Physical chemistry for beginners / by Dr. C.M. Van Deventer ; with a preface by J.H. Van 'T Hoff ; translated by R.A. Lehfeldt, D.Sc.

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University of Bristol. Library

Publication/Creation

London : Edward Arnold, [1897]

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PHYSICAL CHEMISTRY

FOR BEGINNERS

VAN DEVENTER

TRANSLATED BY

R. A. LEHFELDT.

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FOR BEGINNERS

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PHYSICAL CHEMISTRY
FOR BEGINNERS

BY

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WITH A PREFACE BY

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SECOND IMPRESSION

London
EDWARD ARNOLD

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Oxford
HORACE HART, PRINTER TO THE UNIVERSITY

25645

PREFACE

When I was lecturing on Chemistry in Amsterdam, especially for medical students, I had a double purpose in view: on the one side, to develop the systematics of the subject moderately fully, and entirely on an experimental basis, and to show how the fundamental laws of Chemistry are arrived at from this groundwork of facts. Each of my chapters was therefore double; to one part fell the consideration of certain elements, to the other that of the conclusions obtained.

I began with 'matter from the qualitative point of view'; water, oxygen, hydrogen, air, and nitrogen supplied the material; then came the concepts, compound, mixture, element, and the whole table of atoms. The halogens constituted the material of the next chapter, in which the laws of mass were introduced, and so it went on through the session.

That had its advantages, but a book was wanting. For the systematic part there were plenty to hand, but for the theoretical hardly one, till the welcome help of this little book of van Deventer, which is now appearing in German. The author has attended my lectures, worked with me in the laboratory, and proceeded further on his own account; conducted practical classes for medical students, and, moreover, in private hours, carried relief to the suffering portion of the medical studentry.

But, from a more general point of view, the author is much to be thanked for having set himself the task of explaining Physical or General Chemistry, after his fashion, to students of Medicine, Pharmacy, and Chemistry, without putting their physical and mathematical accomplishments to too severe a proof. The subject treated of is one which has shown itself in the last few years remarkably fruitful; Physical Chemistry has appeared in the modern world with a journal of its own, and from it, in conclusion, we will quote a favouring sentence addressed to the Old World:

'The immediately impending development of all the sciences in which Chemistry plays a part, from Geology to Physiology, the entire chemical technics included, may perhaps be more clearly seen at the present moment than at any earlier time; they will all suffer a fundamental reformation by the application of the results in General Chemistry, won in recent times.'

J. H. VAN 'T HOFF.

AUTHOR'S PREFACE

In this small work the author has striven to arrange the leading results of Physical Chemistry in such a way that this important branch of modern Chemistry should be accessible to those who have not carried out advanced studies in Mathematics and Physics. The work is thus intended to meet the needs of students of Medicine and Pharmacy, as well as of chemists.

The book is a translation from the Dutch. The author is glad to acknowledge the help of Mr. F. Leviticus, teacher of the German language and literature in Amsterdam, who took part in the translation.

The author has also to express his best thanks to Mr. J. J. van Laar, to whom he is indebted for many numerical details of the latest results.

CH. M. VAN DEVENTER.

AMSTERDAM, 1897.

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TABLE OF CONTENTS

CHAPTER I

DEFINITIONS

PAGE

§ 1. Chemistry 1

§ 2. Substance, element, compound, mixture 1

Note 1. Relative elements 1

2. Mixture and compound 2

3. Crystalline form 2

CHAPTER II

FUNDAMENTAL LAWS OF COMBINATION.

§ 3. Law of the conservation of mass 3

Note 1. History 3

2. Conservation of mass of each element . . 4

§ 4. Law of constant composition 4

Note. History 4

§ 5. Law of multiple proportions 4

Note 1. History. Chemical equations . . . 5

2. Chemical formulae. Representation of the qualitative and quantitative composition of a substance 5

3. Expression by letters, after Berzelius . . 6

4. Conditions for a correct equation. Method for determining coefficients . . . 7

PAGE
5. The equation usually contains only substances which take part in the reaction . 9
6. Second and third method for determining coefficients 9
Problems 11
§ 6. Law of constant proportions 12
§ 7. Law of equivalence of the elements. Definition of equivalence 13
NOTE. Alternative definition of the equivalent . . 14
§ 8. Explanation of the fundamental laws 14
§ 9. Law of Gay-Lussac on the combination of compounds in the gaseous state 15
NOTE 1. This law is a particular case of the preceding laws 15
2. Gaseous compounds must be compared at the same pressure and temperature . . . 16

CHAPTER III

BEHAVIOUR OF GASES

§ 10. Law of Boyle–Gay-Lussac 16
NOTE 1. The law of Boyle and the law of Gay-Lussac separately 17
2. Perfect gases. Vapours 17
§ 11. Law of Gay-Lussac on the reaction of substances in the gaseous state 17
NOTE. History. The law includes that of § 9 . . 17
§ 12. Density of gases. Vapour- or gas-density 18
NOTE 1. Weight of a gas at 0° and 760 mm. is often only a mathematical fiction . . . 18
2. Specific volume 18
3. Importance of a knowledge of the gas-density 19
§ 13. Some methods of measuring gas-densities. Principle. Methods of Regnault, Dumas, Gay-Lussac, modified by Hoffmann, and Victor Meyer 19

PAGE
NOTE 1. Application of Dumas's method at high temperatures. Disadvantage of the process . 20
2. Method of Victor Meyer is the most used. The gas-density need only be known approximately 22
§ 14. Abnormal gas-densities 23
§ 15. Conceptions of the nature of gaseous bodies. Molecules. Atoms 23
NOTE 1. The conception of the nature of liquids and solids is less completely worked out . . 24
2. History 24
§ 16. Avogadro's hypothesis 24
NOTE. History 24
§ 17. Deductions from Avogadro's hypothesis :
(*a*) Molecular weight 25
NOTE 1. Molecular weights are relative numbers . 25
2. Molecular weight only of substances which can be vaporized without decomposition . 25
3. Weight of a litre of gas at 0° and 760 mm. . 25
4. Molecular quantity. Gram-molecule . . 26
5. Explanation of abnormal gas-densities . . 26
§ 18. (*b*) Atomic weight. Theoretical and experimental definition 26
NOTE 1. Atomic weights are relative numbers . . 26
2. The unit is the sixteenth part of an atom of oxygen 26
3. Existence of the highest common factor . . 27
4. Other methods for determining atomic weights 28
5. It is not necessary to analyze the molecular quantity 28
6. The order of magnitude of the atomic weight is given by the highest common factor . 28
7. Approximate correctness of molecular weights 29
§ 19. (*c*) Number of atoms in the molecule 29
NOTE. Special methods of determining the number in case of elements 29

PAGE
§ 20. (*d*) Number of atoms in the molecule of an element . 30
§ 21. (*e*) Derivation of the molecular formula of a substance . 31
Problems 33
NOTE 1. Determination of the molecular quantity in other ways 34
Isomerism. Constitutional formulae 34
Theory of van 't Hoff and Lebel. Asymmetric carbon atom. Malic acid and tartaric acid 36
NOTE 2. Formulae of bodies whose molecular weight is unknown 39
3. Abnormal gas-densities 39
4. Molecular magnitude of liquids . . . 40
§ 22. (*f*) Valency of the elements 41
Problems 43
Symbolism: double bond, triple bond 44
§ 23. (*g*) Theoretical proof of Gay-Lussac's law on the reactions of gases 44
Problems 45

CHAPTER IV

SOME POINTS OF THERMO-CHEMISTRY

§ 24. Law of Dulong and Petit 45
Table 46
NOTE 1. History. Atomic heat 47
2. Exceptions 47
§ 25. Law of Joule 48
NOTE 1. History. Molecular heat. Applications . 48
2. Neumann's rule 49
3. Table of molecular heats of similar compounds 49
§ 26. Application of the two laws to determine atomic weights 50
§ 27. Heat of formation and decomposition of a compound. Heat of reaction. Endothermic and exothermic processes 52

PAGE

NOTE 1. Influence of state of aggregation . . . 53
2. Molecular symbolism neglected . . . 54
3. Heat of neutralization 54

§ 28. Calorimetric methods 54
Mixture calorimeter 54
NOTE 1. Thermal capacity of dilute solutions . . 55
2. Mercury calorimeter not now used. Combustion calorimeter. Method of explosion . 55

§ 29. Law of Lavoisier and Laplace 56

§ 30. Law of Hess :—
Alternative formulation 56
NOTE. History. Explanation 57

§ 31. Applications of law of Hess :—
(*a*) The evolution of heat in a reaction is equal to the sum of the heats of formation of the products diminished by the sum of the heats of formation of the reagents 57
NOTE. Heat of formation a special case of heat of reaction 58
(*b*) Determination of heat of formation by the last-named rule 58
(*c*) Application of the rule to predict heat of reaction 62
NOTE. Correction for external work 62

§ 32. Some general results of investigations on heat of formation. Stable and unstable compounds. Dissociation. Reversible changes 63
NOTE. Heat of formation of dissociable bodies is a latent heat 64
Magnitude of heat of reaction. Heat of neutralization 64
Law of thermo-neutrality 65
Problems 78

§ 33. Principle of maximum work 79
NOTE. Value of and objections to the principle . . 80

§ 34. Applications of the principle of maximum work :—
(*a*) Law of simultaneous reactions 81
NOTE. *Status nascendi*. Predisposing affinities . . 81

PAGE
(*b*) Prediction of reactions 83
(*c*) Proof of the above rules by experience . . . 84
(*d*) Compounds with negative heat of reaction . . 85
(*e*) Explosive substances and mixtures . . . 85
§ 35. Cause of the commencement of a reaction . . . 87
§ 36. Criticism of the principle of maximum work . . . 88
§ 37. Endothermic reactions at normal temperatures. Freezing mixtures. Solution of salts in water. Evaporation of liquids 88
NOTE. Salts with water of crystallization . . . 89
§ 38. Influence of chemical mass 89
§ 39. Dissociation 90
NOTE. History 90
§ 40. Principle of mobile equilibrium 90
NOTE 1. History 91
Salt solutions as example. Esterification . . . 92
NOTE 2. No dissociation at the absolute zero . . 93
§ 41. Chemical equilibrium 93
§ 42. Schematic expression 94
§ 43. Proof of the existence of equilibrium between simultaneous reactions 95
§ 44. The three kinds of chemical equilibrium: (*a*) Homogeneous; (*b*) heterogenous; (*c*) condensed . . . 96
§ 45. Influence of temperature on equilibrium: (*a*) on homogeneous, (*b*) on heterogeneous, (*c*) on condensed equilibrium 96
NOTE. Determination of equilibrium state by calorimetric, volumetric, and optical methods . 97
Transformation temperature 98
§ 46. Influence of pressure on equilibrium: (*a*) on homogeneous, (*b*) on heterogeneous, (*c*) on condensed equilibrium 99
§ 47. Influence of chemical mass on equilibrium . . . 100

PAGE
NOTE 1. Prevention of the action of a substance . . 100
2. History 101
§ 48. Analogy between physical and chemical changes of state 101
§ 49. Laws of Berthollet 102
NOTE. History 103
Explanation 103
§ 50. Watt's principle 104
Applications. Distillation. Fractional distillation . 105
Liquefaction of gases under their own pressure . . 106
§ 51. Watt's principle applied to the transference of bodies at normal temperature 108
Hygroscopic salts and acids. Deliquescence. Efflorescence 109
NOTE 1. Chemical hygroscopy 110
2. Change in the quantity of moisture in the air 112

CHAPTER V

SOLUTIONS

§ 52. Definition. Saturated and supersaturated solutions . 113
NOTE. Aqueous solutions 113
§ 53. Solubility. Influence of temperature and pressure. Law of Henry 114
NOTE 1. Heat of solution in almost saturated solution 114
2. Liquids which mix in all proportions . . 114
§ 54. Each hydrate has its own solubility 114
NOTE. Graphical expression of solubility . . . 115
§ 55. Osmosis 116
Semi-permeable membranes. Osmotic pressure . . 116
§ 56. Osmotic phenomena in dilute solutions 116
Dilute solutions follow the laws of Boyle, Gay-Lussac, and Avogadro 117
NOTE. Determination of the molecular quantity from the osmotic pressure 118

