, the same solution of antimony was then applied, part of the metal was reduced, though in small quantity, attended with an orange precipitate.

The acids of vinegar and tartar seemed to impede the reduction, the muriatic acid also seemed to have the same effect, though not in so great a degree as

EXPERIMENT XV.

COBALT.

To a bit of silk which was dipped in a solution of nitrate of cobalt and dried in the air, the solution of sulphure in alcohol was applied; the silk soon became brown, but no farther change could be perceived.

To another bit of silk which was immersed in the solution of sulphure in water, a few drops of the same solution of cobalt were applied, the silk immediately acquired a dark colour, and in a little time some of the metal was reduced, attended with a dull blue precipitate, which changed to a blackish brown.

Muriate of cobalt was reduced in the same manner; vinegar promoted the reduction of both these preparations of cobalt.

EXPERIMENT XVI.

IRON.

To a piece of silk which was immersed in a solution of sulphate of iron largely diluted, and dried in the air, the solution of sulphure in alcohol was applied, the silk soon became black, but no other change could be perceived.

Another bit of silk was dipped in the solution of sulphure in water, some of the same solution of iron was then applied, the silk instantly assumed a black colour, but no reduced iron appearing, it was immerged in a glass of water, and transferred a bright film of reduced iron to the surface of that fluid.

Sometimes part of the film has not the metallic lustre, which is very evident in other parts of it, so that the parts completely reduced can be easily distinguished from the dull and imperfectly reduced black oxid of iron, intermixed with these bright films.

The same experiments were repeated on bits of calico with the same result, the calico from its spongy texture is better suited to produce strong films than silk is.

Vinegar did not promote the reduction of iron in these experiments.

EXPERIMENT XVIL

ZINC.

To a bit of silk which was immersed in a largely diluted solution of muriate of zine, and dried in the air, some of the solution of sulphure in alcohol was applied, nothing appeared on the silk, but the yellow colour which the solution of sulphure imparts.

Another bit of silk was dipped in the solution of sulphure in water, and some of the same solution of zinc was applied, the yellow colour which the solution of sulphure gave the silk soon became white; but no reduced zinc could be seen. The silk was then immerged in a glass of clear water and transferred a bright film of reduced zine to its surface.

In another experiment made with white calico, the pellicle transferred to the surface of water was brighter, and more zinc was reduced than in the preceding experiment.

Sulphate of zinc also was reduced both on silk and ealico, with this difference, that black and olive precipitates attended the reduction,

EXPERIMENT XVIII.

MANGANESE.

I dipped a bit of silk in a diluted solution of nitrate of manganese, and dried it in the air, the solution of sulphure in alcohol was then applied, the silk acquired a yellow colour which soon disappeared, but no other change could be observed.

To another bit of silk, which was immersed in the solution of sulphure in water, a drop of the same solution of manganese was applied, instantly a pearl-white precipitate was formed, the margin of which soon acquired a bright film of reduced manganese. Under this film a violet tinge was evident.

The nitrate of manganese used in this experiment was very acid.

A solution of alkaline sulphure in water after a certain length of time loses the power of reducing the metals, in which respect it resembles an old solution of sulphate of iron. Having procured a more neutral solution of nitrate of manganese, I immersed a bit of silk in the solution of sulphure in alcohol, when most of the spirit evaporated; a single drop of this solution of manganese was applied, instantly a bright film of reduced manganese appeared, attended with a violet tinge, and a brown precipitate. After some time the violet tinge disappears.

On another bit of silk immersed in the same solution of sulphure in alcohol, a drop of a solution of sulphate of manganese in distilled water was applied, instantly films of reduced manganese bright as silver appeared, accompanied with a faint violet tinge, and a pearl-white precipitate. These films soon disappear.

A solution of alkaline sulphure in alcohol does not by age lose its power of reducing the metals, as that in water does; I kept the former solution more than two years, and found it at the end of that time as capable of reducing the metals, as when it was made.

It is manifest from the experiments related in this chapter,—

1. That water is essential to the reduction of metals by alkaline sulphure.

- 2. That alcohol does not promote these reductions without the aid of water.
- 3. That alkaline sulphure does not reduce the metals by giving them phlogiston, nor by uniting with, and separating their oxygen, for were either of these opinions true, a solution of alkaline sulphure in alcohol should reduce them as effectually as a solution of the same in water does.
- 4. That acids contribute to these reductions by promoting the decomposition of water.

Now since M. Gengembre has demonstrated, thatwater is decomposed by alkaline sulphure, who can doubt that it is decomposed in these reductions?

The manner in which metals are reduced by this substance, seems to be the following.

An hydrure of sulphur, that is, a combination of hydrogen and sulphur is formed: this hydrure of sulphur attracts the oxygen of the water, while the hydrogen of the latter unites in its nascent state, with the oxygen of the metal, and reduces it.

The experiments in this chapter leave us no room to doubt of the decomposition of water in metallic reductions by alkaline sulphure, and serve to illustrate and confirm the manner in which sulphur, phosphorus, and other combustible bodies, effect the reduction of metals.

CHAPTER V.

REDUCTION OF METALS

BY

SULPHURATED HYDROGEN GAS.

HAVING treated of the effects of hydrogen gas and sulphur separately, I shall next treat of their effects, when combined in the form of sulphurated hydrogen gas.

I obtained this elastic fluid by pouring water, acidulated with sulphuric acid on alkaline sulphure, prepared in the manner mentioned in the preceding chapter; but had it been prepared with a caustic alkali, it is probable the gas would be more powerful. The sulphure of the shops is generally unfit for these experiments.

It is necessary in experiments with sulphurated hydrogen gas, hydrogen gas, &c. to have some mode of conveying them into a chimney, as they are offensive and unwholesome.

EXPERIMENT I.

GOLD.

A piece of silk, which was immersed in a solution of nitro-muriate of gold in water, and dried in the air, was exposed to sulphurated hydrogen gas, the silk got a slight tinge of brown, but no other change occurred; it was then wetted with alcohol, and after some time, the brown became more intense, and white films appeared on some parts of the silk, owing to moisture collected from the gas, which is always replete with water.

Another bit of silk was dipped in the same solution of gold and exposed, while wet, to the gas; the yellow colour, which the solution of gold gave the silk, was immediately changed to a brown, and a white metallic pellicle appeared, and covered the whole surface of the silk opposed to the gas; but no purple or other colours, that usually attend the reduction of this metal by other agents, could be perceived. This pellicle did not entirely disappear as the silk became dry; though it lost most of its lustre and looked more like silver, or some other white metal imperfectly reduced, than gold.

This elastic fluid, and alkaline sulphure, have an effect on the reduction of gold, very different from that of the vapour of sulphur obtained from a burning match, which further appears from the following experiment, made with sulphurated hydrogen gas, that happened to be mixed with some sulphurous acid gas.

EXPERIMENT II.

GOLD.

A piece of silk, which was dipped in a solution of gold in ether and dried in the air, was exposed to a current of sulphurated hydrogen gas, containing some sulphurous acid gas; but no signs of reduction could be perceived: the silk was then wetted with alcohol, still no visible change was produced, except a brown stain where the alcohol most abounded;

this stain, after some minutes exposure to atmospheric air, was covered with a white metallic film, which soon disappeared; after some minutes the silk was wetted with water and exposed again to the gas, a white metallic film immediately appeared, and the brown stain began to change slowly to a purple; the silk was soon covered with various colours, as blue, red, and orange, and some spots of reduced gold of its own proper colour appeared; after some time the white film and all the colours, except the purple, disappeared, some specks of the perfectly reduced gold were permanent.

Another bit of silk, which was immersed in an aqueous solution of gold and exposed to the same mixed gas, exhibited nearly the same appearances.

EXPERIMENT III.

GOLD.

Having found that sulphurated hydrogen gas had a powerful effect in reducing other metals, I was desirous of trying its effects on a larger scale, thinking it might be attended with more success; I therefore immersed a quarter of a yard of silk in an aqueous solution of gold and exposed it while wet, to this gas in close vessels; the silk was soon covered with

a white metallic pellicle, which disappeared in a short time: the experiment was continued about twelve hours, and on withdrawing the silk from the gas, I could not perceive the smallest vestige of reduced metal, or purple, or other colours, that constantly attend the reduction of gold.

The silk had a dull brown hue verging on a slate colour.

EXPERIMENT IV.

SILVER.

A piece of silk, which was immersed in a solution of nitrate of silver in water, and dried in the air, was exposed to a current of sulphurated hydrogen gas, but no change could be perceived for some time; at length, when the silk collected moisture from the gas, some particles of reduced silver were visible, accompanied by a brown stain.

Another piece of silk was dipped in the same solution of nitrate of silver, and exposed while wet, to the gas; the silver was instantly reduced all over the side of the silk opposed to the current, a great variety of beautiful colours, as red, orange, yellow, green, and blue, attended the reduction; most of these disappeared, but part of the silver remained permanently reduced.

I found that, if the silk be immersed in a solution of silver in alcohol and dried, and then moistened with water, and exposed while wet to the gas, none of these colours appear.

This experiment was repeated on a quarter of a yard of silk in close vessels, and immediately both sides of the silk were covered with reduced silver, attended with the same beautiful colours; the silk was left exposed to the gas seven or eight hours, and being then examined, no reduced silver could be seen; nothing remained but a strange medley of colours, chiefly blue, green, purple, and orange, unequally mixed, some prevailing more than others in certain parts of the silk; however, the die is by no means disagreeable.

EXPERIMENT V.

SILVER.

A piece of silk, which was immersed in a solution of fused nitrate of silver in alcohol, and dried in the air, was exposed to a current of the gas; but no change could be perceived for some time: it was then wetted with alcohol, still no alteration could be observed, till the silk attracted moisture from the gas, when small particles of reduced silver began to appear, attended with a brown stain.

If the silk immersed in the solution of silver in alcohol, and exposed while wet to the gas, be kept constantly wet with alcohol, these appearances take place sooner.

A piece of silk, which was dipped in a solution of muriate of silver in ammonia, and exposed, while wet, to the gas, had in a short time its surface covered with reduced silver; but another piece of silk dipped in the same solution of silver and dried, underwent no such change.

DXPERIMENT VI.

PLATINA.

A bit of silk, which was dipped in a solution of nitro-muriate of the ore of platina in distilled water and dried in the air, was exposed to a current of sulphurated hydrogen gas; but underwent no perceptible change.

Another bit of si k was immersed in the same solution of platina and exposed while wet, to the gas; the whole surface of the silk, opposed to the current, was instantly covered with reduced platina, which soon lost its lustre; nothing remaining but a brown colour, with some faint vestiges of the reduced metal.

This experiment was repeated on a bit of linea with the same result.

EXPERIMENT VII

MERCURY.

A hit of silk, which was dipped in a solution of oxygenated muriate of mercury in distilled water, and dried in the zir, was exposed to a current of the gas; the only visible change produced was a slight shade of yellow on part of the silk.

Another bit of silk was immersed in the same solution of mercury and exposed, while wet, to the gas; the mercury was immediately reduced, but soon lost its lustre; the gas reacting changed most of it to a substance of a dull white colour. The same experiments were made with nitrate of mercury, with the same result.

EXPERIMENT VIII.

COPPER.