PAGE
§ 57. Experimental data 118
Osmotic pressure, change of freezing point, boiling point, and vapour pressure 118
NOTE 1. Molecular lowering of the freezing point . 118
2. Relation to the latent heat of fusion of the solvent 119
3. Collection of rules 119
4. Determination of molecular weight . . 119
5. Isotonic coefficients. Plasmolysis. Blood-corpuscle method 120
§ 58 Exceptions 121
These occur in strong acids, bases, and salts; generally in aqueous solutions of electrolytes 121
§ 59. Principle of electrolytic dissociation 122
NOTE. Definition of ions 122
§ 60. Some laws of electrolytic dissociation :—
(*a*) Relation between degree of dissociation and dilution 122
(*b*) The most strongly reacting substances are the most dissociated 123
NOTE 1. Symbolism 123
2. Strongly reacting substances interchange their components the most readily . . 123
3. Reactions are commonly reactions of ions . 123
4. Part played by phenolphthaleïn 123
(*c*) Each ion behaves as a molecule with respect to osmotic pressure 124
§ 61. Verification of the theory of electrolytic dissociation . 125
NOTE. Reduction of the conductivity to a definite concentration of the solution . . . 126

CHAPTER VI

PHOTOCHEMISTRY

§ 62. Coloured flames 127
§ 63. Spectroscope 128

PAGE
NOTE 1. Spectrum of gases and of solids 128
2. Pringsheim's researches 128
3. Spectrum of the rare earths 129
§ 64. Absorption spectrum 129
Explanation of dark lines in the solar spectrum and of the constitution of the sun 130
§ 65. Photo-chemical action. Rules 130
NOTE 1. Violet light is not the only active kind of light. The name 'chemical rays' is incorrect 130
2. Absorption of light is not always accompanied by chemical action 131
3. Combination of the products of decomposition prevents reformation of the substance . 131
§ 66. Photo-chemical extinction and induction 131
NOTE. Explanation of the induction in chlorine and hydrogen 132
§ 67. Formation and fixation of a photographic image . . 132
NOTE. Hypothesis to explain the development . . 133
Negative and positive image 133
§ 68 Colour photography 134
Stationary light-waves 134

CHAPTER VII

THE PERIODIC SYSTEM

§ 69. Definitions 135
NOTE 1. Explanation of the term 'periodic function' . 135
2. Second definition 135
3. History of the system 136
§ 70. Graphical representation 136
§ 71. Tabular expression 137
§ 72. Small and large periods 137
§ 73. Specific gravity, atomic volume, fusibility, volatility, atomic heat, valency 138

PAGE

§ 74. Applications of the periodic law :—
  (*a*) Correction of atomic weights 140
  NOTE 1. Co, Ni, and Te appear not to fit in correctly with the system 140
  (*b*) Prediction of undiscovered elements . . . 140
  (*c*) Determination of atomic weight 141
  (*d*) Unit of the elements 141
  NOTE 2. Methods of atomic weight determination . 141

§ 75. Concluding remark on the meaning of the periodic system 142
  Discovery of argon and helium 142

Index 144

LIST OF TABLES

Specific heat of the elements 46
Molecular heat of similar compounds 49
Heat of formation of compounds of the metalloids . . . 66
Heat of formation of compounds of the metals . . . 68
Heat of combustion and of formation of organic compounds . 71
Molecular Heat of evaporation 74
Heat of neutralization of bases 74
Heat of neutralization of acids by soda 75
Heat of solution 76
Natural system of the elements 143

PHYSICAL CHEMISTRY FOR BEGINNERS

CHAPTER I

DEFINITIONS

§ 1. **Chemistry** is the science of the conditions under which one or more substances give rise to new substances, either from themselves, or by mutual action. The description of the substances also, and the phenomena accompanying their production, belong to the province of Chemistry.

§ 2. **Matter or substance** is the name given in chemistry to any homogeneous body, without regard to its form, or state of aggregation.

An element is a substance which cannot be decomposed into other substances.

A compound is a substance composed of two or more elements; the only property of the compound which can be immediately inferred from the properties of the elements, is its weight.

A mixture is a combination of substances in which the latter retain their leading properties.

NOTE I. The substances now called *elements* are so relatively, i. e. they cannot be decomposed by the forces now known to us. The notion of a '*relative element*' was introduced by Lavoisier.

NOTE 2. It is often difficult to explain intelligibly the boundary between compounds and mixtures. The distinction implies a certain conception: in a compound the elements are imagined as such, but so deeply modified by each other's presence that the properties of the whole —with the exception of the weight—are not the sum of the properties of the components: and the behaviour of the compound towards other substances, is by no means that of the free elements. But in a mixture, the constituents are imagined, each with its own properties, so little influenced by the presence of others, that the components act on another substance just as if they were free.

NOTE 3. Solid bodies often form out of liquids, and then form figures enclosed by flat faces. Such substances are called *crystals*. They show certain regularities, on which the systematic study of crystals is based. They are divided into six groups, so that each crystallized chemical compound has its place in one of these groups.

Crystals grow by the deposition of fresh layers of material on the flat faces already existing. On that account, the form of crystals does not essentially depend on their dimensions, but on the angles between the plane faces, since these are unchanged by the *parallel growth* of the crystals. It is however always possible to reduce a crystal to an ideal form, by a displacement of its faces: in this ideal form a certain degree of symmetry is apparent. The degree of symmetry is conditioned by the number of planes of symmetry.

The position of the crystalline faces is often expressed by their intersection with *axes* chosen in the crystal, bearing a definite relation to the planes of symmetry.

The set of crystalline forms which show the same numbers of planes of symmetry, is called a *system of crystals*. There are six of these, with nine, seven, five, three, one, and no planes of symmetry respectively.

Solid substances which do not crystallize are called *amorphous*.

A definite compound may crystallize in more than one system: such cases are usually conditioned by temperature.

CHAPTER II

FUNDAMENTAL LAWS OF COMBINATION

§ 3. **The law of the conservation of mass** (Lavoisier's law). A system of bodies does not change its mass (or weight) when it is transformed into another system.

Other modes of expression. In chemical action, no mass is gained or lost. The mass of a material system is independent of its chemical *form*. In a chemical action, the total mass is the same before and after.

NOTE I. This law was applied dogmatically by Lavoisier, as a principle of method in experimental chemical research. It was adopted as a fundamental law of chemical science, after his death, and largely in consequence of his work.

NOTE 2. From the law of Lavoisier, together with the notion of an element, it follows that not only the mass of the whole system is independent of its chemical form, but also that *each element* is present in the same mass before and after the reaction.

§ 4. The law of constant composition. The composition of a compound is independent of its mode of formation.

Another mode of expression. A compound, defined by a certain totality of physical and chemical properties, has a definite qualitative and quantitative composition.

Example. Alcohol is produced by fermentation of sugar in water. But the same substance can be obtained by the oxidation of ethane, by the action of ethyl iodide on an aqueous solution of potassium hydroxide, and by other reactions. The product, however, which possesses a density of 0·792 and a boiling point of 78°, is always of the same composition: 46 grams of the substance contain 24 grams of carbon, 6 grams of hydrogen, and 16 grams of oxygen.

NOTE. This law was introduced by Prout at the beginning of this century.

§ 5. The law of multiple proportions. When two elements unite to form more than one compound the *different* masses of one element which combine with the same mass of the other are in a ratio expressible by *rational* numbers.

Another mode of expression. A definite mass of an element combines with *different* masses of a second element, in such a way that the latter are in the same ratio as rational numbers.

Example. In the compounds methane, ethane, ethylene, acetylene, benzene, 12 grams of carbon are combined with 4, 3, 2, 1, and 1 gram of hydrogen respectively. In the substances ammonia, ammonium chloride, nitric acid, methylamine, amidobenzene, nitrotoluene, azoic acid, 14 grams of nitrogen occur, with 3, 4, 1, 5, 7, 7, and $\frac{1}{3}$ grams of hydrogen respectively.

NOTE 1. This law was discovered in 1802 by Dalton.

The law of the conservation of mass enables us, according to Lavoisier's procedure, to express chemical reactions by *equations* in which, on the left-hand side of the sign of equality, are placed the substances in the original system, on the right-hand side the products of the reaction.

E.g. sodium hydroxide + hydrochloric acid = sodium chloride + water.

NOTE 2. Since a definite substance has a definite composition, the substance is often named according to its composition. Further, the substances may be designated by a symbol, or *formula*, which expresses its qualitative and quantitative composition. In these formulae letters occur, which stand for elements, and for *characteristic numbers* belonging to them. Coefficients, following the letters, indicate how many times their characteristic numbers are to be taken. How these numbers, which are called atomic weights, are determined, will be explained later.

The substance potassium chloride is represented by the formula KCl: it contains 39 grams of potassium and 35·5 of chlorine. HNO_3 is nitric acid, a substance which, in 63 grams, contains 1 gram of hydrogen, 14 of nitrogen, and 48 of oxygen.

If the substances taking part in a reaction be represented by their formulae—frequently multiplied by a coefficient—arranged in the form of an equation, this affords an exact account of the substances themselves and their relative quantities as they occur in the reaction: the expression then shows exactly the qualitative and quantitative course of the reaction.

The equation

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$$

shows that in the action of sulphuric acid on potassium nitrate, 98 grams of acid are required for each 101 grams of salt: and that in the process 136 grams of potassium hydrogen sulphate and 63 grams of nitric acid are produced.

From the equation

$$2H_2 + O_2 = 2H_2O$$

one learns that 4 grams of hydrogen combine with 32 of oxygen to form 36 of water.

For substances in the state of gas or vapour the formula has a further special meaning, which will be referred to again later. See § 17, Note 3, and § 23.

NOTE 3. Berzelius was the first to indicate the elements by letters, and compounds by combinations of letters: and to attribute a quantitative meaning to the symbols.

The characteristic numbers attached to the letters, now adopted by nearly all chemists, have only been used for about thirty years past.

NOTE 4. It follows from Lavoisier's law and from the definition of an element that a chemical equation must contain, on each side of the sign of equality, the same elements and the same quantity of each. It is not sufficient to know the substances present at the beginning and end of a reaction, and to write them on the two sides of the equation. Thus oxygen and hydrogen combine to form water, but the equation

$$H_2 + O_2 = H_2O$$ [1]

is *incorrect*. In this case it is at once obvious what must be done: for if one writes

$$2H_2 + O_2 = 2H_2O$$

then the equation is in agreement with Lavoisier's law. It is often, however, not so easy to find the right coefficients, and it is only by a methodical investigation that they can be determined. Since the coefficients are required to bring the equation into harmony with Lavoisier's law, and the latter expresses merely the equality between two quantities, but not the absolute value of either, it is clear that only the relative values of the coefficients have to be found.

To explain the method, we will apply it to a special case.

---

[1] Hydrogen and oxygen, it will be explained later, are not to be represented by the symbols H and O, but by H_2 and O_2.

When potassium manganate (K_2MnO_4) is treated with much water, potassium permanganate ($KMnO_4$), manganese dioxide (MnO_2), and potassium hydroxide (KOH) are produced. The equation that represents this reaction must have the form

$$p\,K_2MnO_4 + q\,H_2O = x\,KMnO_4 + y\,MnO_2 + z\,KOH.$$

According to the definition of an element, and to Lavoisier's law, the following equations must hold:

$$\begin{array}{rcr} p\,K_2 = (x+z)\,K & \text{or} & 2p = x+z \;\ldots(a) \\ p\,Mn = (x+y)\,Mn & ,, & p = x+y \;\ldots(b) \\ p\,O_4 + q\,O = x\,O_4 + y\,O_2 + z\,O & ,, & 4p+q = 4x+2y+z \;\;(c) \\ q\,H_2 = z\,H & ,, & 2q = z \;\ldots\ldots(d) \end{array}$$

Here, it will be seen, are five unknown quantities and only four equations. But, as was remarked previously, we are only concerned with the *ratios* of the coefficients; the number of equations is sufficient, and we may choose arbitrarily any whole number for one of the unknowns. If the calculation then leads to fractions for the other unknowns, we are directed to multiply by an appropriate factor, to reduce to whole numbers. *Irrational numbers cannot possibly appear in the results;* for the equations are necessarily linear and the coefficients rational.

Now put $z = 1$, then from (d) $q = \frac{1}{2}$.

By combining (c) and (b) we arrive at

$$-q = 2y - z, \therefore y = \tfrac{1}{4}.$$

From (b) and (a) $p = z - y$, and thence $p = \frac{3}{4}$.

Finally, according to (a) $\frac{3}{2} = x + 1$, whence $x = \frac{1}{2}$.

Multiplying the results of the arithmetic by 4, and arranging in the forms of an equation, we get

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

It is not possible to have more equations than unknown quantities; but it is quite possible that the number of equations should differ by more than one from that of the unknown. E. g. the reaction according to which potassium chlorate gives oxygen, potassium perchlorate, and potassium chloride on heating:

$$p\,KClO_3 = q\,KCl + r\,KClO_4 + s\,O_2$$

gives two independent relations between four unknowns, so that more than one system of values is possible for them. In fact, experiment shows that on the temperature depends which system occurs. Still the equations are linear and their unknowns have whole numbers for coefficients, so that in this case also only rational values of the coefficients are possible.

It is therefore always possible to express a chemical reaction by means of an equation with integral coefficients.

This law will later, in § 23, be made use of for an important application.

NOTE 5. It must not be overlooked that in the equations, only such quantities of each substance occur as take part in the reaction: in the equation

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KOH + MnO_2$$

only a little water occurs. This does not, however, mean that this small quantity of water is enough to make the reaction possible; for the equation only implies that when the reaction has taken place—and it takes place only in presence of much water—the given quantity of water has been converted into another form.

NOTE 6. The method just explained for finding the right coefficients usually leads to the desired conclusion. But it is often easier to refer the chemical changes to a fictitious reaction, whose coefficients can at once be found: when the latter are known, it is not difficult to write down the true equation with its proper coefficients.

Take again the case of the action of water on potassium manganate. K_2MnO_4 is a derivative of the oxide MnO_3: it yields with water $KMnO_4$, a derivative of Mn_2O_7, and the dioxide MnO_2. The fictitious chemical action of the oxides is their formation of MnO_2 and Mn_2O_7 from MnO_3.

For this fictitious reaction we find at once the equation

$$3MnO_3 = Mn_2O_7 + MnO_2;$$

but $3MnO_3$ means $3K_2MnO_4$; Mn_2O_7 means $2KMnO_4$; and there remain 4K over which appear as 4KOH, and therefore require $2H_2O$.

Finally, the action may be divided into several phases: for each phase which corresponds to a simple reaction the equation may be at once written, and by summation the final equation which expresses the beginning and end of the reaction, arrived at.

One knows, e.g., that by the action of potassium bichromate with dilute sulphuric acid on alcohol, aldehyde, potassium sulphate, and chromium sulphate are produced. We may say then: sulphuric acid and potassium bichromate give potassium sulphate and chromic acid; chromic acid dissociates into water and anhydride; the anhydride oxidizes alcohol, with formation of aldehyde and water, and is itself reduced to chromium trioxide. This treatment may be expressed by the equations:

$$\begin{aligned} K_2Cr_2O_7 + H_2SO_4 + H_2O &= K_2SO_4 + 2H_2CrO_4 \\ 2H_2CrO_4 &= 2H_2O + 2CrO_3 \\ 2CrO_3 &= Cr_2O_3 + 3O \\ 3C_2H_6O + 3O &= 3C_2H_4O + 3H_2O \\ Cr_2O_3 + 3H_2SO_4 &= Cr_2(SO_4)_3 + 3H_2O. \end{aligned}$$

By summing these, and leaving out terms which occur on both sides, we arrive at

$$\begin{aligned} K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_6O & \\ = K_2SO_4 + Cr_2(SO_4)_3 + 3C_2H_4O + 7H_2O. \end{aligned}$$

The disappearance of so many substances has a chemical as well as a mathematical meaning. The decomposition of the whole process into phases is a purely mental operation, and the substances which occur in this operation, but not in the actual process, should not find a place in the final equation. The disappearing terms are all formulae of substances, whose existence has to be assumed to connect the equations with one another, and only those substances occur in the final equation which can be observed at the beginning and the end of the reaction.

Problems. Find the equations by which the following reactions may be expressed:

1. The action of dilute nitric acid (HNO_3) and copper (Cu) gives rise to formation of copper nitrate ($Cu(NO_3)_2$), nitric oxide (NO), and water (H_2O).

2. By the action of strong sulphuric acid (H_2SO_4) on copper (Cu), copper sulphate ($CuSO_4$), sulphur dioxide (SO_2), and water (H_2O) are formed.

3. Oxalic acid ($C_2H_2O_4$) is oxidized in presence of dilute sulphuric acid (H_2SO_4) and potassium permanganate ($KMnO_4$) to carbon dioxide (CO_2) and water (H_2O), while potassium sulphate (K_2SO_4) and manganese sulphate ($MnSO_4$) appear as bye-products.

4. Potassium bichromate ($K_2Cr_2O_7$) is decomposed by heating with concentrated hydrochloric acid (HCl), with formation of chromium trichloride (Cr_2Cl_6), chlorine (Cl_2), potassium chloride (KCl), and water (H_2O).

5. Potassium iodide (KI) is oxidized in neutral or alkaline solution of potassium permanganate ($KMnO_4$) to potassium iodate (KIO_3) with formation of MnO_2 and KOH.

§ 6. **Law of constant proportions.** The elements combine in definite ratios of mass, and these ratios often recur when they enter into combination with other elements.

Examples. Ethylene is composed of six parts of carbon to one of hydrogen. Carbon and hydrogen occur in the same proportion in all the hydrocarbon compounds of the ethylene series, and further in all the fatty acids, aldehydes, and dihalogen derivatives of ethylene; the latter substances containing, besides, oxygen or a halogen respectively.

200 grams of mercury combine with 32 grams of sulphur to form mercurous sulphide. The same quantities occur, together with 64 grams of oxygen, in mercurous sulphate.

39 parts of potassium combine with 35·5 of chlorine to form potassium chloride. In potassium chlorate there

is the same quantity of potassium, combined with the same quantity of chlorine, and 48 parts of oxygen.

As a supplement to this law, the following rule may be stated. The ratio of masses of two elements combined with a third are often reproduced when the two are combined with another element.

Examples. 48 parts of oxygen and 14 of nitrogen form a compound with 108 of silver; but one finds also 48 parts of oxygen and 14 of nitrogen combined with 31·75 of copper, with 103 of lead, with 100 of mercury, with 32·5 of zinc, with 68·5 of barium, with 20 of calcium, with 39 of potassium, with 23 of sodium, with 1 of hydrogen.

32 parts of sulphur and 64 of oxygen combine with 216 of silver; but one finds also the same quantity of sulphur and oxygen combined with 206 parts of lead, with 63·5 of copper, 200 of mercury, 65 of zinc, 137 of barium, 40 of calcium, 78 of potassium, 46 of sodium, and 2 of hydrogen.

§ 7. **Law of equivalence of the elements.** The elements in many cases enter into combination in definite relations of mass to one another. The number of grams of an element which are capable of replacing one gram of hydrogen is called the *equivalent* of that element.

Examples. 1 gram of hydrogen combines with 8 grams of oxygen. But the hydrogen can be replaced in its combination with 8 grams of oxygen by 23 grams of sodium, 39 grams potassium, 20 grams calcium, 68·5 grams barium, 9 grams aluminium, 32·5 grams zinc, 31·75 grams copper, 103 grams lead, 100 grams of mercury.

NOTE. The equivalent of an element can accordingly be determined from the amount which combines with 8 grams of oxygen, or with so much of another element as forms a saturated compound with one gram of hydrogen.

§ 8. **Explanation of the fundamental laws.** Only the first three of the six laws mentioned are independent, in that each states something which is not contained in those that precede. The law of constant proportions, and the law of equivalence, may be regarded as particular cases of the law of multiple proportions. Still the formulation of those particular cases is useful: it brings out the existence of important phenomena: without such formulation, important special cases might easily be overlooked.

In order to express the fact that one element often takes the place of another in a combination, the word *substitution* is employed. One may say copper chloride is hydrochloric acid, in which copper is substituted for hydrogen. It should be remarked, however, that the substitution cannot always be accomplished directly. Thus there is no difficulty in substituting zinc for copper in copper sulphate, by merely immersing a zinc rod in the solution of the copper sulphate; but the reverse substitution is not so easy to carry out, and can only be done by more complicated processes. In some circumstances the substitution may be with quantities of an element other than its so-called equivalent. For instance, it is possible to obtain from hydrochloric acid a chlorine compound in which not 31·75 grams copper, but twice that quantity, replace 1 gram of hydrogen.

Especially in organic chemistry, this fact puts difficulties in the way of determining the equivalent—for which substituting quantity is to be called *the* equivalent?—and the manifold substitution made it difficult to express substances by generally applicable formulae at a time when the meaning attributed to the letters was that of equivalents. The atomistic theory developed below spares us the trouble of deciding which is the right equivalent, and avoids the indeterminateness of the nomenclature formerly used. Atomic weight and equivalent stand in a certain relation to one another, but in any stage of experimental chemistry there exists only one atomic weight, while opinions may always differ on the correct equivalent weight.

§ 9. **Law of Gay-Lussac on the combination of elements in the gaseous state.** When a gaseous compound is formed from gaseous elements, the volume of a given mass of the compound bears to the volume of the elements composing it a ratio expressible by whole numbers.

Examples. *Two* litres of gaseous hydrochloric acid are formed by the combination of *one* litre of chlorine and *one* litre of hydrogen. *Two* litres of steam decompose into *two* litres of hydrogen and *one* of oxygen, and can be reformed from the same quantities. *Two* litres of ammonia give, on decomposition, *three* litres of hydrogen and *one* of nitrogen.

Note 1. This law is a special case of a more general one, discovered by Gay-Lussac in 1808, which will be explained below in § 11.

NOTE 2. In comparing the volume of substances in the gaseous state, it is assumed that their temperature and pressure are the same.

CHAPTER III

THE PROPERTIES OF GASES

§ **10. Law of Boyle-Gay-Lussac.** Many substances are changed into the gaseous state by heating, or by reduction of pressure: many others are gaseous at *normal* temperature and *normal* pressure, i.e. at 15° C. and 760 mm. of mercury. For most substances there are limits of pressure and temperature within which for a given mass of substance the relation between pressure, temperature, and volume is given with close approximation by the following equation:

$$\frac{PV}{T} = \frac{PV}{273+t} = C.$$

In this equation V is the volume of a given mass of substance at the *absolute* temperature T and under the pressure P.

Examples. 1 gram of hydrogen at 0° and 760 mm. occupies a volume of 11·16 litres, 1 gram of chlorine 0·324 litres.

NOTE 1. This law is a combination of the law of Boyle,

$$PV = A \quad . \quad . \quad . \quad . \quad (T \text{ constant}),$$

with the law of Gay-Lussac:

$$V_T = V_0 T/273 \quad . \quad . \quad . \quad (P \text{ constant}),$$

or

$$V_T = V_0 (1 + t/273) \quad . \quad . \quad (P \text{ constant}).$$

NOTE 2. Gases are called *perfect* in so far as they obey the above law. *Vapours* may be treated as perfect gases when they are somewhat far removed from the point of condensation. The deviation of gases from the Boyle–Gay-Lussac law belongs rather to the domain of Physics: in this book only the particular case known as that of *abnormal vapour densities* will be touched on (see § 14).

§ 11. Law of Gay-Lussac on the reaction of substances in the gaseous state. When gaseous substances take part in a reaction their volumes bear to one another a ratio expressible by whole numbers, and usually simple.

Examples. Two litres of hydrogen combine with one of oxygen to two of steam (see note to § 12). One litre of chlorine combines with one of hydrogen to two of hydrochloric acid. One litre of methane gives with two of oxygen one litre of carbon dioxide and two of steam. One gram of diamond combines with 1·9 litres of oxygen to 1·9 litres of carbon dioxide.

NOTE. This law was deduced by Gay-Lussac in 1808 from his own researches, and was verified by Humboldt. It includes the law given in § 9.

§ **12. Density of gases.** In chemistry the density of a gas is expressed by comparison with that of air, or more commonly of hydrogen, at the same temperature and pressure. According to the law of Boyle–Gay-Lussac, the ratio of the mass of the same volume of a gas and of hydrogen under the same conditions must be the same, whatever the temperature and pressure chosen. When the volume of a measured weight of gas, under measured pressure and temperature, is known, we can calculate the weight of 1 litre under 0° and 760 mm. according to the law of Boyle–Gay-Lussac. This weight, expressed in grams, divided by 0·0896 grams (the weight of 1 litre of hydrogen at 0° and 760 mm.) gives the *gas-density* of the substance.

NOTE 1. The weight of a substance in the gaseous state at 0° and 760 mm. is often only a *mathematical fiction*, viz. when the maximal pressure at 0° is less than 760 mm. If one says that the density of steam at 0° and 760 mm. is 0·8 grams per litre, that expression is fictitious, for the pressure of steam at 0° cannot exceed 4 mm. The density *would be* 0·8 if steam at 0° could be compressed to 760 mm. without condensation and it obeyed Boyle's law. The fiction is useful because it enables us immediately to compare all gases and vapours with hydrogen; the density of the latter gas at 0° and 760 mm. being accurately determined, and vapour-densities thus easily arrived at.