A bit of silk was immersed in a solution of sulphate of copper in distilled water, and suspended in the air to dry; it was then exposed to a current of the gas, the silk assumed a brown colour; but no other change appeared.

Another bit of silk was dipped in the same solution of copper, and exposed while wet to the gas, a white metallic film attended with a brown stain, immediately appeared, some parts had a yellow film approaching to the colour of copper; these films all disappeared leaving behind a brown stain; the parts which were covered with the yellow film resembling copper, exhibited after some time, a dull bluish disagreeable matter.

EXPERIMENT IX.

LEAD.

Having dipped a piece of silk in a solution of acetite of lead in distilled water and dried it in the air, I exposed it to a stream of the gas; the silk became a little brown, but no other change could be observed.

Another bit of silk was immersed in the same solution of lead, and exposed while wet to the gas; no sooner did it touch the silk, than a brown tinge diffused itself like a passing shadow over the whole surface of the silk, accompanied with a bright coat of reduced lead, which resembled silver.

The brown tinge, which the silk acquires, resembles what happens when white paper is slightly singed by holding it near a burning body.

This experiment was repeated on a quarter of a yard of silk in close vessels, and the silk was immediately covered with a coat of reduced lead, which had the brilliance of silver, and was attended with a brown tinge; the experiment was continued several hours, after which the silk was examined, and found to have lost all the argentine lustre, which was succeeded by a sparkling gray die; a sulphure of lead, or galena, being formed in the fibres of the silk. The same experiment was repeated on two other pieces of silk with the same result.

This elastic fluid is so powerful a reducer of the metals, that if chambers painted with white lead,

have any considerable degree of moisture, and are exposed to its influence, the lead on the surface of the walls is reduced, and that chiefly where the humidity is most abundant; this effect I observed, was produced, even at the distance of three chambers from the place where the gas was formed; and the lead was reduced most evidently behind the window shutters where the moisture of the wall was most considerable.

It is a common experiment with chymists, in order to shew the effects of this gas, to draw characters with a solution of sugar of lead on paper, which they place over a glass of water containing some alkaline sulphure; in some time the characters drawn on the paper acquire a brown, or black colour, and become visible; which amuses the spectators.

But it is surprising, that the metal has never been reduced in this experiment even by chance; and not less so, why lead should be singled out for this trial of skill, in preference to other metals, which are equally affected by this gas.

EXPERIMENT X.

TIN.

A piece of silk was dipped in a solution of muriate of tin in distilled water and dried in the air; the silk on exposure to a current of the gas, scarce underwent any change, except a few brown specks dispersed over its surface.

Another bit of silk was immersed in the same solution of tin, and exposed while wet to the gas, which no sooner touched the silk, than the surface opposed to the current was covered with reduced tin of greatbrightness; in some time various colours, as blue, orange, and a faint purple, appeared, and became more evident, as the reduction proceeded.

The gas does not re-act on this metal so much as on mercury, and some other metals, part of the reduced tin remained permanent, but most of it disappeared, and left behind a disagreeable brown stain.

EXPERIMENT XI.

ARSENIC.

A bit of silk was immersed in a solution of muriate of arsenic in distilled water and dried in the air, it was then exposed to a stream of sulphurated hydrogen gas, but no change could be observed, except a faint tinge of citron yellow, which appeared on some parts of the silk.

Another bit of silk was dipped in the same solution of arsenic and exposed while wet to the gas, the arsenic was instantly reduced all over the surface, opposed to the gas, attended with a citron yellow colour.

The gas soon re-acted on the reduced arsenic; and nothing remained but the yellow stain.

EXPERIMENT XII.

BISMUTH.

I dissolved some bismuth in nitric acid, and evaporated the solution to dryness, the salt was then dissolved in distilled water, and the solution deposited a copious white precipitate, but retained a quantity of the metal sufficient for these experiments.

In this solution of bismuth a piece of silk was immersed, and dried in the air, it was then exposed to a stream of the gas, and the only visible effect produced was a very faint tinge of brown.

Another bit of silk was dipped in the same solution of bismuth, and exposed wet to the gas, the silk was instantly covered with a bright pellicle of reduced bismuth, which soon lost most of its metallic lustre, being changed by the reaction of the gas to a sulphure.

Mr. Kirwan in his experiments on hepatic air, found that nitrous solution of bismuth, by mixture with a solution of hepatic air in water, changes to a reddish brown, and even assumes a metallic appearance.

He also found that nitrates of silver, lead, and acetite of lead, were precipitated black.

EXPERIMENT XIII.

ANTIMONY.

A piece of silk, which was immersed in a solution of tartrite of antimony in distilled water and dried in the air, was exposed to a stream of the gas, but suffered no visible change, except that a few specks of yellow and orange appeared.

A bit of silk was dipped in the same solution of antimony, and exposed while wet, to the gas, the antimony was immediately reduced to its metallic form, attended with a deep orange colour; in some time, most of the metallic lustre disappeared, a few specks only remaining permanent.

EXPERIMENT XIV.

IRON.

A piece of silk was immersed in a diluted solution of sulphate of iron in distilled water and dried; it was then exposed to a current of the gas, but underwent no visible change.

Another bit of silk was dipped in the same solution of iron and exposed while wet, to the gas; the silk soon began to acquire a dark colour, which gradually increased, and at length became black, attended with an obscure metallic film. The silk was immersed in water, and deposited a bright metallic film on the surface of that fluid.

EXPERIMENT XV.

ZINC.

A bit of silk which was immersed in a diluted solution of sulphate of zinc in distilled water and dried in the air, was exposed to a current of the gas, but underwent no visible change.

Another bit of silk was dipped in the same solution of zinc and exposed while wet, to the gas, but no change in the colour of the silk, or sign of reduction could be perceived; the silk was then immerged in a glass of clear water, and transferred to its surface a bright metallic film of the colour of zinc.

When a languid stream of gas was employed in these experiments the films transferred to water were scarce visible.

EXPERIMENT XVI.

ZINC.

A piece of silk, which was immersed in a largely diluted solution of muriate of zinc and dried in the air, was exposed to a brisk current of sulphurated hydrogen gas, but underwent no visible alteration.

Another bit of silk was dipped in the same solution of zinc, and exposed while wet, to the same brisk current of gas; instantly the surface of the silk opposed to the gas, was covered with a bright coat of reduced zinc, attended with faint orange and purple colours.

Though the reduced zine was quite evident, yet I had the curiosity to examine its appearance on the surface of water; I therefore immersed the silk in a glass of that fluid, and a bright metallic pellicle, which retained the texture of the silk, as wax retains the impression of a seal, was transferred to its surface.

Another bit of silk, dipped in the same solution of zinc, and exposed for a longer time to the gas,

lost its metallic lustre, the zinc being changed to a sulphure by the re-action of the gas.

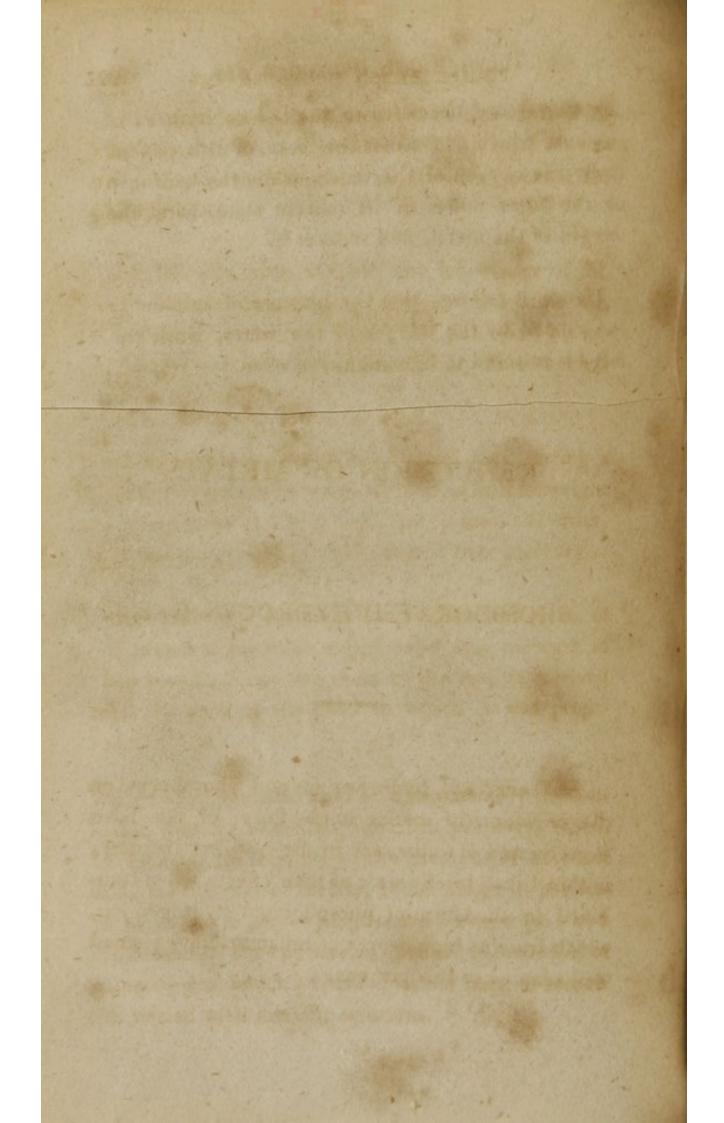
These experiments, on sulphate and muriate of zinc, show that the acid in which the metal is dissolved, influences the reduction in a remarkable manner.

It is evident from the experiments related in this chapter,

- 1. That water is essential to the reduction of metals by sulphurated hydrogen gas.
- 2. That alcohol does not promote these reductions without the aid of water.
- 3. That sulphurated hydrogen gas does not reduce the metals by giving them phlogiston, nor by uniting with and separating their oxygen; for, were either of these opinions well founded, metallic solutions in alcohol should be as effectually reduced by this gas, as metallic solutions in water are.

When we consider that alkaline sulphure reduces the metals by decomposing water, we have every reason to conclude, that sulphurated hydrogen gas reduces them in the same manner, since the same circumstances are necessary to both; the hydrure of sulphur, which constitutes the base of this gas attracts the oxygen of the water, while the hydrogen of the latter unites in its nascent state, with the oxygen of the metal, and reduces it.

Hence it follows, that the hydrure of sulphur is oxygenated by the oxygen of the water, while the metal is restored to its combustible state.



CHAPTER VI.

REDUCTION OF METALS

BY

PHOSPHORATED HYDROGEN GAS.

THE effects of hydrogen gas and phosphorus on the reduction of metals in the fibres of silk have been treated of separately in the two first chapters; in this, I shall briefly treat of their effects, when combined in the form of phosphorated hydrogen gas, which from its high degree of inflammability seemed well adapted to this purpose. The spontaneous inflammation of this kind of air was known to M. Gengembre in 1783, and his experiments were published in Rosier's journal for October 1785.

Mr. Kirwan also, without any knowledge of M. Gengembre's experiments, discovered the same air, which he calls phosphoric air; and published his experiments in the 76th volume of the Philosophical Transactions for 1786.

This elastic fluid may be obtained by digesting a solution of potash in water with about half its weight of phosphorus in a heat sufficient to melt the latter, and may be received in glass vessels over mercury.