NOTE 2. The specific volume of a gas is the volume of 1 gram of the gas at 0° and 760 mm., expressed in litres. E. g. for hydrogen this quantity is 1/0·0896 = 11·16 litres.

Note 3. A knowledge of the gas-density is of great importance in chemistry, not only because it is a property of the substance, but because it has been found that a relation exists between the gas-density of a substance and the mass in which it takes part in reactions: relations exist, moreover, between vapour-density and the laws of combination, which find their most complete exposition in the atomistic theory, which will be dealt with shortly (see § 14 et seqq.).

§ 13. Some methods of measuring gas-densities. *General principle.* To calculate the gas-density of a substance—the mass of 1 litre of hydrogen at 0° and 760 mm. being assumed known—one must know the mass of substance employed, its volume in the gaseous state, and the pressure and temperature at which the volume is measured. From these quantities the mass of 1 litre at 0° and 760 mm. may be calculated. This principle is the basis of the following methods:

(*a*) *Regnault's method.* A glass globe whose volume is accurately known is weighed first evacuated, and then filled with the gas, at atmospheric pressure and temperature. The method is adapted to such substances as are gaseous under ordinary conditions, and gives very exact results.

(*b*) *Dumas's method.* Often used for liquids whose boiling point is not high. In a glass globe whose weight and volume are known a small quantity of the liquid to be measured is introduced, and heated in a bath whose temperature is a few degrees above the boiling point of the liquid. The liquid boils, and the vapour, escaping from the narrow neck, drives out the air.

Eventually the bulb is full of the vapour at the temperature of the bath and the pressure of the air: the neck is then sealed off, the bulb removed and weighed.

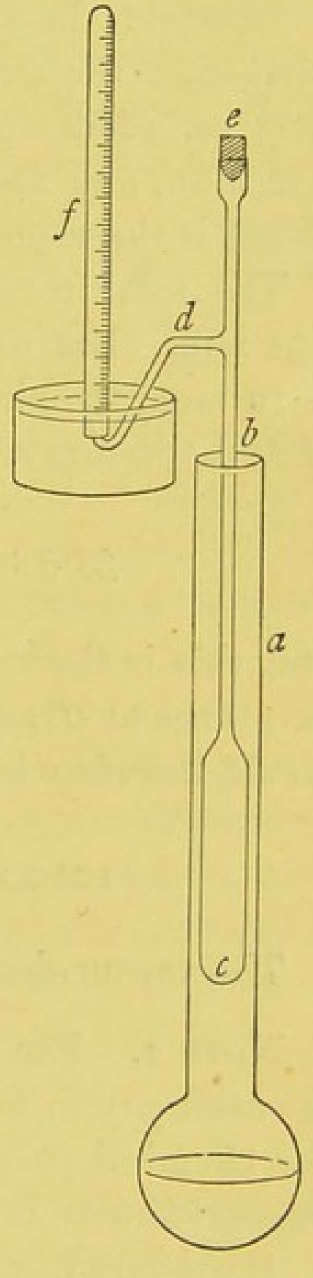
NOTE 1. With some modifications this method is available up to very high temperatures: the glass bulb being replaced by one of porcelain. Dumas's method has the disadvantage that liquids are often mixed with a small quantity of impurity of higher boiling point, so that in the final state the impurity may become of consequence.

(*c*) *Gay-Lussac's method, modified by Hofmann.* Available for liquids of low boiling point. A small bulb, weighed first empty and then full of the liquid, is sealed off and introduced into the empty space of a graduated barometer tube. The latter is surrounded by a jacket, through which passes the vapour of a boiling liquid. The substance is in this way vaporized; the bulb bursts, and the mercury is depressed. The volume is read off the graduation of the tube; the pressure of the vapour is that of the atmosphere diminished by that of the mercury column remaining in the tube; and the temperature is that of the vapour in the jacket.

(*d*) *Victor Meyer's method* (method of displacement of air). In this method the volume of the vapour is not measured directly, but that of the air it displaces is determined instead.

A long glass tube *e c* is provided with the side tube *d*, and the lower part is widened. The jacket *a* which surrounds the greater part of the tube holds a liquid whose vapour on boiling raises the part *c* to a constant temperature. The opening *e* is closed with a stopper;

while *d* delivers into a graduated tube *f* filled with water, inverted over a dish filled with water. The liquid is boiled: the vapour surrounds the tube *c*, the air in it expands and escapes through *d* till the expansion ceases. The opening of *d* is only then brought under the tube *f*: and next, the stopper being taken out for a moment, a little bulb containing a weighed quantity of the substance whose vapour-density is required is slipped in through *e*; the stopper being immediately replaced. The substance evaporates in the lower part of the apparatus, and drives out a volume of air equal to the volume of vapour generated: this air passes through the delivery tube *d* into *f*. When the evaporation of the substance is complete, the production of air bubbles ceases. Since the vapour has driven out an equal volume of air, the volume of the air in *f* is that which the vapour would occupy if it could be cooled to atmospheric temperature, at the atmospheric pressure. The gas-volume is thus reduced to atmospheric pressure and temperature in the experiment itself. The volume of air is measured in the appropriate way, pressure and temperature read, and the former diminished by the saturation pressure of water at the



temperature of observation. When the mass volume, temperature, and pressure have been determined in this way, it is easy to calculate the mass of a litre of the vapour at 0° and 760 mm.

Example. In a vapour-density experiment by Meyer's method, 0·184 grams of a liquid were evaporated, and 37·5 cc. of damp air collected. The barometer read 752 mm., and the temperature of the room was 14° C. What is the vapour-density of the body?

The total pressure of air and water vapour is thus 752 mm. But as the pressure of water vapour at 14° is 12 mm., the air exercised a pressure of 740 mm. At 0° and 760 mm. the volume is accordingly

$$37{\cdot}5 \times \frac{740}{760} \times \frac{273}{273+14} = 35 \text{ cc.}$$

and this is the volume of 0·184 grams of the vaporized substance at 0° and 760 mm. A litre of the substance would therefore have at 0° and 760 mm. a mass

$$1000 \times \frac{0{\cdot}184}{35} \text{ grams} = 5{\cdot}3 \text{ grams.}$$

The vapour-density is therefore $5{\cdot}3 \div 0{\cdot}0896 = 59$.

NOTE 2. For measurements of moderate accuracy it is customary to use Victor Meyer's method; and usually for chemical purposes an approximate measurement of vapour-density is sufficient.

It appears from the description that it is not necessary to know the temperature of the bath in this process, provided it is certainly high enough to evaporate the substance to be studied. If the tube *ec* is made of appropriate material the method can be used up to very high temperatures.

§ 14. **Abnormal gas-densities.** Most gases and vapours behave in such a way that the volume of a given quantity can be measured at any temperature and pressure, and, reduced as above described to 0° and 760 mm., will give always the same density. Each substance has therefore a single gas-density, independent of the temperature and pressure to which it is exposed in the experiment. This rule holds for all bodies which, within certain limits of pressure and temperature, obey the law of Boyle–Gay-Lussac.

But there are substances, such as peroxide of nitrogen and acetic acid, which behave differently: their gas-density depends on the temperature or pressure at which it is determined. For such substances there is a maximum value of the gas-density at low temperatures, and a minimum at high, which does not vary further by further rise of temperature. The latter constant value is taken as correct for acetic acid and similar substances. The density of certain gases is constant over a very wide range of temperature, but diminishes at higher temperatures. This is the case with chlorine. The case of sulphur is noteworthy, as its density at 464° is about four times as great as at 1100°, while from 1100° to 1700° it does not change.

The cases quoted are said to be *abnormal gas-densities.* An explanation of this behaviour is given below (see § 17, note 5; cf. also § 21, note 3).

§ 15. **Conceptions of the nature of gaseous bodies. Molecules. Atoms.** Physics, and also chemistry, makes use of the following conception: a gas consists of a large number of composite particles moving through space in straight lines. Each of these particles, called *molecules*, possesses the same chemical composition as the whole mass of the body. If the latter is a compound, each molecule is composed of heterogeneous parts, of which each consists of a single element. These parts are called *atoms*: they are, according to our present knowledge of chemical processes, indivisible, either by physical or chemical means. A molecule of a gaseous element may also be composed of atoms, but they are in this case of the same kind. The space occupied by the molecule itself is small compared with the space in which it moves.

NOTE 1. The theory of the constitution of liquids has not been worked out so far as that of gases, and that of solids even less.

NOTE 2. The existence of atoms was assumed by Democritus (circa 400 B.C.). In modern chemistry the distinction between the meanings of atom, molecule, and equivalent is chiefly due to Laurent, who worked in the middle of this century.

§ 16. **Avogadro's hypothesis.** At the same temperature and pressure, the same volume of different gases contains the same number of molecules.

NOTE. This hypothesis was put forward by Avogadro in 1811, and by Ampère in 1814, but only in the latter half of the century recognized by most chemists as the basis of a system.

§ 17. Deductions from Avogadro's hypothesis. (*a*) *Molecular weight.* The ratio of the masses of equal volumes of different gases, taken at the same temperature and pressure, is the ratio of the mass of a molecule of the one substance to the mass of a molecule of the other. Taking the mass of a molecule of hydrogen as 2, the mass of the molecule of another gas is called its *molecular* weight.

The molecular weight is thus a *relative number*, expressing the ratio of the mass of a molecule of the substance in the gaseous state to that of a half-molecule of hydrogen. The molecular weight may, however, *also* be defined as the doubled quotient of the weight of a litre of the substance in the gaseous state at 0° and 760 mm., divided by 0·0896 grams.

Briefly, the molecular weight of a substance is twice its gas-density (see § 12).

Note 1. The value 2 for the molecular weight of hydrogen is not one experimentally found, but conventionally *assumed*; consequently all the molecular weights employed in chemistry are only *relative numbers.* The determination of the absolute dimensions of molecules belongs to physics; chemistry needs for the solution of its problems only the relative values.

Note 2. The molecular weight can only be determined directly for such bodies as volatilize without decomposition (cf. § 21, note 3).

Note 3. From the molecular weight of a body its density in the gaseous state can be immediately found: the latter is half the molecular weight multiplied by 0·0896 grams per litre.

NOTE 4. The *molecular quantity* of a substance is the number of grams which contains as many units as the molecular weight.

That quantity is commonly called a gram-molecule of the substance.

NOTE 5. *Explanation of the existence of abnormal gas-densities.* Substances whose gas-densities change with the temperature change also their molecular weights. That may be explained by supposing that their molecules, at low temperatures, consist of more complicated groups than at higher temperatures, and that on rise of temperature these groups break up. This explanation of the phenomena is supported by the fact that for substances with abnormal gas-densities the specific heat is abnormally great and variable; the heat absorbed goes in part only to raise the temperature, the remainder is used up in decomposing the complex molecular groups into simpler.

§ **18.** (*b*) *Atomic weight. Theoretical and experimental definition.* The atomic weight of an element is the ratio of the weight of an atom of that element to the weight of a half-molecule, or atom, of hydrogen.

NOTE 1. The atomic weight also is a ratio—*a relative number.*

NOTE 2. In the table at the end of the book the unit of atomic weight is, for special reasons, chosen not as the atom of hydrogen, but as the sixteenth part of an atom of oxygen. The atomic weight of hydrogen comes, accordingly, to 1·007. If, therefore, the atomic weights given be divided by 1·007 they will give the ratios to one atom of hydrogen.

The atomic weight of an element is the *greatest common divisor* of the *different quantities* of the element which occur in the *molecular quantity of its compounds*.

Examples:

I. Compounds of oxygen.

Name.	Molecular quantity.	Oxygen-content.
Oxygen	32	32
Water	18	16
Carbon monoxide	28	16
Carbon dioxide	44	32
Sulphur dioxide	64	32
Sulphur trioxide	80	48
Nitric acid	63	48
Arsenic trioxide	396	96

Greatest common factor = 16 = atomic weight of oxygen.

II. Compounds of chlorine.

Name.	Molecular quantity.	Oxygen-content.
Chlorine	71	71
Hydrochloric acid	36·5	35·5
Methyl chloride	50·5	35·5
Ethylene dichloride	99	71
Chloroform	119·5	106·5
Carbon tetrachloride	154	142

Greatest common factor = 35·5 = atomic weight of chlorine.

Note 3. The existence of a greatest common factor is in agreement with the law of multiple proportions, but is not a deduction from it. If the molecular quantities of compounds of the elements A and B all contain the same quantity of A, then the law of multiple proportions would necessitate a highest common factor for the quantities of B. But that necessity is not contained in the law. The existence of the highest common factor, which is the actual basis of atomic weights, is a fact which cannot be deduced from any of the laws previously stated, but is derived anew from experience.

It is clear that the atomic weight of an element must be changed if new compounds of it are discovered whose analysis leads to a lower value of the highest common factor.

NOTE 4. We shall give below other methods for determining the atomic weight. But in these the correctness of Avogadro's hypothesis is assumed, so that their results cannot in general invalidate the atomic weight determined by the method just described. When there are but few volatile compounds of an element, the value of the highest common factor does not possess much certainty, and other methods are desirable for the determination and criticism of the atomic weight.

NOTE 5. To determine the composition of the molecular quantity it is not necessary to analyze that quantity. The numbers are calculated from the known percentage composition and the gas-density.

NOTE 6. The highest common factor here considered is a number whose accuracy depends on molecular weights, and therefore on gas-densities. The latter cannot be measured with very high accuracy; but from the highest common factor we can find the *order of magnitude* of the required number, and are in a position to choose it from several possible values, each of which can be determined accurately. Since analysis of pure hydrochloric acid shows that it contains 1 gram of hydrogen to 35·46 grams of chlorine, and its molecular weight is about 36·5, the atomic weight of chlorine can only be 35·46, or an aliquot part of that. The highest common factor is, however, of the order 35·5, so it follows that the exact atomic weight is 35·46.

NOTE 7. The molecular weight too can only be obtained approximately from the gas-density. Here too, then, the results should be corrected by the data derived from analysis, as will be explained later (see § 21).

§ **19.** (*c*) *Number of atoms in the molecule.* When in a compound we know the qualitative and quantitative composition, the molecular quantity, and the atomic weights of the elements, it is easy to find the number of atoms in the molecule. For that purpose it is only necessary to divide the quantity of each element that occurs in the molecular quantity of the compound by its atomic weight.

Examples. The molecular quantity of ethyl alcohol is 46 grams: these 46 grams contain 24 grams of carbon, 16 of oxygen, and 6 of hydrogen. The atomic weights of carbon, oxygen, and hydrogen are 12, 16, and 1. The molecule of ethyl alcohol accordingly contains 2 atoms of carbon, 1 of oxygen, and 6 of hydrogen.

The molecular quantity of oxygen is 32 grams. The molecule of oxygen, therefore, contains 2 atoms.

The molecular quantity of phosphorus is 126; the atomic weight is 31, and the number of atoms, therefore, 4.

NOTE. Certain reactions lead to a knowledge of the number of atoms in the molecule, without investigating the molecular quantity or the atomic weight.

1 litre of hydrogen and 1 of chlorine unite to form 2 litres of hydrochloric acid gas. If hydrogen and chlorine were monatomic gases, then after the reaction there would be only half as many molecules as before, and—according to Avogadro's rule—the volume of the acid would be only half that of the reacting gases. But if chlorine and hydrogen, as well as hydrochloric acid, are assumed to consist of diatomic molecules, then the number of molecules, and therefore the volume, will not be affected by the reaction. As a matter of fact, no contraction occurs in the reaction considered.

It may be put thus: the litre of hydrogen occupies, after the reaction, two litres, so that each molecule must have split into two parts.

In the same way we may consider the formation of two litres of steam from two litres of hydrogen and one of oxygen, or the decomposition of two litres of ammonia gas into one of nitrogen and three of hydrogen.

From these facts it may be concluded that hydrogen, chlorine, oxygen, and nitrogen are not monatomic, but at least diatomic. But such reasoning does not lead to certain results; for theory and observation would still be in agreement if the number of atoms in the molecule were greater than two. It is better, therefore, to solve the problem by means of the molecular quantity and the atomic weight.

§ 20. (*d*) *Number of atoms in the molecules of the elements.* Many elements are diatomic in the gaseous state, e. g. hydrogen, nitrogen, oxygen, chlorine (H_2, N_2, O_2, Cl_2).

Phosphorus vapour is P_4 up to 1040°; at higher temperature its molecules partially split up into P_2. Sulphur vapour at the boiling point of sulphur is S_8; the molecules split into S_2 at higher temperature, and these are stable at the highest temperatures observed. Monatomic are potassium, sodium, zinc, cadmium, and mercury (K, Na, Zn, Cd, Hg)[1]. The vapour-density of the four first-named elements has been determined at very high temperatures, and their atomic weights have not been deduced from the molecular quantity, but in other ways.

The vapour-density of mercury is 100, so that its molecular quantity is 200 grams. The volatile compounds of that element which have been measured all contain 200 grams of it in the molecular quantity. The number of such compounds is, however, small, and doubts might be raised whether mercury really is monatomic. But the atomic weight of 200 is in agreement with the specific heat of solid mercury (cf. § 24); and Kundt's researches on the velocity of sound in mercury vapour give 1·67 for the so-called factor of Laplace; and according to the kinetic theory of gases that is the value it should have for a monatomic gas.

§ 21. (*e*) *Derivation of the molecular formula of a substance.* The molecular formula of a substance expresses in a definite symbolic manner its qualitative and quantitative composition, and the number of atoms present in a molecule in the gaseous state.

This symbolic expression has already been used. The

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[1] The newly-discovered argon [and the others of the same class, helium, &c.] are probably to be counted amongst the monatomic elements.

elements are represented by letters, and each letter stands for not merely an element, but for the quantity represented by its atomic weight. Moreover, the formula gives the gas-density, for that is half the sum of the weights of the atoms.

The substance H_2SO_4, for example, contains for each 2 grams of hydrogen 32 grams of sulphur and 64 of oxygen; its gas- or vapour-density is 49.

We will explain the derivation of the molecular formula from experimental data by means of an example.

Elementary analysis of acetic acid shows that 100 parts of that substance contain 39·9 of carbon, 6·7 of hydrogen, and therefore 53·4 of oxygen. The atomic weights are $C = 12$, $H = 1$, $O = 16$, and the vapour-density has been found to be 30·5.

From the last-mentioned fact it follows immediately that the molecular weight is about 61.

By help of the atomic weights, the expression of the composition may be found in the following way:

Let the formula be $C_pH_qO_r$, i.e. the substance contains $12p$ parts of carbon, q of hydrogen, and $16r$ of oxygen. But the quantities are in the ratio 39·9 : 6·7 : 53·4, so that the formula $C_{\frac{39\cdot9}{12}}H_{6\cdot7}O_{\frac{53\cdot4}{16}}$ shows the results of the analysis. From this we obtain $C_{3\cdot325}H_{6\cdot7}O_{3\cdot337}$, and thence $CH_{2\cdot015}O_{1\cdot004}$. The latter formula may be rounded off into CH_2O.

The results of the analysis are therefore accurately expressed by the formula CH_2O; but that does not prove its correctness, for the formula $C_xH_{2x}O_x$ would equally well agree with the analysis: so that all we can conclude is that the substance possesses a formula of the form $C_xH_{2x}O_x$.

Such a substance, however, would have the gas-density $15x$. But as the gas-density has been found by experiment to be 30·5, it follows that $x = 2$, and the formula for acetic acid $C_2H_4O_2$.

This example shows, what was mentioned in § 18, note 6, that the gas-density need only be determined approximately. What is needed is a value which will decide with what factor to multiply the simplest formula CH_2O.

So to find the molecular formula from experimental data the following procedure is to be adopted:—Divide the percentage number of each element by its atomic weight; round off the quotients thus obtained to the whole numbers they approach; the gas-density corresponding to the *simplest formula* thus found is divided into the gas-density found by experiment, and the round whole number so obtained multiplied into the simplest formula.

Problems. To find the molecular formulae in the following cases.

1. An organic substance of the following composition:

$$C = 51{\cdot}9$$
$$H = 13{\cdot}1,$$
and therefore $$O = 35{\cdot}0,$$

the gas-density being 22·7.

2. A hydrocarbon containing

C 92 per cent.
H 7·7 per cent.,

the gas-density being 38·8.

3. A substance containing in 100 parts
73·8 of carbon,
8·7 of hydrogen,
17·1 of nitrogen,
the gas-density being 80·2.

NOTE 1. If the molecular quantity is known by any other method, the molecular formula may be found in the same way.

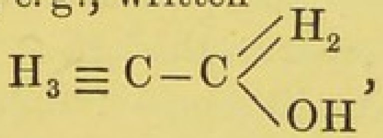
The molecular formula therefore expresses the results of the analysis and the gas-density, and further, the number of atoms in the molecule, but not the mode of arrangement of the atoms. But it is essential to be able to express the arrangement if two different substances have the same molecular formula. In point of fact, that case—known as isomerism—occurs frequently in organic chemistry. Moreover, the conception of a definite arrangement of the atoms in a molecule puts us in a position to express the behaviour of the substance in many reactions.

A formula in which the arrangement of the atoms is indicated is called a *constitutional formula* or *structural formula*; and although the value of such formulae should not be overrated—for all the reactions of the substance do not always lead to the same conclusion as to structure, and which reaction should be taken as decisive of the constitution?—yet in the practice of chemistry their use is very great, for they always bring under one expression many relations of the substance.

Examples. Ethyl alcohol and dimethyl ether—whose molecular formulae are both C_2H_6O—are isomers. The first of the two is attacked by sodium, with formation of sodium ethylate, whose composition is given by the formula C_2H_5ONa. Dimethyl ether has no action on sodium. This difference in chemical properties may be expressed by giving the alcohol the structural formula C_2H_5OH, and the ether $(CH_3)_2O$; for according to these formulae there exists an analogy between alcohol, C_2H_5OH, and water, HOH, which makes the reaction with sodium appear natural, whilst in the structural formula $(CH_3)_2O$ this analogy does not exist.

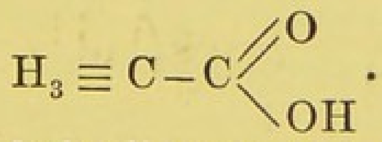
Acetic acid and methyl formate are isomeric, having the molecular formula $C_2H_4O_2$. In acetic acid one hydrogen atom can be replaced by sodium, by the action of soda: methyl formate is not suited to such a substitution; when it is boiled with soda it is decomposed into methyl alcohol and sodium formate. This difference in behaviour towards sodium is expressed in the formulae CH_3COOH for acetic acid, and $HCOOCH_3$ for methyl formate.

The decomposition into groups may be carried further, and ethyl alcohol, e.g., written



$$H_3 \equiv C - C\begin{matrix} \diagup H_2 \\ \diagdown OH \end{matrix},$$

and acetic acid



$$H_3 \equiv C - C\begin{matrix} /\!\!/ O \\ \diagdown OH \end{matrix}.$$

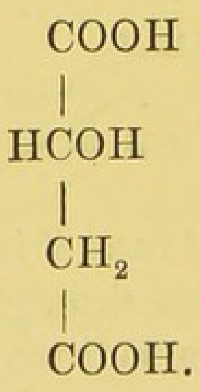
The meaning of the lines in these formulae will be explained later (cf. § 22).

In the above-mentioned cases it is enough to designate the groups; but often this description is not sufficient to express the difference between isomers, and it is necessary to determine exactly the position of the groups in their mutual relations, and to treat the molecule as a figure in three dimensions, and not as a flat figure whose parts can lie in one plane, e. g. that of the paper.

Considerations on this point led van 't Hoff and Le Bel to a theory (1877) which puts us in a position to explain many important cases of isomerism, and express them by formulae. We will develop and explain here one of the most important results of that theory.

There are cases in which two substances have the same chemical properties and, accordingly, the same constitutional formula, whilst they differ in that the solution of the one turns the plane of polarization to the right, while the other turns it to the left by an equal amount. The phenomenon follows this rule: When in the molecule of an organic compound a carbon atom appears in the constitutional formula combined with four *mutually different atoms or groups* the compound is optically active, and there exist two forms, of which one rotates the polarization plane as much to the right as the other to the left.

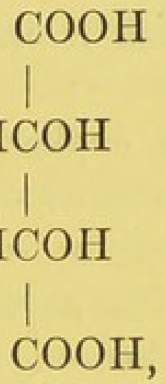
Example. The constitutional formula of malic acid is the following:



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{COOH.} \end{array}$$

The carbon atom of the group $\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}OH}$ is a so-called *asymmetric* carbon atom; it is connected with four different groups (COOH), H, OH, and $(\mathrm{CH_2COOH})$; malic acid is accordingly optically active.

Tartaric acid has the constitutional formula:



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{COOH,} \end{array}$$

and thus contains two asymmetric carbon atoms: it is optically active.