But finding it inconvenient to introduce pieces of silk prepared for these experiments over mercury in close vessels, I exposed them to the gas, as it issued from the neck of the phial in which it was prepared.

Part of this elastic fluid is spontaneously inflammable, but the other has not that property, which M. Gengembre imputes to the presence of carbonic acid; for the sake of brevity, I shall designate the latter by the term gas, or phosphorated hydrogen gas; and the former by the epithets spontaneously inflammable, or detonating gas, which I found does not burn or scorch silk wetted with metallic solutions.

EXPERIMENT I.

GOLD.

A piece of silk, which was immersed in a solution of nitro-muriate of gold in distilled water, and suspended in the air twelve hours to dry, was divided into three parts.

One of these was exposed to a stream of phosphorated hydrogen gas: the silk became brown, and its margins, which happened to touch the sides of the phial, acquired a violet tinge: but no reduction took place.

Another of these parts was wetted with alcohol, and exposed to the gas; but no signs of reduction could be perceived.

The remaining part was wetted with water, and was no sooner exposed to the gas, than the reduction commenced over the whole silk, which was soon covered with a bright coat of reduced gold.

EXPERIMENT II.

SILVER.

A piece of silk was dipped in a solution of fused nitrate of silver in alcohol, and dried in the air: it was then divided into three parts.

One of these, in order to dissipate moisture more effectually, was dried still better by a gentle heat, and exposed to the gas; the silk acquired a brownish dark colour: but no other alteration could be perceived.

Another of these parts, which was also better dried by a gentle heat, was wetted with alcohol, and exposed to the gas: the silk acquired a dark brown colour; but no other change could be observed.

The remaining part was wetted with water, and exposed to the gas: the reduction commenced immediately, and in a short time the silk was covered with reduced silver.

EXPERIMENT III.

PLATINA.

A piece of silk was immersed in a solution of nitro-muriate of the ore of platina in distilled water, and dried in the air; it was then divided into three parts.

One of these parts was exposed to the gas; but suffered no visible change.

Another of them was wetted with alcohol, and exposed to the gas; but underwent no perceptible change.

The remaining part was wetted with water, and exposed to the gas: in about three or four minutes, a bright metallic film, of great lustre, appeared on the side of the silk, opposed to the gas.

Another bit of silk, which was dipped in the same solution of platina, and exposed, while wet, to the spontaneously inflammable gas, was immediately covered with reduced platina, which being transferred

to the surface of water, looked bright as silver, and retained the impression of the silk.

EXPERIMENT IV.

MERCURY.

A bit of silk, which was immersed in a solution of nitrate of mercury in distilled water, and dried in the air, was exposed to the gas; but underwent no visible change.

Another bit of silk was dipped in the same solution of mercury, and dried: it was then wetted with alcohol, and exposed to the gas; but no sign of reduction appeared.

Another bit of silk was immersed in the same solution of mercury, and exposed to the gas; the metal was instantly reduced all over the silk; a great variety of beautiful colours attending.

A piece of silk was dipped in a solution of oxygenated muriate of mercury in distilled water, and dried in the air: it was then divided into two parts.

One of these was exposed to the gas: no change appearing, it was wetted with alcohol, and exposed

again to the gas; but still no alteration could be per-

The remaining part was wetted with water, and was no sooner exposed to the gas, than the mercury was reduced over the whole silk. No colours attended the reduction.

Mr. Kirwan introduced some precipitate per se to a small portion of phosphoric air: the precipitate soon grew black, and a white smoke appeared; in two days the precipitate remained solid, yet acquired a pale white colour like that of steel: the air lost its spontaneous inflammability.*

EXPERIMENT V.

COPPER.

A piece of silk, which was immersed in a solution of sulphate of copper in distilled water and dried in the air, was divided into two parts.

One of these was exposed to the gas, but no visible change occurred.

^{*} M. Kirwan. Phil. Trans. for 1786.

The remaining part was wetted with water and exposed to the gas, in a few minutes a brownish matter appeared in the silk, but nothing metallic could be seen; the silk was then dipped in a glass of clear water, and transferred a small white metallic pellicle to its surface.

In another experiment made with the spontaneously inflammable gas, a white metallic pellicle was immediately formed, attended with a brown stain; this pellicle resembled silver or a white metal; but the gas soon re-acted on it, and formed a disagreeable brown matter in the fibres of the silk.

EXPERIMENT VI.

LEAD.

A bit of silk, which was dipped in a solution of acetite of lead in distilled water and dried in the air, was exposed to the gas, but suffered no visible change.

Another bit of silk was immersed in the same solution of lead, and exposed while wet to the gas, but nothing metallic could be seen; the silk, however, on immersion in water, transferred a few minute bright films to the surface of that fluid. In another experiment made with the detonating gas, the reduced films were more evident.

EXPERIMENT VII.

TIN.

A bit of silk, which was dipped in a solution of muriate of tin in distilled water and dried in the air, was exposed to the action of the gas without suffering any visible alteration.

Another piece of silk was immersed in the same solution of tin and exposed while wet to the gas, but no signs of reduction could be perceived; the silk was then immersed in water and transferred a delicate metallic film to its surface.

EXPERIMENT VIII.

ARSENIC.

A bit of silk, which was immersed in a solution of muriate of arsenic in distilled water and dried in the air, was exposed to the gas, but no change could be perceived.

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Another bit of silk, immersed in the same solution of arsenic and exposed while wet to the gas, acquired in a few minutes a brown stain, but nothing metallic could be seen on the silk; which, however, on being dipped in water, transferred a very minute film of reduced arsenic to its surface.

In another experiment made with the detonating gas, the films of reduced arsenic were much more evident, of greater brilliance and attended with a brown stain produced in the fibres of the silk.

EXPERIMENT IX.

BISMUTH.

A piece of silk, which was dipped in a solut on of nitrate of bismuth in distilled water and dried in the air, was exposed to the gas but no alteration could be observed.

Another bit of silk was immersed in the same solution of bismuth, and exposed while wet to the gas; the silk in two or three minutes got a brown stain, which gradually became more intense, and a very delicate metallic film appeared; the silk was then immerged in water, and transferred a bright film of reduced bismuth to the surface of that fluid; the film retained the impression of the silk.

EXPERIMENT X.

ANTIMONY.

A bit of silk immersed in a solution of tartrite of antimony in distilled water and dried in the air was exposed to the gas, but suffered no apparent change.

Another piece of silk was dipped in the same solution of antimony, and exposed while wet to the gas, but no signs of reduction appeared; the silk was then immerged in water, to the surface of which it transferred one small spangle.

This experiment was repeated with the detonating gas, which with difficulty produced some sparkling films; the silk was immersed in water and transferred the films to its surface.

A white matter was visible in the fibres of the silk.

EXPERIMENT XI.

COBALT.

A piece of silk immersed in a solution of muriate of cobalt and dried in the air, was exposed to the gas, but suffered no visible alteration.

Another bit of silk was dipped in the same solution of cobalt, and exposed while wet to the gas, but no sign of reduction appeared; nor did the silk transfer a film to water.

Another bit of silk was immersed in a solution of nitrate of cobalt, and exposed while wet to the detonating gas, no signs of reduction were visible for some time; but at length a few small spangles of the metal appeared on the silk, and were very brilliant, and when transferred to water were still more so; a white matter could be seen in the fibres of the silk.

EXPERIMENT XII.

IRON.

A bit of silk was immersed in a largely diluted solution of sulphate of iron in distilled water, and dried; it was then exposed to the action of the gas; but no alteration could be perceived.

Another bit of silk was dipped in the same solution of iron and exposed while wet to the gas, in a few minutes some parts of the silk acquired a light brown colour; but no reduced iron could be seen on the silk, which however, transferred a very minute and delicate film to water.

This experiment was repeated with a strong detonating gas, and a very brilliant metallic film about four lines in diameter was reduced on the silk, accompanied with a brown stain, but nothing like the black oxid of iron appeared.

EXPERIMENT XIII.

ZINC.

A bit of silk, which was immersed in a largely diluted solution of muriate of zinc was exposed dry to the gas, but underwent no visible alteration.

Another piece of silk was dipped in the same solution of zinc and exposed wet to the gas; no signs of reduction appearing, the silk was immerged in water, and left a very minute metallic film on its surface, which could with difficulty be seen. The experiment was repeated with the detonating gas, and a very bright metallic film of zinc, four or five lines in diameter, was reduced on the silk.

This experiment succeeded also with a largely diluted solution of sulphate of zinc.

The silk, viewed by transmitted light, exhibited a brown stain beneath these films of iron and zinc.

The experiments detailed in this chapter shew,

- 1. That water is essential to the reduction of metals by phosphorated hydrogen gas.
- 2. That alcohol does not promote these reductions without the aid of water.
- 3. That this elastic fluid does not reduce metals by giving them phlogiston, nor by combining with, and separating their oxygen; for, were either of these suppositions true, it should reduce them as well with alcohol as with water.

After explaining the manner, in which sulphurated hydrogen gss reduces the metals, the mode of agency of phosphorated hydrogen gas is sufficiently obvious.

The gas attracts the oxygen of the water, while the hydrogen of the latter unites in its mascent state with the oxygen of the metal and reduces it.

Hence it follows that the hydrure of phosphorus, which constitutes the base of this gas, is oxygenated by the oxygen of the water, while the metal is, at the same time, restored to its combustible state.

By hydrure of phosphorus, is meant a combination of hydrogen and phosphorus, containing less caloric than is necessary to the gaseous state.

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CHAPTER VII.

REDUCTION OF METALS

BY

CHARCOAL.

FINDING several combustible bodies, as hydrogen, phosphorus, sulphur, and combinations of these, capable of reducing the metals in the ordinary temperature of the atmosphere; I was desirous of knowing if charcoal also possessed that power.

Charcoal may be applied with this view in several forms. M. Rouelle has observed that caustic fixed alkali dissolves a considerable quantity of this substance.

Charcoal also exists in a very attenuated state in ether, alcohol, gum, &c.

I have examined some of its effects on the reduction of metals, in these different forms, in which it probably exists combined with hydrogen, and also some of its effects in the solid form.

EXPERIMENT J.

GOLD.

A small bit of well burned charcoal was suspended by a thread in a phial containing a diluted solution of nitro-muriate of gold in distilled water; some air bubbles soon appeared on the charcoal; and in about two hours reduced gold was evident on its lower surface, and increased gradually, till the charcoal was nearly coated with gold of its proper colour.

This experiment was repeated with a richer solution of gold; the reduction did not commence near so soon, nor was the quantity reduced so great, or brilliant, as in the preceding experiment.

EXPERIMENT II.

GOLD.

A small bit of charcoal was suspended in a solution of gold in ether: an effervescence immediately commenced, and continued for a considerable time: but the solution suffered no change of colour, nor was there a particle of the gold reduced.

I should not be surprised if the gold were reduced in this experiment, as charcoal contains a large quantity of water, which it powerfully attracts from the surrounding air: however not a vestige of reduced gold could be perceived.