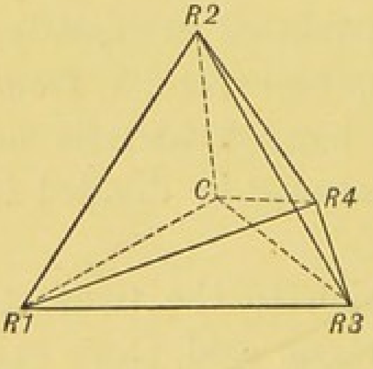
As has been mentioned, the presence of such a carbon atom causes the existence of two active forms; but there is always a third form which is inactive, produced by union of the two active modifications. An important example of these double molecules, which are commonly formed when the substance is produced artificially, is racemic acid, which is inactive, and results from a combination of right- and left-handed tartaric acid. Such a substance, however, may always be divided into the two active components.

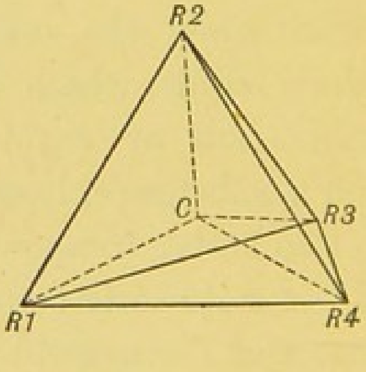
It is noteworthy that in addition to the two active forms and the neutral form of tartaric acid, there exists a fourth modification, which, like racemic acid, is inactive, but cannot be decomposed. This is not in contradiction with the theory; for tartaric acid contains two asymmetric carbon atoms, of exactly equal influence, since the molecule consists of two similar halves. Each half causes an equal rotation of the plane of polarization, and the two may, according to their geometrical arrangement, both rotate to the right, or both to the left, or in opposite senses.

In the latter case the rotations compensate, and a molecule results, which is not divisible, although it is optically inactive.

The following is an explanation of this behaviour of optically active substances :—

Van 't Hoff pictured an active substance as a figure in three dimensions. The asymmetric carbon atom is at the centre of a tetrahedron, and from it four forces are exerted in the direction of the corners, which unite the asymmetric carbon atom with the groups placed at the corners of the tetrahedron. If the central carbon is asymmetric, that implies that the four groups are different, and the substance having the formula $CR_1R_2R_3R_4$ may form the two following figures.





These two figures are not congruent; for it is not possible to rotate them so that all the similar groups agree in position. Moreover, each in itself is completely asymmetric—possessing no plane of symmetry. But if two of the groups are alike, then one plane of symmetry arises, and it is possible to turn the figures so as to be precisely similar.

The conception of the molecule as a tetrahedron thus puts us in a position to represent optical isomerism by formulae.

This connexion between the structure of the molecule and optical activity follows from experience, in so far that in all optically active bodies the presence of one or more asymmetric carbon atoms has been proved. The theory is, moreover, supported by the fact that in solids the property of rotating the plane of polarization is associated with crystallization in asymmetric forms.

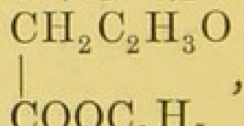
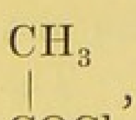
NOTE 2. A molecular formula only, properly speaking, exists for bodies which can be vaporized without decomposition. Thus the molecular weight is derived from the gas-density, or sometimes in other ways—e. g. from the osmotic pressure in solution (cf. § 57, note 4), or from considerations on the constitution. If the molecular weight is unknown, the simplest formula in accordance with the results of analysis is used, and the formula is then nothing more than the expression of the qualitative and quantitative composition.

NOTE 3. In many cases when the molecular weight has not been found from the gas-density, but from other data, the experimentally found gas-density has not agreed with that calculated from the formula. The molecular formula of ammonium chloride, for example, is NH_4Cl. According to that the gas-density should be 26·75 : just half that is found to be the case. This depends on the fact that ammonium chloride is not vaporized as such, but in evaporating dissociates into NH_3 and HCl. A molecule of ammonium chloride thus yields, on vaporization, two molecules, which, according to Avogadro's hypothesis, take up twice as much space. This phenomenon will therefore occur in general when a substance splits up into simpler molecules on conversion into vapour.

If we treat these cases as cases of *abnormal gas-densities* we may say: The gas-density of a substance is abnormal when it does not accord with the molecular formula (cf. § 14 and § 17, note 5).

Note 4. A notion of the size of liquid molecules has lately been attained from the phenomena of surface tension treated from the molecular point of view. It appears that in liquids *association* frequently occurs, i.e. that the molecules of a liquid are frequently multiples of the molecules in the gaseous form.

The liquid molecules are associated in water, all the alcohols, glycols, and organic acids, most ketones, propionitril, nitroethane, phenol, nitric acid, sulphuric acid.

The liquid molecules are not associated in, e.g., CS_2, N_2O_4, $SiCl_4$, PCl_3, $POCl_3$, S_2Cl_2, $SOCl_2$, SO_2Cl_2, $Ni(CO)_4$, C_8H_{18}, CH_4, C_2H_5I, C_2H_5SH, $(C_2H_5)_2O$, CCl_3CHO, $HCOOCH_3$, $ClCOOC_2H_5$,  $\begin{array}{l}CH_2C_2H_3O\\ |\\ COOC_2H_5\end{array}$,  $\begin{array}{l}CH_3\\ |\\ COCl\end{array}$, C_6H_6, C_6H_5Cl, $C_6H_5NO_2$, $C_6H_5NH_3$, pyridine, quinoline.

It has been shown further that the degree of association depends on temperature. The size of the liquid molecule usually, on rise of temperature, approaches that of the gas molecule, and at moderately low temperatures there exists in the liquid an equilibrium between associated and unassociated molecules. The relation between temperature and degree of association for certain bodies is shown in the following table:—

	−89·8° C.	+ 20°	100°	140°	200°	280°
Methyl alcohol	2·65	2·32	2·08	1·97	1·81	—
Ethyl alcohol .	2·03	1·65	1·39	1·27	1·09	—
Water . .	—	1·64	1·41	1·29	—	—
Acetic acid .	—	2·13	1·86	1·72	1·53	1·30

Sulphuric acid at moderate temperatures consists of liquid molecules $(H_2SO_4)_{32}$; above 130° C. these decompose into smaller complexes.

§ 22. (*f*) *Valency of the elements.* The so-called *doctrine of valency* is connected with Avogadro's hypothesis. If we study how many atoms of any element one atom of a certain element can take up to form a *saturated* compound, we find that the number is different for different elements. This capacity is called the *valency* of the element; it may be measured by the number of hydrogen atoms with which an atom of the element in question can combine to form a molecule.

The elements of which one atom can take up the same number of hydrogen atoms are of equal valency; and those elements are clearly of equal valency which can combine with one another to form a molecule containing one atom of each.

Chlorine, bromine, iodine are univalent, for they form the compounds HCl, HBr, HI. Oxygen and sulphur are divalent, forming H_2O, H_2S. Nitrogen and phosphorus are trivalent, with NH_3 and PH_3; carbon and silicon tetravalent, CH_4, SiH_4. Of the same valency are chlorine, bromine, and iodine; oxygen and sulphur; nitrogen and phosphorus; carbon and silicon.

The valency may, under some conditions, be derived from the number of atoms of some other *univalent* element with which an atom of the element considered can unite. *Multivalent* elements cannot, however, as a rule, be used to determine valency, since *mutual* saturation of the atoms of such elements often takes place. Moreover it is amongst the multivalent elements that *variable valency* often occurs, i. e. the fact that the same element may appear in different compounds with different valencies.

In ferrous chloride, $FeCl_2$, iron is divalent; in ferric chloride, $FeCl_3$, trivalent. From the formulae of nitric peroxide, NO_2, and sulphuric anhydride, SO_3, it is not possible to settle the valency of nitrogen or sulphur with certainty.

If the theory of valency were a logical deduction from sharply defined conceptions, it would be possible to determine *a priori* the formulae of compounds from the valency of the elements. Actually, the application of the theory is much restricted in consequence of variable valency and unsaturated compounds. There is no general rule, either, that the highest valency of an element occurs in its most stable compounds. $MnCl_4$ is less stable than $MnCl_2$, while ferrous compounds, on the other hand, are easily oxidized to ferric. It is only in saturated compounds of C, O, and H that it is possible to assume that those elements have a valency of 4, 2, and 1 respectively, and so in many cases to determine the constitution of a saturated organic compound from its molecular formula.

E.g. the molecular formula C_2H_6O can only belong to *two* isomeric substances. The carbon and oxygen have between them ten valencies, of which six are needed to saturate the six univalent hydrogen atoms. If these six are supplied by the carbon atoms, there remain only two to this element which the oxygen can utilize, and we get the formula $H_3C.O.CH_3$ of methyl oxide.

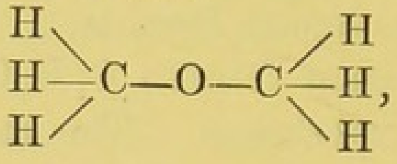
But if one of the valencies of the oxygen is saturated with hydrogen (the oxygen atom cannot, in this case, be saturated with two hydrogen atoms), the other valency of the oxygen must serve to connect it with a carbon atom. The latter element, therefore, uses five of its eight valencies to unite with the hydrogen, one for oxygen, and the remainder saturate one another, giving the formula $HO.CH_2.CH_3$, that of ethyl alcohol.

Problems. 1. Deduce the constitutional formulae of *saturated* substances possessing the molecular formula C_3H_8O.

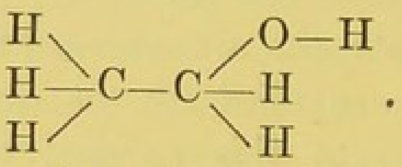
2. Find the constitutional formulae of the substances whose molecular formula is $C_2H_4O_2$, remembering that in those compounds *one* oxygen atom occurs, both of whose valencies are saturated by the same carbon atom.

3. The same problem for substances of the molecular formula $C_3H_6O_3$, assuming that they all contain the univalent group carboxyl OC.OH.

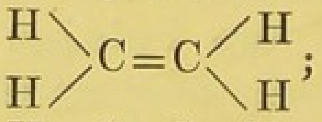
The valencies (bonds) or *units of affinity* are commonly written as strokes proceeding from an atom, mutual saturation being expressed by a joining stroke. Thus methyl oxide may be written



and ethyl alcohol



In unsaturated carbon compounds (i. e. compounds in which the carbon atoms are unsaturated) this condition is usually indicated by joining the carbon atoms by two or three strokes: e. g. ethylene



acetylene $H{-}C{\equiv}C{-}H.$

One should beware of regarding these symbols as representing *forces*; they express nothing more than certain unsaturated states as they occur in ethylene and acetylene.

The terms double and triple bond must not therefore be taken to mean stronger forces between the atoms, but only the degree of saturation.

The quadrivalence of carbon forms the point of departure for the stereochemical theory of van 't Hoff and Le Bel. We cannot here enter into the discussion of the treatment of unsaturated compounds by this theory.

§ **23.** (*g*) *Theoretical proof of Gay-Lussac's law on the reactions of gases.* In § 5, note 4, it was shown how the coefficients in a chemical equation may be found. It appeared that whole numbers for the coefficients can always be found, and that therefore any chemical equation has the form:

$$pAB + qCD + \ldots = rAD + sBC + \ldots,$$

in which p, q, r, s... are whole numbers.

If now gaseous substances occur in the equation, then—since according to Avogadro's hypothesis each molecule occupies one unit of volume—the volume of each substance must be in proportion to its coefficient in the equation, and as the latter are rational numbers must be in rational proportion.

Problems. 1. One litre of methane, CH_4, is burnt with the required amount of oxygen to carbon dioxide and steam. What is the volume of the oxygen, and of the products of combustion?

2. Ten grams of ethyl alcohol are burnt in air. What is the volume of air required, and that of the products of combustion?

CHAPTER IV

SOME POINTS IN THERMO-CHEMISTRY

§ **24. Law of Dulong and Petit.** The product of the atomic weight and the specific heat of all elements in the solid state is nearly the same, viz. 6·4.

TABLE OF THE ELEMENTS WHICH APPROXIMATELY FOLLOW DULONG AND PETIT'S LAW.

Element.	Atomic weight (approximate).	Specific heat.	Product or atomic heat.
Lithium	7	0·9408	6·6
Sodium	23	0·2934	6·76
Magnesium . . .	24·4	0·2499	6·09
Aluminium . . .	27	0·214	5·80
Phosphorus (yellow)	31	0·174–0·190	5·40–5·87
Sulphur (rhombic) .	32	0·1776	5·70
Potassium	39	0·1665	6·47
Calcium	40	0·169–0·172	6·74–6·9
Scandium	44	0·153	6·7
Chromium	52	0·1216	6·32
Manganese	55	0·1217	6·69
Iron	56	0·1138	6·37
Cobalt	59·5	0·1067	6·35
Nickel	59	0·1092	6·44
Copper	63·5	0·093–0·095	5·9–6·0
Zinc	65·5	0.0956	6·26
Gallium	70	0·079	5·53
Arsenic	75	0·0814	6·11
Selenium	79	0·0746	5·9
Bromine	80	0·0843	6·74
Zirconium	90	0·0660	5·94
Molybdenum . . .	96	0·0722	6·92
Ruthenium . . .	102	0·0611	6·23
Rhodium	103	0·058	5·98
Palladium	106	0·0593	6·28
Silver	108	0·0570	6·15
Cadmium	112	0·0567	6·36
Indium	113·5	0·0565–0·0574	6·42–6·53
Tin	118	0·0562	6·64
Antimony	120	0·0508	6·11
Tellurium	125	0·0474	5·94
Iodine	127	0·0541	6·86
Lanthanum . . .	138·5	0·0448	6·20
Cerium	140	0·0448	6·27

Element.	Atomic weight (approximate).	Specific heat.	Product or atomic heat.
Tungsten	184	0·0334	6·15
Osmium	191	0·0311	5·9
Iridium	193	0·0326	6·30
Platinum	195	0·0324	6·31
Gold	197	0·0324	6·39
Mercury (solid) . .	200	0·0319	6·38
Thallium	204	0·0336	6·86
Lead	207	0·0314	6·49
Bismuth	208	0·0308	6·40
Thorium	233	0·0276	6·41
Uranium	239	0·0277	6·65

NOTE 1. This law was discovered in 1819. It may be expressed in the following way: The *atomic heat* is a nearly constant quantity for all solid elements.

NOTE 2. The deviation from the value 6·4 is so great for certain elements—C, Si, B, and Be—that they cannot be included under Dulong and Petit's law. But their atomic heat approaches the normal value with rise of temperature. At ordinary temperatures we have:

Element.	Atomic weight.	Specific heat.	Atomic heat.
Beryllium	9·1	0·408	3·7
Boron	11	0·238	2·6
Carbon (diamond) .	12	0·12	1·44
Silicon	28·1	0·170	4·77

but at high temperatures:

Element.	Atomic weight.	Specific heat.	Atomic heat.
Beryllium at 257° C.	9·1	0·58	5·28
Boron at 600° C. . .	11	0·5	5·5
Carbon at 1000° C. .	12	0·459	5·5
Silicon at 232° C. .	28·1	0·203	5·7

It should be noted that the specific heat of each allotropic modification of a solid element is different.

§ 25. **Joule's law.** An element in a solid compound has the same atomic heat as in the solid free state.

NOTE 1. This law was announced in 1844. It may also be formulated in the following way: The molecular heat of a compound is the sum of the atomic heats of the elements composing it. Elements which show deviation from the law of Dulong and Petit carry those deviations into their compounds. The law of Joule enables us to determine approximately the atomic heat of those elements which cannot be studied in the solid state free. From the molecular heat of silver chloride, diminished by that of silver, it appears that the atomic heat of chlorine is 6 to 6·4. Further, the following values have been obtained from the molecular heat of compounds:

Element.	Atomic weight.	Atomic heat.
Hydrogen	1	2·3
do. (as palladium hydride) . .	1	5·9
Oxygen	16	4
Nitrogen	14	6·4 (?)
Fluorine	19	5
Chlorine	35·5	6·4

The law of Joule may also be applied with good effect in the case of elements which cannot be prepared in sufficient quantity and purity to determine their specific heat directly.

Example. From the atomic heat of lead, and the molecular heat of $PbCO_3$, we get the heat for the group CO_3; subtracting that from the directly measured molecular heat of $BaCO_3$, $SrCO_3$, and $CaCO_3$, the remainder will be the atomic heats of Ba, Sr, and Ca. On the same principle the atomic heat of the following elements has been found :

Element.	Atomic weight.	Atomic heat.
Rubidium	85·4	6·4
Strontium	87·5	6·4
Barium	137	6·4

NOTE 2. The following rule was stated by Neumann as early as 1831. The equivalent quantities of chemically similar substances have the same capacity for heat. E. g. the product of the molecular weight into the specific heat is nearly the same for calcspar, dolomite, magnesite, spathic iron ore, zinc carbonate.

NOTE 3. The following table will serve to test the constancy of the molecular heat of similar compounds :

Substance.	Specific heat.	Molecular heat.	Substance.	Specific heat.	Molecular heat.
Ag_2S . . .	0·0746	18·5	CuCl . . .	0·1383	13·7
CoAsS . . .	0·1070	17·8	HgCl . . .	0·0521	12·3
Cu_2S	0·12	19·1	KCl	0·1730	12·9
FeAsS . . .	0·1012	16·5	LiCl . . .	0·2821	12·0
			NaCl . . .	0·214	12·5
AsS	0·1111	11·9	RbCl . . .	0·112	13·5
CoS	0·125	11·4	NH_4Cl . .	0·373	20·0
FeS	0·1357	11·9			
HgS	0·0512	11·9	$BaCl_2$ . . .	0·0896	18·6
NiS	0·1281	11·6	$CaCl_2$ . . .	0·1642	18·2
PbS	0·0509	12·2	$HgCl_2$ . . .	0.0689	18·7
SnS	0·0837	12·6	$MgCl_2$ . . .	0·1946	18·5
ZnS	0·1230	12·0	$MnCl_2$ . . .	0·1425	18·0
			$PbCl_2$ . . .	0·0664	18·5
AgCl	0·0911	13·1	$SnCl_2$ . . .	0·1016	19·2

Substance.	Specific heat.	Molecular heat.
$SrCl_2$	0·1199	19·0
$ZnCl_2$	0·1362	18.6
$AgBr$	0·0739	13·9
KBr	0·1132	13·5
$NaBr$(impure)	0·1384	14·3
AgI	0·0616	14·5
CuI	0·0687	13·1
HgI	0·0395	12·9
KI	0·0819	13.6
NaI	0·0868	13·0
Cu_2O	0·111	15·9
H_2O (solid)	0·474	8·5
CuO	0·142	11·3
HgO	0·0518	11·2
MgO	0·276[1]	11·0
MnO	0·1570	11·1
NiO	0·1623	12·1
PbO	0·0512	11·4
ZnO	0·1248	10·1
Al_2O_3	0·2173	22·3
As_2O_3	0·1279	25·3
B_2O_3	0·2374	16·6
Bi_2O_3	0·0605	28·3
Fe_2O_3	0·1670	26·7
Sb_2O_3	0·0901	26·3
MnO_2	0·159	13·8
SiO_2	0·1913	11·5
SnO_2	0·0933	14·0

Substance.	Specific heat.	Molecular heat.
TiO_2	0·1703	14·0
K_2CO_3	0·2162	29·9
Na_2CO_3	0·2728	28·9
Rb_2CO_3	0·123	28·4
$BaCO_3$	0·1078	21·2
$CaCO_3$	0·2085	20·9
$PbCO_3$	0·0791	21·1
$SrCO_3$	0·1448	21·4
K_2SO_4	0·1901	33·1
Na_2SO_4	0·2312	32·8
$(NH_4)_2SO_4$	0·350	46·2
$BaSO_4$	0·108	25·2
$CaSO_4$	0·1966	26·7
$CuSO_4$	0·184	29·3
$MgSO_4$	0·2216	26·6
$MnSO_4$	0·182	27·5
$PbSO_4$	0·0872	26·4
$SrSO_4$	0·1428	26·2
$ZnSO_4$	0·174	28
$CoSO_4 + 7H_2O$	0·343	96·4
$FeSO_4 + 7H_2O$	0·346	96·2
$MgSO_4 + 7H_2O$	0·407	100·1
$ZnSO_4 + 7H_2O$	0·347	99·7
KNO_3	0·2388	24·1
$NaNO_3$	0·2782	23·6
NH_4NO_3	0·455	36·4
BaN_2O_6	0·1523	39·8
PbN_2O_6	0·110	36·4
SrN_2O_6	0·181	38·3

§ 26. Application of the two laws to determine atomic weights. When an element forms no, or only

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[1] According to another experiment 0·2439.

a few, volatile compounds, it is not possible to determine the atomic weight from the gas-densities. Knowledge of the specific heats may, however, lead to the quantity required, as the following example will show.

To find the atomic weight of platinum. The true formula of the chloride is unknown: let us call it Pt_pCl_q. Then the quantitative composition may be expressed by the formula $Pt_{\frac{p}{q}}Cl$; but from the analysis it is known that 35·5 grams of chlorine combine with 48·6 of platinum. Moreover, the specific heat of platinum has been measured, and found to be 0·0324; the atomic weight is therefore of the *order of magnitude*

$$6{\cdot}4 \div 0{\cdot}0324 = 197{\cdot}5.$$

The fraction $\frac{p}{q}$ must be the ratio of two whole numbers, and must be near to $\frac{48{\cdot}6}{197{\cdot}5}$. It is at once obvious that this fraction is about $\frac{1}{4}$, so that $\frac{p}{q}$ may be assumed as $\frac{1}{4}$. The formula of the chloride is therefore $PtCl_4$, and the atomic weight of platinum $4 \times 48{\cdot}6 = 194{\cdot}4$. This conclusion is not invalidated by the objection that the formula of platinum chloride may be a multiple of $PtCl_4$.

The law of Joule may be used in the following way to determine, e. g., the atomic weight of barium. 1 kg. of lead combines with 0·0582 kg. of carbon and 0·233 kg. of oxygen to form white lead, whose specific heat is 0·080. The thermal capacity of 1·2912 kg. of white lead is therefore 0·1033 calories. The capacity of 1 kg. of lead is 0·031 calories, so that 0·0582 kg. of carbon + 0·233 kg. of oxygen have together a capacity of 0·0723 calories. But 0·665 kg. of barium combine with the same mass of carbon and oxygen to form 0·956 kg. of barium carbonate. The capacity of the latter is 0·108 calories × 0·956 = 0·1032 calories. So the capacity of 0·665 kg. of barium is 0·0309 calories, and of 1 kg. of barium 0·0465 calories. From this it follows that the atomic weight of barium is of the *order of magnitude* 6·4 ÷ 0·0465 = 138. In barium chloride, however, 35·5 parts of chlorine go to 68·5 of barium. If we give the substance the formula $BaCl_2$ the atomic weight of barium appears as 137, in sufficient agreement with the value 138.

§ **27. Heat of formation and heat of decomposition of a compound. Heat of reaction. Endothermic and exothermic reaction.** The *heat of formation* is the number of calories developed when the molecular quantity of a compound is formed from its elements. E.g. when 78 grams of sodium sulphide are formed from 46 grams of solid sodium and 32 grams of solid sulphur, and the product of reaction has been brought back to the original temperature, the number of calories[1] given out in the process to the calorimeter is 87, and this quantity is the heat of formation of sodium sulphide.

This fact is expressed in the equation:

$$Na_2, S = 87 \text{ Cal.}$$

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[1] 1 Cal. means a large calorie, i.e. the quantity of heat required to raise 1 kg. of water 1°. A small calorie is the thousandth part of that, and may be designated with c. A quantity of 100 small calories is frequently written 1 K. In this book only large calories will be used.

The expression *heat of decomposition* needs no further explanation. The *heat of reaction* is the quantity of heat given out by the molecular quantities of the reacting substances, when the system has recovered its original temperature.

Thus 87 Cal. is the heat of reaction for

$$2Na\,(\text{solid}) + S\,(\text{solid}) = Na_2S\,(\text{solid}).$$

Heat of reaction is also written in the following way :

$$2Na\,(\text{solid}) + S\,(\text{solid}) = Na_2S\,(\text{solid}) + 87\text{ Cal.}$$

$$NaOH\,(\text{dissolved}) + HCl\,(\text{dissolved}) = NaCl\,(\text{dissolved}) + H_2O + 13{\cdot}7\text{ Cal.}$$

$$Na\,(\text{solid}) + H_2O\,(\text{liquid}) = NaOH\,(\text{dissolved}) + H\,(\text{gaseous}) + 43{\cdot}4\text{ Cal.}$$

NOTE 1. The state of aggregation of the reagents must not be neglected as a rule, for the heat of reaction depends on it. Thus

$$NaOH\,(\text{dissolved}) + HCl\,(\text{dissolved}) = NaCl\,(\text{dissolved}) + H_2O\,(\text{liquid}) + 13{\cdot}7\text{ Cal.}$$

but $NaOH\,(\text{dissolved} + HCl\,(\text{gaseous}) = NaCl\,(\text{dissolved}) + H_2O\,(\text{liquid}) + 31\text{ Cal.}$

$$C\,(\text{diamond}) + O_2\,(\text{gaseous}) = CO_2\,(\text{gaseous}) + 94{\cdot}3\text{ Cal.}$$

$$C\,(\text{charcoal}) + O_2\,(\text{gaseous}) = CO_2\,(\text{gaseous}) + 97{\cdot}6\text{ Cal.}$$

The physical state of the substances is often expressed by differences of printing. In this book, however, we shall write down the state, as in the preceding examples.