Bits of charcoal were suspended in the same manner in most of the metallic solutions treated of in this essay: no change was perceived on those immersed in solutions of arsenic, manganese, and fused nitrate of silver in water: but a bit immersed in a solution of the same nitrate in alcohol, had parts of it covered with bright sparkling particles, which seemed to vegetate from the charcoal, and were evidently reduced silver: for they were not soluble in water, on the surface of which the bit of charcoal deposited some small spangles of great lustre. The

bits immersed in solutions of sulphate of iron and zinc exhibited some very faint signs of reduction.

But these experiments were not repeated, nor sufficiently varied, to enable us to form a just opinion of the power of charcoal in reducing metals in this way.

A small quantity of charcoal, reduced to fine powder, was digested several days in a strong solution of caustic potash in alcohol; the phial was frequently shaken to promote the solution.

Some of the clear solution, which was of a reddish colour, was poured into a phial for use.

EXPERIMENT III.

GOLD.

A few drops of this solution of charcoal, or carbon, were applied to a bit of silk; after the alcohol evaporated, a solution of gold in ether was dropped on, and immediately produced a brown, which, in about half an hour, was changed to a purple hue, owing to water attracted from the air; but no other sign of reduction appeared.

Another bit of silk was immersed in the solution of carbon, and when the alcohol evaporated, a few

drops of an aqueous solution of gold were applied; a brown stain was instantly formed; the silk was kept wet with water; the stain gradually assumed a purple tinge, and in about five minutes, some reduced gold of its proper splendour and colour appeared: and in some time after every part of the silk, to which the solutions of carbon and gold were applied, was coated with reduced gold, which remained permanent. During the experiment, it is necessary to keep the silk constantly wet with water.

If the solution of gold be applied before the alcohol evaporates, a black precipitate is formed, along with the brown stain. In an experiment made in this manner, a metallic film, whitish and obscure, appeared in the beginning; but soon vanished: and in some time after, the gold was reduced of its proper colour; and a speck of ruby red appeared on the margin.

The silk viewed by transmitted light presented various colours, as purple, blue, and some green.

EXPERIMENT IV.

SILVER.

A few drops of the solution of carbon were applied to a bit of silk: when the alcohol evaporated,

a solution of fused nitrate of silver in alcohol was applied: a light brown stain was immediately produced in the silk; but no reduced silver could be seen.

The solution of carbon was applied to another bit of silk, and when the alcohol evaporated, an aqueous solution of fused nitrate of silver was dropped on: a brown stain was instantly formed, and in about ten minutes, minute films of reduced silver were visible.

The silk was kept wet with water during the experiment; and the brown stain was gradually changed to black. In some little time the metallic films disappeared.

If the solution of silver be applied to the silk, before the alcohol evaporates, black and brown precipitates are immediately formed; and commonly no reduced silver can be seen; but sometimes very minute films appear.

EXPERIMENT V.

PLATINA.

To a bit of silk, which was immersed in a solution of nitro muriate of platina in distilled water, and dried in the air, a few drops of the solution of carbon were applied; but no visible change was pro-

Another bit of silk was dipped in the solution of carbon, and when the alcohol evaporated, a few drops of the solution of platina were applied: a yellow precipitate was immediately formed, and in about ten minutes delicate films of reduced platina were visible: these metallic films soon vanished; and nothing but a yellow stain and the precipitate remained.

A bit of calico, on which this experiment was repeated, transferred a bright film of reduced platina to the surface of water.

During these experiments, the silk and calico were kept wet with water.

EXPERIMENT VI.

MERCURY.

On a bit of silk, which was immersed in a solution of oxygenated muriate of mercury in distilled water and dried in the air, a little of the solution of carbon was dropped, but the silk underwent no visible change. Another bit of silk was dipped in the solution of carbon, and when the alcohol evaporated, a little of the same solution of mercury was applied, a yellow precipitate was immediately formed, and soon after small films of reduced mercury appeared on the margin of the stain.

This experiment was repeated with a solution of nitrate of mercury, and the reduction of the metal was very evident on the margin of the stain, which was black; the precipitate on the bit of silk was 9f the colour of sulphur.

EXPERIMENT VIL.

COPPER.

To a bit of calico, which was immersed in a solution of acetite of copper in distilled water and dried in the air, a few drops of the solution of carbon were applied, but no visible change was produced.

On another bit of calico which was dipped in the same solution of copper, some of the solution of carbon was dropped, the calico acquired a slight tinge of brown; it was kept wet with water, and in about twenty minutes several white metallic films were evident.

A bit of silk on which this experiment was made, acquired a beautiful red colour, similar to the ruby red with which copper tinges glass, and depending on the same cause, viz. the quantity of oxygen combined with the metal.

EXPERIMENT VIII.

LEAD.

A bit of white calico was immersed in a solution of acetite of lead in distilled water and dried in the air, then a few drops of the solution of carbon were applied, but no visible alteration took place.

On another bit of the same calico, which was dipped in the solution of carbon, a little of the same solution of lead was dropped, and in a few seconds films of reduced lead bright as silver appeared, the calico was then immerged in water, and transferred a continuous pellicle of reduced lead to its surface.

This experiment was often repeated, both on silk and calico; sometimes the lead is reduced in an instant, but at other times five or six seconds elapse before any reduced lead becomes visible.

I also found that a solution of potash in alcohol reduces lead; but not so soon, or effectually, or in

such quantity as the former solution does, but it is evident, that these solutions differ only in the quantity of carbon which they contain.

EXPERIMENT IX.

TIN.

To a bit of calico, which was immersed in a solution of muriate of tin in distilled water, and dried in the air, some of the solution of carbon was applied; but no signs of reduction appeared, nor was the colour of the calico much altered.

On another bit of calico which was dipped in the solution of carbon, some of the same solution of tin was dropped, a white precipitate was instantly formed, attended with bright films of reduced tin; the calico was immerged in water, and left a bright metallic film on the surface of that fluid.

The same experiment succeeds on silk.

EXPERIMENT X.

BISMUTH.

A piece of silk which was immersed in a solution of nitrate of bismuth in distilled water and dried in

the air, suffered no visible alteration on applying the solution of carbon.

To a bit of calico which was dipped in the solution of carbon, a few drops of the same solution of bismuth were applied, and immediately films of reduced bismuth were evident. The calico was immerged in water, and transferred a bright metallic film to its surface.

This experiment succeeded also on silk.

EXPERIMENT XI.

ARSENIC.

A bit of silk was immersed in a solution of muriate of arsenic in distilled water and dried in the air, then a little of the solution of carbon was dropped on the silk, but no visible alteration took place.

Another bit of silk was dipped in the solution of carbon, and when the alcohol evaporated, some drops of the same solution of arsenic were applied; and in a short time a few minute metallic films were visible on the silk, which when transferred to water, were still more so.

Tartrite of antimony treated in the same manner, transferred a very delicate film, scarcely visible, to the surface of water.

EXPERIMENT XII.

IRON.

A bit of calico which was dipped in a largely diluted solution of sulphate of iron, and dried in the air, suffered no perceptible change on applying the solution of carbon, except a slight tinge of brown.

Another bit of calico was immersed in the same solution of iron, and placed on a bit of deal board, a few drops of the solution of carbon were then applied, the calico was kept constantly wet with water, and in about fifteen minutes films of reduced iron were visible, the calico was immersed in water and left a bright metallic film on its surface.

EXPERIMENT XIII.

ZINC.

To a bit of silk which was dipped in a largely diluted solution of muriate of zinc, and dried in the air, a few drops of the solution of carbon were applied, but scarce any alteration of colour, or other visible change occurred.

A piece of calico was immersed in the same solution of zinc, and placed on a bit of thin deal board, a few drops of the solution of carbon were then applied, the calico was kept constantly wet with water, and in about fifteen minutes films of reduced zinc were evident; the calico was immerged in water and transferred a very bright metallic film of the colour of zinc to its surface.

I also reduced muriate of cobalt in this manner.

EXPERIMENT XIV.

MANGANESE.

To a bit of silk which was dipped in a diluted solution of nitrate of manganese, and dried in the air, some drops of the solution of carbon were applied, but nothing appeared except a brown stain.

Another bit of silk was immersed in the solution of carbon, when the alcohol evaporated, a few drops of the same solution of manganese were applied; a brown stain was soon produced, the silk was kept wet with water, and in about twenty minutes films of re-

duced manganese of a bluish white colour were evident on the silk.

This experiment did not succeed with a strong solution of nitrate of manganese.

The same experiment succeeds also on linen and oalico, both with nitrate and sulphate of manganese, the reduction is attended with violet and purple colours, such as this metal imparts to glass and other substances, in which it exists combined with different proportions of oxygen; this difference is the cause of the different colours which solutions of manganese assume.

The bright films of reduced manganese soon disappear, the cause of which has been explained in the first chapter of this essay; the explanation there offered is confirmed by the following facts.

"Regulus of manganese," says Mr. Bergman, when well fused, generally persists in a dry place, but sometimes undergoes spontaneous calcination, and falls down in a brownish black powder.

"Moisture, but particularly the access of aerial acid assists this operation. A small piece put into a dry bottle well corked, remained perfect for the space of six months, but afterwards exposed to the

" open air of a chamber for two days, contracted a brownness on its surface, together with so much friability as to crumble between the fingers. The

" internal parts however, retained an obscure metal-

" lic splendour, which disappeared in a few hours."*

I shall now relate a few experiments made with ether, alcohol, and gum.

EXPERIMENT XV.

GOLD.

I evaporated a solution of gold in nitro-muriatic acid to dryness, and dissolved the salt in pure alcohol, the solution was poured into a phial carefully dried in hot sand, and rinced with pure alcohol; the solution filled about three-fourths of the phial, which was carefully corked, and though it was nine months exposed to the gray light, no films of reduced gold appeared.

Part of the same solution was poured into a phial, and diluted with water, films of reduced gold soon appeared.

^{*} Chem. Essay, Vol. II. p. 206 and 207, Eng. trans.

EXPERIMENT XVI.

GOLD.

A phial half filled with a solution of gold in sulphuric ether was exposed nine months to the gray light; but no films of reduced gold were produced.

On a bit of silk, which was dipped in part of the same solution of gold, and exposed to the gray light, and kept wet with water, reduced gold appeared in the space of a few hours.

EXPERIMENT XVII.

GOLD.

I mixed an aqueous solution of gold with a solution of gum arabic in distilled water, in such proportion, as to prevent the solution from spreading in the silk.

With this solution I drew several stripes on a piece of silk, and exposed it to the gray light of a chamber; in some time the gold was reduced attended with blue and purple colours. Similar stripes were drawn on another piece of silk, which, after the stripes became sufficiently dry, was placed over the vapour of hot water; and in about fifteen minutes the gold was reduced in a beautiful manner.

This solution was applied to another bit of silk, which after it became sufficiently dry, was placed between the leaves of a blank book, to exclude the action of light: the gold, after some time, was reduced.

I found that small stripes and spots, made with this solution, were reduced by breathing on them for some time.

Sugar also, mixed with the solution of gold, promotes the reduction; but not so well as gum.

A bit of silk was dipped in a solution of nitrate of silver in distilled water, and exposed, while wet, to the smoke of a common fire; in a short time reduced silver appeared.

The following inferences are deducible from the experiments related in this chapter.

1. Charcoal is capable of reducing the metals in the ordinary temperature of the atmosphere.

- 2. Water is essential to the reduction of metals by charcoal: for these experiments prove, that the reduction cannot be effected without water.
- 3. Charcoal does not reduce the metals by giving them phlogiston; nor by uniting with and separating their oxygen; for were either of these opinions true, metallic solutions in ether and alcohol, should be as effectually reduced by charcoal, as metallic solutions in water are.
- 4. Ether and alcohol do not promote the reduction of metals without the aid of water; but when this is present in sufficient quantity, they effect the reduction, in the same manner, that charcoal and other combustible bodies do.

It is evident then that charcoal reduces the metals by decomposing water; which seems to be effected in the following manner.

The carbon of the charcoal attracts the oxygen of the water, while the hydrogen of the latter unites in its nascent state, with the oxygen of the metal, and reduces it.

Hence it follows that the carbon is oxygenated by the oxygen of the water, and forms carbonic acid, while the metal is restored to its combustible state. This explanation is supported by the following facts: M Gengembre has observed, that if charcoal be impressed in water, and kept at a temperature of thirty degrees of the thermometer of M. De Reaumur, the water is gradually decomposed, and inflammable gas is formed.*

That charcoal effects the reduction of metals, in high degrees of heat also, by decomposing water, is evident from the following observations.

The great force with which charcoal attracts water is a fact sufficiently established; Dr. Priestley is so convinced of this, that he expresses himself in the following strong terms. "I did not know, nor could believe the powerful attraction, that charcoal, or iron appear to have for water; when they are intensely heated, they will find and attract it in the midst of the hottest fire through any pores in the retort."

Now since water is essential to the reduction of metals in low degrees of heat; and since that fluid is always present, when metals are reduced by charcoal in high degrees of heat; it is manifest, that charcoal acts in the same manner in both these temperatures;

^{*} Essay on Phlogiston, new ed. by M. Kirwan, p. 61.

⁺ Phil. Trans. 1785. Vol. LXXV. p. 289.

and since water is easily, and instantly, decomposed by charcoal at a red heat, as the Antiphlogistians themselves allow; it clearly follows that their theory of metallic reduction is erroneous: for since the water is instantly decomposed by the charcoal, it is a necessary consequence, that its carbon must unite with the oxygen of the water, while the hydrogen of the latter unites in its nascent state, with the oxygen of the metal, and reduces it, forming a new quantity of water equal to that decomposed: this new quantity of water may be decomposed in its turn: so that a thimble full of water would be sufficient to reduce any quantity of metal; provided the water were prevented from escaping, and time enough allowed.

Beside this source of water, the air of the atmosphere, which contributes to support the fire is an inexhaustible magazine of water: and the hotter the air is, the more water it holds in solution; as M. Le Roy has demonstrated.* Moreover all metallic oxids and ores contain a large proportion of water.

From this view it appears, that the manner in which charcoal and other combustible bodies effect the reduction of metals, is by assisting to decompose water, the hydrogen of which is therefore the only reducer of the metals.

^{*} El. Nat. Hist. & Chem. Eng. Trans. in three volumes, p. 163. Vol. I.

In order to point out the difference between this opinion and that of the Antiphlogistians, I shall present the reader with M. Lavoisier's idea of metallic reduction.

"It cannot be doubted," says that celebrated chymist, "that charcoal at a red heat takes oxygen from all metallic substances; this is a fact against which no exception can be made; and it is the foundation of the whole theory of metallic reduction."

But the experiments in this essay demonstrate, that this assertion is erroneous in every instance of metallic reduction; for, so far is it from being true, that charcoal takes oxygen from all metallic substances; it never does so in one single instance, since its carbon always unites with the oxygen of the water, the hydrogen of which unites immediately to the oxygen of the metal, and reduces it.

"But this action of charcoal on oxygen," adds M. Lavoisier, "this property, which it possesses of ta"king it from metallic substances, is not so strong in
"the cold, as at a red heat, since we are unacquaint"ed with any metallic revivification effected by char"coal without heat."*

^{*} Essay on Phlog. a new ed. by M. Kirwan, p. 60.

It is evident that this mode of reasoning is no longer of any weight, since charcoal does reduce metals in the ordinary temperature of the atmosphere.

The reason charcoal is more powerful in high degrees of heat, than other reducers of the metals, is its great fixity in the fire, and the immense force with which it attracts and imprisons water in its pores, thus preventing its escape till it be decomposed by an affinity, which is much more complex than has been hitherto imagined.

Another reason of the superior power of charcoal in metallic reduction is, that it forms a volatile elastic fluid with the oxygen of the water, which flies off, and consequently does not re-act on the metal, or disturb, or impede by its presence, the action of the reducing powers; advantages that phosphorus or any other combustible substance, which forms a fixed acid, that re-acts on the metal, can never possess.

CHAPTER VIII.

REDUCTION OF METALS

BY

LIGHT.

THE next substance I shall treat of, is Light, which seems well adapted to illustrate the theory of metallic reduction; as in experiments made with this substance, water can be more effectually excluded, than in trials with any other reducer of the metals.

Before any decisive experiments could be made on light, or indeed any other reducer of the metals, it is obvious that we should first ascertain the effects of water itself in the ordinary temperature of the atmosphere; to determine this point the two following experiments were made.

EXPERIMENT I.

GOLD.

A piece of silk was immersed in an aqueous solution of nitro-muriate of gold, and suspended in a phial over water; the phial was corked, covered with black silk, and placed in a dark closet to prevent the action of light. The experiment was continued from the 20th of July to the 20th of October, during which time the silk was frequently observed, and found to continue moist, but no alteration could be perceived, except that the yellow colour which the solution of gold gave the silk, was changed to a light brown.

The silk was now taken out of the phial, and a solution of phosphorus in ether applied to it; shortly after, a white metallic film appeared; the silk was then kept wet with water, and in some time reduced gold of its proper colour appeared.

EXPERIMENT II.

SILVER.

A bit of silk which was dipped in an aqueous solution of nitrate of silver, was suspended in a phial over water, and placed in a dark closet from the 20th of July to the 20th of October, and examined from time to time, but no alteration could be observed, its white colour continued pure and unchanged.

The silk was now taken out of the phial, and the silver was immediately reduced by means of a solution of phosphorus in ether.

Hence it appears, that water alone has not the power of reducing metals in the ordinary temperature of the atmosphere.

EXPERIMENT III.

GOLD.

On the 24th of July a piece of silk was immersed in a solution of nitro-muriate of gold in water, and dried by a gentle heat; it was then suspended in a window exposed to the sunbeams as much as possible; no change was perceived on it till the 26th, when the margin of the silk began to assume a purple tinge, which increased gradually, and on the 29th exhibited a few obscure specks of reduced gold on the side of the silk opposed to the light.

The purple tinge continued to increase, and the yellow which the solution of gold gave the silk decreased gradually, till on the 27th of August the colour was a mixture of purple and light brown.

The reduction of the gold seemed to keep pace with these changes of colour, and was very evident on some parts of the silk even in the gray light, but much more so in sunshine; these changes were observed till the 20th of October; the experiment was then discontinued, and scarce any reduced gold could be seen on the side of the silk not opposed to the light.

That this slight reduction of the gold and changes of colour in the silk, depended on water absorbed from the air of the chamber, will appear from the following experiments.

EXPERIMENT IV.

GOLD.

A bit of silk which was dipped in the solution of gold employed in the preceding experiment was dried and suspended in a chrystal phial over dry carbonate of potash; the phial was then corked, and further secured from external humidity by covering the cork with wax: it was now placed in a dark closet twenty-four hours, that the carbonate of potash might have sufficient time to attract all the moisture it could from the air of the phial, before exposing it to the action of light.

The phial was then placed in a window exposed as much as possible to the solar light, from the 24th of July to the 20th of October, and carefully observed; the same side of the silk was always opposed to the light, and had the yellow tinge, which the solution of gold gave, altered to a brownish yellow: but the other side of the silk suffered no visible change whatever, nor could any purple tint, or the smallest vestige of reduced gold be perceived.

Another bit of silk which was immersed in the same solution of gold and dried by a gentle heat,

was suspended over some dry carbonate of potash, contained in a chrystal phial covered with black silk, and placed in a dark closet during the same space of time, but underwent no visible change whatever.

Both these bits of silk were now taken out of the phials, and the gold was instantly restored to its metallic splendour by means of water and a solution of phosphorus in ether; a proof that the nitro-muriate of gold in these bits of silk, suffered no change during that space of time.

EXPERIMENT V.

GOLD.

A piece of silk, which was dipped in the same solution of gold, and placed on a china plate exposed to the sunbeams, was kept moderately wet with water during the experiment; the first alteration observed was, that the yellow colour of the silk began to change to a faint green, succeeded by a purple tinge, which in about fifteen minutes exhibited some particles of reduced gold; soon after the threads of the silk, which acquired this purple tint were gilded with gold; and, in about an hour, the whole of the silk was covered with a superb coat of reduced gold, exhibiting the texture of the silk in a beautiful manner.

The purple tinge, which attended the reduction, verged in some parts on red, and in others on blue.

This experiment, which is very amusing, I have repeated times unnumbered; and when the sun is powerful, and the solution of gold properly prepared and of due strength, the coat of reduced gold is so bright and dazzling, as to distress the eye of the beholder.

I find that the best way of preparing a solution of gold for this purpose, is to separate the oxid of gold from its solution in nitro-muriatic acid by means of good ether.

The silk may be dipped in this solution, and when the ether evaporates, kept moderately wet with distilled water.

It was with this solution in ether that I first reduced gold in the fibres of silk, and it was by means of the same I discovered, that water was a necessary condition in these reductions by light.

EXPERIMENT VI.

GOLD.

A bit of silk, which was dipped in a solution of nitro-muriate of gold on alcohol, and placed in a china saucer exposed to the sunbeams, was kept wet with alcohol for the space of an hour, but no change even in the colour, which the solution of gold gave the silk, could be perceived.

The alcohol diffused the solution of gold unequally through the silk, the rays of the sun being intercepted, suspended the experiment; there was no sunshine on the following day: on the third day the silk was again exposed to the sunbeams, and kept wet with alcohol, which extracted a yellow tincture; a proof that the gold in the silk suffered no degree of reduction; the sun shone pretty strong for an hour or more, and at length a faint tinge of purple, followed by some reduced gold, appeared.

The preceding experiments leave us no room to doubt that the purple tinge, and the small quantity of reduced gold, that appeared in this experiment, depended on water attracted from the air, or deposited in the silk by the alcohol during its evaporation.

Mr. Scheele reduced a solution of nitro-muriate of gold in water by exposing it in a phial for a fortnight to the rays of the sun.*

^{*} Experiments on Air and Fire. Eng. Trans. p. 82.

Mr. Lewis also made many experiments on the staining of marble, and other substances with metallic solutions, and light.

EXPERIMENT VII.

SILVER.

A piece of silk, which was immersed in a solution of nitrate of silver in water, was dried by a gentle heat, and exposed to the light of the sun as much as possible, in the window of a chamber from the 20th of July to the 20th of October.

In less than an hour the silk acquired a reddish brown colour; next day the colour became more intense and gradually increased, till on the third day it bordered on black, which increased slowly; at length part of it became gray, and a few minute particles of reduced silver could be distinguished; the black tinge gradually disappeared, and the silk was of a reddish brown colour; the reduced silver had a gray east.

The following experiments demonstrate, that the changes of colour and the few particles of semi-reduced silver, depended on water attracted from the atmosphere.

⁺ Commerce of the Arts.

EXPERIMENT VIII.

SILVER.

A bit of silk was immersed in part of the same solution of nitrate of silver in water, and dried in the dark, the silk retained its white colour; it was then suspended over dry carbonate of potash in a chrystal phial, which was corked and secured from the ingress of moisture by covering the cork with wax.

The phial was left in a dark closet twenty-four hours, that the salt might imbibe as much moisture as possible from the silk and air.

The phial was then placed in a window, exposed as much as possible to the rays of the sun, from the 24th of July to the 20th of October; the silk scarcely suffered any visible change, except a very faint tinge of reddish brown, which was best seen by transmitted light; for the silk viewed by reflected light appeared nearly white; but that even this tinge, slight as it was, depended on a minute quantity of moisture, which the carbonate of potash was unable to extract, appears from the next experiment.

EXPERIMENT IX.

SILVER.

A piece of silk was dipped in a solution of fused nitrate of silver in alcohol and carefully dried; it was then suspended over a quantity of concentrated sulphuric acid in a chrystal phial, which was coated with a double fold of black paper and gum arabic, reaching somewhat above the level of the acid to prevent the light from acting on it; the phial was corked, and to exclude moisture more effectually, the corkwas covered with wax.

The phial was now placed in a dark closet twentyfour hours, that the humidity of the enclosed silk and
air might be attracted by the acid; it was then placed
in a window, exposed as much as possible to the rays
of the sun, from the 19th of July to the 26th of
October, but the silk underwent no visible change
whatever; its white colour remained pure and unaltered.

The silk at the end of this period was taken out of the phial, and wetted with water, a solution of

phosphorus in ether was then applied to it, and instantly the metallic splendour of the silver appeared.

Another bit of silk which was immersed in a solution of nitrate of silver in water, and dried in the dark, was suspended over dry carbonate of potash in a phial, and placed in a dark closet about two months; the silk underwent no visible alteration whatever; its white colour remained pure.

I was desirous of knowing if the nitrate of silver in this bit of silk suffered any change, that might render it incapable of reduction; I therefore took it out of the phial, and divided it into two parts; one of these was wetted with water, and the silver was instantly reduced by a solution of phosphorus in ether. The other part, which was suspended in a window, exposed to the air of the chamber and rays of the sun, soon acquired a reddish brown colour.

Hence it is evident, that these changes of colour indicate partial reductions of the metal, and that they never happen without the presence of water.

EXPERIMENT X.

SILVER.

A bit of silk, which was dipped in a solution of nitrate of silver in water, was placed on a China saucer, exposed to the rays of the sun, and kept moderatelywet with water; in a few minutes the white colour of the silk was changed to a reddish brown, which by degrees became darker, and in about three or four hours, though the solar rays were often languid and intercepted, acquired a blackish gray colour, most of the reddish brown having disappeared; next day there was no sunshine, but towards the evening, particles of reduced silver were visible on the side of the silk opposed to the light.

EXPERIMENT XI.

SILVER.

A bit of silk, which was immersed in a solution of nitrate of silver in alcohol, and exposed to the beams of the sun, as in the preceding experiment, was kept moderately wet with alcohol, but resisted the action of the light much longer than the preceding; however in some time, specks and lines of a reddish brown began to appear on some parts of the silk;

next day, though there was no sunshine, the reddish brown colour increased a little; on the third day it became more intense, but no black, or gray colour, or particle of reduced silver, could be observed.

Whoever compares this with the preceding experiments, can have no doubt that the changes of colour which appeared in this experiment, depended on water attracted from the air, or deposited in the silk by the alcohol during its evaporation.

The experiments detailed in this chapter, prove beyond the power of contradiction,

- 1. That water is essential to the reduction of metals by light; for these experiments demonstrate that the reduction cannot take place without water, and that it is always in proportion to the quantity of that fluid present.
- 2. That light does not reduce metals by giving them phlogiston, as Messrs. Macquer and Scheele supposed; for was this opinion true, light should reduce them without the aid of water, and as well with alcohol as with water.
- 3. Light does not reduce metals by fusing and expelling their oxygen, as the Antiphlogistians imagine; for were this its mode of agency, the reduction should happen without the assistance of water, and as well with alcohol as with water.

4. Light is a combustible body, for it acts like hydrogen, phosphorus, sulphur, and charcoal, in the reduction of metals.

Since water then is essential to the reduction of metals by light, and since light does not reduce metals by giving them phlogiston, nor by fusing and expelling their oxygen, it follows, that the water is either decomposed, or that it unites with metallic earths, and constitutes their phlogiston, or that it unites with and separates their oxygenous principle; but as the two last suppositions are inadmissible, it is obvious that light reduces the metals by decomposing water.

After explaining the manner in which other combustible bodies reduce the metals by decomposing water, it will not be difficult to explain how light too produces the same effect.

But in order to facilitate the explanation, it must be premised,

- 1. That it is a law of attraction, that when any body is deprived to a certain degree, of another, for which it has a strong affinity, the attraction of the former for the latter is much increased.
- 2. That light has a strong attraction for oxygen, or the base of vital air.

- 3. That when oxygen is condensed, and fixed in any substance, it contains much less light and caloric than it does in the gaseous state.
- 4. That the oxygenous principle exists in water in this condensed state, and consequently has a strong attraction for light.

Therefore when light reduces the metals, it attracts the oxygen of the water, while the hydrogen of the latter unites in its nascent state to the oxygen of the metal and reduces it, forming at the same time a quantity of water equal to that decomposed.

Hence it follows that the light is oxygenated and changed into vital air, while the metal is restored to its combustible state.

CHAPTER IX.

REDUCTION OF METALS

BY

ACIDS.

IT is well known that solutions of gold throw up films of the reduced metal to the surface of the fluid, and sides of the phials that contain them.

It has been shewn in the seventh chapter, that this effect depends on the presence of water, which is further illustrated by the following experiments.

EXPERIMENT I.

SILVER.

A drachm of saturated solution of nitrate of silver in distilled water was mixed with half an ounce of vinegar, in a few minutes a precipitate was formed; the whole was then poured on a filter and washed with distilled water; the precipitate acquired a bluish gray metallic appearance; the liquor which passed the filter, got a brown colour and became blackish; next day bright films of reduced silver floated on the liquor, and in some months after, a considerable part of the inner surface of the phial was coated with reduced silver. Distilled vinegar did not produce this effect.

EXPERIMENT II.

PLATINA.

If a solution of the ore of platina in nitro-muriatic acid be evaporated to dryness, and the salt dissolved in water, films of a livid white metallic appearance are thrown up to the surface.

EXPERIMENT III.

TIN.

Some tin, which was dissolved in a china cup in muriatic acid and evaporated to dryness, was dissolved in distilled water; immediately white metallic films appeared on the surface of the liquor, and after some hours, the whole surface of the solution was covered with a continuous metallic pellicle, which reflected all the colours of the rainbow, in a beautiful manner.

EXPERIMENT IV.

MERCURY.

Mr. Bergman says, "calcined mercury is reduced by digestion in acid of salt; but the cause has not yet been sufficiently explored."*

As this reduction of mercury by muriatic acid is doubted of by some, I made the following experiment.

^{*} Elective Attractions. Eng, trans. p. 223.

A quantity of precipitate per se was put into a china cup placed on hot sand, and some muriatic acid was poured on it; the oxid was gradually dissolved, and the digestion continued till the acid was nearly evaporated, some distilled water was then poured on the salt, and minute films of a bright metallic appearance floated on the surface.

A nitrate of mercury was evaporated to dryness; the salt acquired a slight tinge of yellow; the cup was removed from the hot sand, and some water poured on the salt; immediately bright films of reduced mercury appeared, and in about three or four hours the whole surface of the solution was covered with a metallic pellicle, parts of which had the colour and splendour of the metal, and other parts reflected a wonderful variety of the most beautiful colours.

EXPERIMENT V.

ARSENIC.

A quantity of white oxid of arsenic and muriatic acid was digested in the same manner in a china cup, a smart heat was continued till most of the acid evaporated and left behind a mass of the consistence of tar, the surface of which had a gray appearance; after it cooled, some distilled water was poured on, it diffused a disagreeable smell, and films of reduced arsenic were thrown up to the surface; these were for some time remarkably bright, but soon became of a dull gray colour, owing to the rapid tendency of this metal to spontaneous calcination.

EXPERIMENT VI.

MANGANESE.

Some concentrated sulphuric acid was poured on a quantity of the him a cup, placed on hot sand; an effervescence was visible, but no sulphurous acid gas was exhaled; the cup was removed from the sand, before any perceptible quantity of the acid evaporated; then some water was poured on the mixture, and instantly the surface of the fluid was covered with very brilliant metallic films, and at the same time the solution acquired a rose colour.

Some of the same oxid of manganese was dissoluted in nitric acid, in which a bit of sugar was put, the solution was poured into a china cup placed on hot sand, and as the evaporation proceeded, bright metallic films appeared on the surface.

Mr. Bindheim of Moscow relates, that he reduced the aërated calx of manganese dissolved in nitrous acid; "the solution was placed upon an open fire in "a glass retort."*

Happening to pour out a very largely diluted solution of sulphate of iron, I was surprised to find the flags of the court in an hour or two after, covered with large films of a livid white metallic aspect, these films after the water evaporated, remained on the flags several days.

In consequence of this I poured a largely diluted solution of sulphate of iron into several shallow vestovered with abundance of bright metallic films.

I also found that a largely diluted solution of muriate of zinc throws up bright metallic films to the surface.

The reduction of metals by acids is a very convincing proof of the decomposition of water, and seems inexplicable on any other principle.

The reduction and calcination of metals by heat and electricity are naturally explained on the same

^{*} Crell's Chem. Journal, Vol. II. p. 48, Eng. trans.

principle; Dr. Priestley informs us in his History of Electricity, Vol. I. p. 344, that S. Beccaria revived several of the metals by the electric shock. It is obvious that the electric fluid produces this effect in the same manner, that other combustible bodies do, viz. by decomposing water. When the red oxid of mercury is reduced in close vessels by heat, the latter attracts the oxygen of the water, contained both in the oxid and in the air of the vessels, while the hydrogen of the water unites to the oxygen of the mercury, reduces it, and forms a quantity of water equal to that decomposed.

It is found, that if light and caloric act both at the same time, the reduction is effected with more facility than if either acted separately; in this case, the superior efficacy of the combined action of light and caloric resembles that of other compound reducers of the metals; as that of sulphurated hydrogen gas, phosphorated hydrogen gas, alkaline sulphure, &c. which are more powerful than simple hydrogen gas, sulphur, or phosphorus.

This superior efficacy of compound reducers, is similar to what happens with some other combinations of combustible bodies, as pyrites, pyrophori, a mixture of lead and tin, &c. which have a more powerful attraction for oxygen, than any of their ingredients in a separate state.

Other acids, as the gallic, the tartarous, the formic, &c. and also alkalis, as ammonia and soda, have the power of reducing some of the metals, facts well known to chymists.

CHAPTER X,

OXYGENATION

OF

COMBUSTIBLE BODIES.

IT has been shewn, in the preceding chapters, that water is essential to the reduction of metals; that it is always decomposed in that process, and that the reducing substances are oxygenated by the oxygen of the water, while the hydrogen of the latter reduces the metals.

That water is also decomposed in every instance of oxygenation, and that the oxygen of water alone

oxygenates combustible bodies will appear from the following observations.

AZOTE.

The first case of oxygenation, we shall consider, is that of Azote, in an experiment of Dr. Priestley, which has been urged by Mr. Kirwan with great success against the Antiphlogistians.

"If the electric spark be taken in nitrous air, it will be reduced to one-third of its bulk, and the residuum is mere phlogisticated air, and a little acid is deposited. Now the Antiphlogistians own that nitrous air contains both pure air and phlogisticated air; since therefore this pure air disappears, is it not evident that it was converted into water? and since the formation of water requires the presence of inflammable air, does it not follow that the nitrous air contained this also?"*

To this objection M. Berthollet replies, that the diminution of the nitrous gas "is owing to the combination of the mercury with the oxygen, which existed in the gas."

^{*} Essay on Phlogiston, new Ed. p. 82.

⁺ Ibid. p. 122.

But this answer is insufficient, as it does not account for the water and acid that appeared; and indeed by this experiment, the Antiphlogistians are refuted on their own principles, and the decomposition of water is incontestably proved; for as nitrous acid could not be formed without more oxygen than what existed in the nitrous air, is it not evident that this oxygen must be derived from the water contained in the nitrous air? It is obvious then, that the water of the gas was decomposed, which seems to have been effected in the following manner.

The electric spark diminishes the attraction of the constituent principles of the water for each other; hence the azote of the gas unites with the oxygen of the latter combines with the oxygen of the gas; and thus water and introus acid are formed.

The formation of nitrous acid in Mr. Cavendish's noted experiment, cannot be explained on any other principle than the decomposition of water: when the electric spark is taken in a mixture of azotic gas and vital air, the water of these airs is decomposed; the electric flame lessens the force with which the oxygen and hydrogen of the water adhere; hence the azote seizes the oxygen of the water and forms nitrous acid, while the hydrogen of the water unites with the oxygen of the vital air, and forms a quantity of water equal to that decomposed.

When nitrous and vital air are mixed, the whole mass "hisses, turns red, grows warm, and contracts in bulk," the azote of the nitrous air attracts the exygen of the water and forms nitrous acid, while the hydrogen of the water unites in its nascent state with the oxygen of the vital air, and forms a quantity of water equal to that decomposed.

Hence while the azote of the nitrous air is oxygenated, the caloric is restored to its combustible state.

"But it is to be observed," says M. Bergman, treating of this experiment, "that the decomposition of nitrous air is the effect of a double attraction; the phlogiston is attracted by the phlogiston is attracted by the phlogiston is attracted by the part by the water. Therefore, when the mixture is made in a phial immersed in mercury, the experiment fails."*

HYDROGEN.

The combustion of hydrogen gas with vital air is explicable only on the decomposition of the water contained in these airs; thus when flame, or a glowing body is applied to a mixture of them, the attraction of the principles of the water for each other is dimi-

^{*} Elec. Attr. Eng, Trans. p. 211.

nished; therefore the hydrogen of the inflammable air unites with the oxygen of the water, while the hydrogen of the latter seizes the oxygen of the vital air; thus the whole bulk of the airs which are changed into water disappears, and their light and caloric are restored to the combustible state.

Hence it appears that water is not formed during the combustion of vital and inflammable air, in the manner the Antiphlogistians suppose.

Indeed it is obvious, that if these airs contained no water they could never be burned; for since they are already saturated with light and caloric, they can have no attraction for any additional quantity of these fluids; and consequently can suffer no other change from the light or caloric of a glowing body than a greater degree of expansion, and therefore could never unite.

The same reasoning applies to the combustion of all elastic fluids.

PHOSPHORUS.

Vital air always contains a large proportion of water; when phosphorus is burned in this air it attracts the oxygen of the water, and forms phosphoric acid, while the hydrogen of the water unites with the oxygen of the gas, and forms water which unites with the acid.

Hence the weight of the acid formed is equal to the weights of the oxygen gas and phosphorus consumed; and the light and caloric, which appear during the combustion are restored to their combustible state.

This explanation is confirmed by an observation of Mr. Bergman, who says,

"In vital air, without the aid of external heat, phosphorus is consumed very slowly, and scarce at all unless water be present."*

Therefore the phosphorus does not unite to the oxygen of the vital air as M. Lavoisier supposes, but to the oxygen of the water contained in the oxygen gas.

SULPHUR.

When sulphur is burned in vital air it attracts the oxygen of the water and forms sulphuric acid, while the hydrogen of the water attracts the oxygen of the gas, and forms a quantity of water equal to that de-

^{*} El. Att. Eng. Trans. p. 213.

composed: the light and caloric are at the same time restored to their combustible state.

The sulphur then does not unite with the oxygen of the vital air as the Antiphlogistians imagine, but with the oxygen of the water contained in that gas.

CHARCOAL.

In like manner during the combustion of charcoal in vital air, the carbon attracts the oxygen of the water, and forms carbonic acid, while the hydrogen of the water unites with the oxygen of the vital air, and forms a new quantity of water equal to that decomposed.

Hence the carbon of the charcoal does not unite with the oxygen of the vital air as M. Lavoisier supposes, but with the oxygen of the water contained in that gas.

That water is decomposed in every instance of combustion, is further proved by attending to what passes during the burning of a common fire; the carbon of the fuel combines with the oxygen of the water and forms carbonic acid, while the hydrogen of the water unites partly with the oxygen, and partly with the azote of the atmosphere, and forms water, and the ammonia which abounds in soot.

From these observations it is evident, that M. Lavoisier's account of the formation of water and acids is erroneous, and inadequate to explain the phenomena.

The different kinds of fermentation are so many instances of the decomposition of water; in every case of them, combustible bodies are oxygenated by the oxygen of the water, while others are restored by its hydrogen to their combustible state.

Hence the azote, ammonia, and carbonic acid of fermentation, the inflammable air of marshes, mines, &c.—the azotic and hydrogen gases ascend into the atmosphere, and there meeting the vital air discharged from the water of plants, &c. form new quantities of air and water.

When the azote is oxygenated, it unites with the oxygen of the water contained in the air and forms atmospheric air, and sometimes perhaps nitrous acid; the hydrogen of the water combines at the same time with the oxygen of the vital air, and forms a quantity of water equal to that decomposed.

But when the hydrogen is oxygenated, a quantity of water double that decomposed is regenerated; for the hydrogen of the gas unites with the oxygen of the water, while the hydrogen of the latter seizes the oxygen of the vital air; and thus a quantity of water double that decomposed is formed, and that part of it which the atmosphere cannot suspend descends in the form of rain.

When these decompositions are rapid, the phenomena of thunder and lightning appear.

This account of the renovation of our atmosphere explains why the phenomena of thunder and lightning appear sometimes with, and sometimes without rain; and also accounts for the production of the nitrous acid, which Mr. Margraaf discovered in the purest snow.

The breathing of fishes is a striking proof of the decomposition of water in respiration.

For this view of the formation of our atmosphere-I am indebted to a friend well acquainted with the experiments related in this essay, and also for the application of the opinion which I venture to advance to the respiration of animals.

The phenomena of vegetation cannot be explained on any other principle, than the decomposition of water by heat and light, which uniting to the oxygen of the water contained in vegetables, change it into streams of vital air that serve to renovate our atmosphere; the hydrogen of the water at the same time contributes to form the oil and other principles of plants, and when these are decomposed by the various processes of combustion, forms a quantity ofwater equal to that consumed in their formation.

The changes, which nitric acid suffers by exposure to heat or light, are explained with ease on this principle; the light unites with the oxygen of the water contained in the nitric acid and forms vital air, while the hydrogen of the water combines with the oxygen of the acid, and forms a new quantity of water equal to that decomposed; thus the nitric is converted into the ruddy nitrous acid.

METALS.

According to the Antiphlogistians, "In every metallic solution by an acid, the metal in order to become oxided, decomposes either the acid itself or the water of solution, or it obtains from the atmosphere the requisite quantity of oxygene. In the second case, hydrogenous gas in a state of greater or less purity is disengaged, and the acid remains entire without decomposition, which is proved by the quantity of alkali necessary to saturate it. In the first case, one of the principles of the acid, or the acid deprived of part of its oxygene is disengaged and fused in the caloric, which is separated at the same time; such are ni-

neither the water nor the acid are changed; such is the solution of copper by the acetous acid.

"The muriatic acid and the vegetable acids, which are formed of radicals, or acidifiable principles, which have more affinity with oxygene than the metals have, are not decomposed by these metals, and the oxygene is always afforded to these last by the water or atmosphere. Hence the solutions by these acids afford only hydrogenous gas, or do not effervesce at all.

"There are some cases in which the water and the acid, are at the same time decomposed by the metal, as in the solution of tin in the nitric acid, according to the observation of M. De Morveau.

a quantity for its saturation, that after having absorbed that of the nitric acid, and reduced it to the state of azote, it decomposes likewise the water, and disengages hydrogen. These two principles being separated from their first compounds, unite together and immediately form ammoniac. Hence there is no disengagement of elastic fluid. In this case it appears, that the formation of ammoniac, in the solution of tin by the nitric acid always takes place; for by throwing quicklime or caustic fixed alkali into this

solution, there is always a disengagement of ammo-

It is evident then that this account of the oxygenation of metals, given by the Antiphlogistians, is equally complex as their account of metallic reduction, and improbable; since every case, in which they deny the decomposition of water, and derive the oxygen from other sources, is easily and naturally explained on that principle, as will appear from what follows.

Thus when mercury or silver is dissolved in nitricacid, the metal attracts the oxygen of the water, while the hydrogen of the latter unites with and separates more or less of the oxygen of the acid, which is thus changed into nitrous air.

The same thing happens during the solution of other metals in this acid, the only difference being the greater or less energy and rapidity with which they combine with the oxygen of the water.

This decomposition of water is confirmed by the solution of tin in this acid, in which the Antiphlogistians allow the decomposition of the acid, and the

^{*} Essay on Phlog. new Ed. by Mr. Kirwan, p. 233-235.

water too, for ammonia is formed by part of the hydrogen of the water, and azote of the acid.

In every case of metallic solution by sulphuric and muriatic acids, whether concentrated or diluted, water is decomposed; the metals attracting the oxygen of the water, while its hydrogen escapes in the form of inflammable air, or unites partly with the oxygen of the acid, and partly with caloric; hence the volatile sulphurous acid, and muriatic acid air obtained, always contain some hydrogen gas, as appears from the following observation of M. Bergman.

"By means of vitriolic acid, inflammable air is obtained from zinc and iron, as also by means of marine acid; but from the other metals dissolved in vitriolic acid, we obtain another species of air, called vitriolic acid air; and by the marine acid, another similar to the former, called muriatic air, but both more or less mixed with inflammable air."*

Again, when copper is dissolved in the acetous acid, the copper attracts the oxygen of the water, while the hydrogen of the latter unites with the oxygen of the atmosphere and forms water; hence no effervescence appears.

^{*} Chem. Essays, Vol. II. p. 358. Eng. trans.

When alkalies dissolve metals, the latter are always oxygenated at the expense of the water, which holds the alkali in solution; thus when lead and copper are dissolved, the metals combine with the oxygen of the water, while its hydrogen unites to the oxygen of the atmosphere and forms water; hence no hydrogen gas appears.

The oxygenation of metals and other substances by heat and air is easily explained on the same principle; the metals, &c. unite with the oxygen of the water contained in atmospheric air, while the hydrogen of the water combines with the oxygen of the air, and forms a quantity of water equal to that decomposed.

This explanation is clearly proved by an experiment of Mr. Bergman on the regulus of manganese, which if kept in a dry place, retains its metallic splendour, but if exposed to moisture, is soon oxygenated, and loses its lustre.*

It is further confirmed by the authority of the distinguished Mr. Scheele, who says that "the water contained in common atmospheric air is the chief cause of the ignition of pyrophorus," which he proved by the following experiment.

^{*} Chem. Essays, Vol. II. p. 206 and 207. Eng. trans-

"I made a very dry air by putting some very small pieses of quicklime into a small matrass, then I put the neck of another matrass into that of the first, so that the air of both might communicate, and I luted the crevices with wax. Two days afterwards I separated the empty matrass, and poured half an ounce of pyrophorus from my phial into it, and immediately carefully shut the aperture up; but I did not observe that it grew in the least warm; an hour after this I put a sponge moistened in water into the matrass, and shut it up again: a few minutes after the pyrophorus began strongly to be heated, and some pieces kindled spontaneously."*

Many other facts might be adduced to prove, that oxygenation cannot take place without water, as the combustion of mixtures of iron filings, sulphur and water, of alkaline sulphure and water, &c. in which the water is decomposed, and the combustible bodies oxygenated by its oxygen.

It is evident then from the experiments and observations related in this essay, that water is essential to the oxygenation of combustible bodies, and that it is the only source of the oxygen that oxygenates them: it is also evident that when one body is oxygenated,

^{*} Exp. on Air and Fire, Eng. trans. p. 112 and 130.

another at least is restored to the combustible state: hence it appears that the oxygenation of combustible bodies is never effected by a single affinity.

The Antiphlogistians treating of the precipitation of metals by each other say,

"Since the metals cannot remain united to the acids, but in the state of oxides of a determinate degree, it is easily conceived, that by plunging into a metallic solution a metal which has a stronger affinity with oxygene than that which is dissolved, the former must deprive the latter of its oxygene, take its place in the acid, and cause the second to subside in a form more or less metallic, accordingly as it has deprived it of more or less oxygene. This is the reason of the precipitation of silver by copper, copper by iron,"*

But this account of the precipitation of metals by one another cannot be admitted, for it has been proved in every instance of reduction related in this essay, that water is decomposed, and that its hydrogen, is the only substance that restores bodies to their combustible state.

^{*} Essay on Phlogiston. new edit. by Mr. Kirwan, p. 236 and 237.

There is no reason then to suppose that nature deviates in this particular case, from that uniform simplicity, which she constantly observes in all her operations.

Therefore it is obvious, that when one metal precipitates another in a form more or less metallic, the precipitant unites with the oxygen of the water, while the hydrogen of the latter combines with and separates the oxygen of the precipitated metal, and thus reduces it.

The experiments made with phosphorus and metallic solutions in ether, alcohol, and water, prove the truth of this explanation, and shew that when one metal precipitates another in the metallic form, it acts like a stick of phosphorus, decomposing the water.

This account of the reduction of one metal by another is supported by the opinion of Mr. Bergman, who says,

"It is well known, that the calx of copper dissolved in vitriolic acid is precipitated in its metallic form on the addition of iron; and that by means of a double elective attraction, for the iron dissolving in the acid would form an inflammable air by its phlo-

giston, were not the copper present, which takes it up."*

The same author remarks, that a small excess of acid is necessary, and that without it no precipitation begins.

Now since water is decomposed by iron and sulphuric acid, it must be allowed, that when iron is immersed in a solution of sulphate of copper, the water is decomposed by the iron and excess of acid, the iron attracting the oxygen of the water, while the hydrogen of the latter unites to the oxygen of the copper, reduces it, and forms a quantity of water equal to that decomposed.

The precipitation of silver in its metallic form by iron and other metals is to be explained in the same manner, and not by a single affinity as the Antiphlogistians imagine.

The reduction of gold and some other metals, by solutions of sulphate of iron and muriate of tin, is readily accounted for on the principles advanced here; for fresh made solutions of sulphate of iron and muriate of tin contain hydrogen, and have the power of

Chem. Essays, Vol. H. p. 384, Eng. trans.

decomposing water; the oxygen of which unites with the iron and tin, while its hydrogen seizes the oxygen of the gold, &c. reduces it, and forms a quantity of water equal to that decomposed.

The decomposition of water is further proved by the large dilution necessary to form the arbor Dianæ, the purple precipitate of Cassius, and other instances of the reduction of metals by one another.*

* It appears impossible to explain, except by the play of double affinity here pointed out, (by which the decomposition of one substance is accompanied with the formation of another,) the uniform state of the atmosphere at all times, and in all places: without this wise provision, let us for a moment consider the immense consumption of oxygen from the atmospheric mass, by the constant processes of respiration from one thousand million inhabitants of the globe; from at least as many animals, and probably myriads of insects, &c. which all require their proportion of this vivifying element. To these we must add the consumption from domestic and volcanic fires, from fermentation and other processes continually going on in every region—and with these data, let us estimate the probable amount.

By Hale's experiments, a candle with a flame of half a cubic inch, consumed per minute twenty-six cubic inches of air; which by calculation amounts to about six hundred and fifty nine cubic feet per annum. Now supposing each person, in respiration, to consume the same per annum, it will afford an amount of six hundred and fifty nine thousand millions of cubic feet; as much for animals; probably as much for insects; certainly as much for fires, candles, and other sources

of combustion; and the same for every species of fermentative process; and we have the above amount five times multiplied, without extending the view to fish: or equal to three billions, two hundred and ninety-five thousand millions of cubic feet of pure air annually expended; to supply which, nothing but the constant extrication of a similar quantity by co-instantaneous operations, can be supposed adequate to keep the atmosphere in the same uniform state of purity. This apparently could not be the case, were atmospheric oxygen, the sole, or even principal source of supply in these extensive operations: and this view however imperfect, may serve to corroborate the sentiments of the ingenious author.

Am. Ed.

CHAPTER XI.

CONCLUSION.

I SHALL conclude with a general view of the inferences, which I ventured to advance in this essay.

- 1. Neither the Phlogistians nor Antiphlogistians account in a satisfactory manner for the increase of weight, which bodies acquire during combustion.
- 2. Their account of the formation of water, acids, and oxids, is erroneous; for it has been shewn that the oxygen of water alone oxygenates combustible bodies.

- 3. Combustible bodies, as hydrogen, phosphorus, sulphur, charcoal, light, &c. are capable of reducing the metals in the ordinary temperature of the atmosphere; and indeed I might add at a much lower temperature, as I frequently experienced.
- 4. Combustible bodies do not reduce the metals by giving them phlogiston, as the Phlogistians suppose; nor by uniting with and separating their oxygen, as the Antiphlogistians maintain.
- 5. Water is essential both to the reduction and oxygenation of bodies, and is always decomposed in these operations.
- 6. Water does not contribute to metallic reduction merely by dissolving and minutely dividing the particles of metallic salts, and thus removing the impediment opposed to chymical attraction by the attraction of cohesion; for were this the case, metallic solutions in ether and alcohol, in which that impediment is equally removed, should be as readily and effectually reduced as metallic solutions in water are.

This circumstance, in which all the experiments on metallic reduction detailed in this essay exactly coincide, merits particular attention, and shews that the manner, in which combustible bodies effect the reduction, is the same in them all.

- 7. When one body is oxygenated, another at least, is restored at the same time to its combustible state; and vice versa when one body is restored to its combustible state, another at least is at the same time oxygenated.
- 8. Quantities of air and water, equal to those decomposed in the different species of combustion, are constantly forming.

Thus nature by maintaining this balance of power between combustible and oxygenated bodies, prevents the return of original chaos.

Since then in every act of combustion, one body at least is oxygenated, and another restored at the same time to its combustible state, the phenomena of combustion may be referred to two heads, viz.

Oxygenation, or the union of oxygen with combustible bodies, and

Reduction, or the restoration of oxygenated bodiesto their combustible state.

And since in every instance of combustion water is decomposed, and one body oxygenated by the

oxygen of the water, while another is restored to its combustible state by the hydrogen of the same fluid, it follows,

- 1. That the hydrogen of water is the only substance, that restores bodies to their combustible state.
- 2. That water is the only source of the oxygen, which oxygenates combustible bodies.
- 3. That no case of combustion is effected by a single affinity.

This view of combustion may serve to shew how nature is always the same, and maintains her equilibrium by preserving the same quantities of air and water on the surface of our globe; for as fast as these are consumed in the various processes of combustion, equal quantities are formed, and rise regenerated like the Phenix from her ashes.

NOMENCLATURE OF CHYMICAL TERMS

USED IN THIS ESSAY.

NEW NAMES.	OLD NAMES.
Ammonia	Caustic volatile alkali,
Acetite of lead	Sugar of lead.
copper	Verdigris.
Azote (nitrogen)	Base of phlogisticated air.
Azotic gas	Phlogisticated air.
Alkaline sulphure	Liver of sulphur.
Alcohol	Highly rectified spirit of
	wine.
Carbon	Pure coal.
Carbonic acid	Fixed air.
Caloric	Heat.
Hydrogen	Base of inflammable air.
gas	Inflammable air.
Hydrure of sulphur	A compound of hydrogen
	and sulphur.
phosphorus	A compound of hydrogen and phosphorus.
Muriate of tin	Salt of Jupiter.
silver	Luna cornea.
arsenic	Arsenic combined with muriatic acid.
zinc	Marine salt of zinc.
cobalt	Marine salt of cobalt.

NEW NAMES.	OLD NAMES.
Nitric acid	Dephlogisticated nitrous acid.
Nitro-muriatic acid	Aqua regia.
Nitro-muriate of gold	A compound of gold and aqua regia.
platina platina	A compound of platina and aqua regia.
Nitrate of silver	Lunar nitre, chrystals of the moon.
——— mercury	Mercurial nitre.
bismuth	Nitre of bismuth.
- manganese	manganese.
Oxygen	Base of vital air.
——— gas	Vital air.
Oxygenated muriate of mercury.	Corrosive sublimate.
Prussiate of mercury	A compound of mercury and prussic acid.
Phosphorated hydrogen	Phosphorie air.
gas	Coustic wegetable alkali
Potash Sulahuwia athan	Caustic vegetable alkali. Vitriolic ether.
Sulphureous acid gas	Volatile sulphureous acid.
Sulphureted bydrogen gas	
Sulphurated hydrogen gas Sulphate of copper	Blue vitriol.
zinc	White do
iron	Green do.
manganese	Vitriol of manganese.
Soda	Caustic mineral alkali.
Tartrite of antimony	Emetic tartar.

THE END.





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