An *exothermic* reaction is one in which heat is given out : an *endothermic* one in which heat is absorbed.

The reaction

$$2H_2\,(\text{gas}) + O_2\,(\text{gas}) = 2H_2O\,(\text{liquid}) + 136{\cdot}8\text{ Cal.}$$

is exothermic ; but

$$N_2\text{ (gas)} + 3Cl_2\text{ (gas)} = 2NCl_3\text{ (liquid)} - 77\text{ Cal.}$$

is endothermic.

NOTE 2. When a reaction is only considered from the thermal point of view it is not necessary to adhere strictly to molecular nomenclature. Thus one may be permitted to write

$$2H\text{ (gas)} + O\text{ (gas)} = H_2O\text{ (liquid)} + 68{\cdot}4\text{ Cal.}$$

NOTE 3. In certain important cases the heat of reaction has received special names. E. g. that of *heat of neutralization* is commonly used.

§ **28. Calorimetric methods.** Reactions which are to be studied calorimetrically must be completed in a few minutes. The most important of them may be put in two groups. The first group includes the formation and mutual action of salts, processes of solution, and dilution; the second class consists of combustions. The *mixture calorimeter* is a vessel, sometimes of glass but commonly of platinum, in which the solution of a reacting substance is placed. The calorimeter is provided with a jacket to protect it from the temperature variations of its surroundings, and, with its contents, is brought approximately to the temperature of the room. A delicate thermometer is sunk in the liquid, and is continuously moved. A second jacket, near the first, contains a small glass bulb, also with a thermometer; and in this bulb is placed the second reagent. The mercury of the thermometers is only occasionally steady; but as soon as the movement of the mercury is regular, the bulb is emptied into the calorimeter, the liquid well stirred, the highest point reached by the thermometer noted, and the variation of temperature observed for a few minutes after the highest reading has been noted.

In order to carry out the calculations it is necessary to know the thermal capacity of the liquids (the calorimeter and the thermometer), the reading of the two thermometers at the moment of mixing, the highest reading of the thermometer in the calorimeter after mixing, and the mass of the reagents; whilst a correction to the observed rise of temperature is applied by means of the observed variation of temperature before and after the mixing.

NOTE 1. In calorimetric investigations on salt-formation and the mutual action of salts, it is usual to work with very dilute solutions, which show hardly any heat of dilution. In such solutions the thermal capacity is very nearly equal to that of the contained water. To measure a heat of dilution, the solution is placed in the calorimeter, and the glass bulb filled with water.

Heat of solution is determined by bringing the substance to be investigated into water contained in the calorimeter.

NOTE 2. The mercury calorimeter of Favre and Silbermann is no longer used. The *combustion calorimeter* is a calorimeter inside the water of which a combustion chamber is fixed. The gases needed for combustion are led into this chamber, and the products of combustion led away from it in such a manner that they give up all their heat to the water of the calorimeter.

In the *method of explosion* the substance is introduced into the combustion chamber, the latter filled with compressed oxygen, and the whole brought to explosion by an electric spark. The method is applicable both to gaseous and to liquid bodies.

§ **29. Law of Lavoisier and Laplace.** Each compound has a definite heat of formation, which is the same as its heat of decomposition.

It is only in consequence of the correctness of the first part of this law that we are enabled to speak of a definite heat of formation. The second part of the law follows from the principle of the conservation of energy.

§ **30. Law of Hess.** The total evolution of heat by a chemical system in passing from one state to another is independent of the intermediate states.

Special case. The heat of formation of a substance is independent of its mode of formation.

Alternative expression. The evolution of heat accompanying a chemical process is the same, whether the process occurs directly or by stages.

Example:

$$\text{K (solid)} + \text{HCl (dissolved)} = \text{KCl (dissolved)} + \text{H} + 61{\cdot}8 \text{ Cal.}$$

This reaction may be divided into two parts:

$$\text{K (solid)} + n\text{H}_2\text{O}^{1} = \text{KOH (dissolved)} + \text{H} + (n-1)\,\text{H}_2\text{O} + 48{\cdot}1 \text{ Cal.}$$

and $$\text{KOH (dissolved)} + \text{HCl (dissolved)} = \text{KCl (dissolved)} + \text{H}_2\text{O} + 13{\cdot}7 \text{ Cal.}$$

The sum of the heat evolved in these two reactions is equal to that evolved in the first.

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[1] $n\text{H}_2\text{O}$ stands for an indefinitely large quantity of water.

Note. This law was first stated by Hess (1840). It is also called the law of the 'constant heat-total.' It is a particular case of the law of conservation of energy, and so considered it may be stated as: The energy of a material system is a function of its state, and not of the processes by which that state is arrived at; or, The change of energy of a system in passing from one state to another depends on the initial and final states, but not on the intermediate state.

§ 31. **Applications of the law of Hess.** (*a*) *The evolution of heat in a reaction is equal to the sum of the heats of formation of the products diminished by the sum of the heats of formation of the reagents.*

That this highly important result follows from the law of Hess may be easily seen in this way.

Consider the reaction

$$\mathrm{AB + CD + \ldots = AC + BD + \ldots + q\ Cal.},$$

in which AB, &c., are compounds of the elements A, B, &c.

Both the left- and the right-hand side of the equation is a form of the system

$$(\mathrm{A + B + C + D + \&c.}).$$

The first form may be arrived at by the reaction

$$\mathrm{A + B + C + D + \ldots = AB + CD + \ldots} + r\ \mathrm{Cal.},$$

and the second by

$$\mathrm{A + B + C + D + \ldots = AC + BD + \ldots} + s\ \mathrm{Cal.}$$

According to the nomenclature of § 27

$$r = \mathrm{A,\ B + C,\ D}\ ; \qquad s = \mathrm{A,\ C + B,\ D}.$$

If the form (AC + BD) is arrived at by first forming

(AB + CD) from the elements, and then allowing it to undergo a double decomposition, according to the law of Hess we have

$$r + q = s, \quad \text{or} \quad q = s - r,$$

or finally,

$$q = (\mathrm{A}, \mathrm{C} + \mathrm{B}, \mathrm{D}) - (\mathrm{A}, \mathrm{B} + \mathrm{C}, \mathrm{D}).$$

NOTE. If the reaction considered is the formation of a compound from its elements, the heat of reaction is the same as the heat of formation of the compound, and the formation appears as a particular case of the rule. Thus in the reaction

$$\mathrm{K}\ (\text{solid}) + \mathrm{Cl}\ (\text{gas}) = \mathrm{KCl}\ (\text{solid}) + 105{\cdot}6\ \text{Cal.},$$

the heat of reaction, 105·6 Cal., is the heat of formation of KCl.

(*b*) *Determination of the heat of formation by the preceding rule.* This rule is important because by means of it the heat of formation can be found for substances, to produce which by direct union of their elements is either impossible or difficult. For if such a substance takes part in a reaction which proceeds rapidly and can be carried out in the calorimeter, and the heats of formation of the other substances in the reaction are known, from those heats of formation and the heat of reaction the heat of formation of the substance considered may be found.

Examples:

Heat of formation of KOH. We have the reaction

$$\mathrm{K}\ (\text{solid}) + \mathrm{H_2O}\ (\text{liquid}) + \mathrm{Aq}^{1}$$
$$= \mathrm{KOH}\ (\text{dissolved}) + \mathrm{H}\ (\text{gas}) + \mathrm{Aq} + 48{\cdot}1\ \text{Cal.}$$

---

[1] Aq means *much* water.

According to the above rule

$$48{\cdot}1 \text{ Cal.} = \text{K, O, H, Aq} - \text{H}_2\text{, O (liquid)},$$

but $2\text{H (gas)} + \text{O (gas)} = \text{H}_2\text{O (liquid)} + 68{\cdot}4 \text{ Cal.},$

i. e. $\text{H}_2\text{, O (liquid)} = 68{\cdot}4 \text{ Cal.},$

consequently $\text{K, O, H, Aq} = 116{\cdot}5 \text{ Cal.};$

but in the solution of KOH in water

$$\text{KOH} + \text{Aq} = \text{KOH Aq} + 13{\cdot}3 \text{ Cal.};$$

therefore

$$\text{K, O, H} = \text{K, O, H, Aq} - \text{KOH, Aq} = 103{\cdot}2 \text{ Cal.}$$

Heat of formation of KCl. The immediate formation of KCl from its elements cannot be carried out in the calorimeter; but the heat of formation can be deduced from the following reaction, which can be performed in a calorimeter easily:

$$\text{KOH (dissolved)} + \text{HCl (dissolved)} = \text{KCl (dissolved)} + \text{H}_2\text{O} + 13{\cdot}7 \text{ Cal.}$$

For according to the rule

$$13{\cdot}7 \text{ Cal.} = \text{K, Cl, Aq} + \text{H}_2\text{, O (liquid)} - \text{H, Cl, Aq} - \text{K, O, H, Aq}.$$

Of all the quantities in this equation, only K, Cl, Aq is unknown. Inserting the numerical values, we get

$$13{\cdot}7 = \text{K, Cl, Aq} + 68{\cdot}4 - 39{\cdot}3 - 116{\cdot}5,$$

whence $\text{K, Cl, Aq} = +101{\cdot}1 \text{ Cal.};$

but $\text{KCl, Aq} = -\ 4{\cdot}4 \text{ Cal.},$

therefore $\text{K, Cl} = +105{\cdot}5 \text{ Cal.}$

From the heat of formation of KCl, KOH, and H_2O, that of KClO may be found by means of a reaction which easily takes place in the calorimeter:

$$2\text{KOH (dissolved)} + 2\text{Cl (gas)} = \text{KCl (dissolved)} + \text{KClO (dissolved)} + 25{\cdot}4 \text{ Cal.}$$

Heat of formation of ammonia gas. The combustion of ammonia in oxygen can be observed in the calorimeter:

$$2NH_3\text{ (gas)} + 3O\text{ (gas)}$$
$$= 2N\text{ (gas)} + 3H_2O\text{ (liquid)} + 181{\cdot}2\text{ Cal.},$$
$$3H_2, O\text{ (liquid)} = 3 \times 68{\cdot}4 = 205{\cdot}2\text{ Cal.},$$
$$\text{whence}\quad N, H_3 = \tfrac{1}{2}(205{\cdot}2 - 181{\cdot}2) = +12\text{ Cal.}$$

Heat of formation of carbon monoxide. This is deduced from the heat of combustion of diamond to carbon dioxide, and the heat of combustion of carbon monoxide to carbon dioxide.

$$C\text{ (diamond)} + 2O\text{ (gas)} = CO_2\text{ (gas)} + 94{\cdot}3\text{ Cal.},$$
$$CO\text{ (gas)} + O\text{ (gas)} = CO_2\text{ (gas)} + 68\text{ Cal.},$$
$$\text{therefore}\quad C, O = C, O_2 - CO, O = 26{\cdot}3\text{ Cal.}$$

Heats of formation of the hydrocarbons. It is well known that of all the hydrocarbons only acetylene can be formed by direct combination of its elements, and that formation is not suitable for calorimetric study. But most hydrocarbons burn easily in oxygen, and commonly they can be made to explode with that gas; in either case the heat of combustion can be found. The products of combustion are always carbon dioxide and water, the heats of formation of which are known, so that in the thermal equation for the combustion, only the heat of formation of the hydrocarbon is unknown.

This indirect process has, however, a disadvantage, viz. that the heats of combustion of the hydrocarbons are large, while their heats of formation are usually small. So that an error which cannot be avoided even in a careful determination of the heat of combustion will appear somewhat large in comparison with the heat of formation, and as this error will be introduced into the value of the heat of formation, the latter may differ sensibly from its true value.

These circumstances account for the noticeable differences often existing between the results of even the best experimentalists. Thus J. Thomsen found for the *heat of combustion* of ethane 370 calories, Berthelot 390, the difference being 5 or 6 per cent. But if from these values we try to deduce the *heat of formation* of ethane, Thomsen's measurements give 23 calories, while Berthelot's gives 4 calories—numbers in complete disagreement with one another.

The measurements of the heat of combustion of acetylene have given results in good agreement :

$$C_2H_2\,(\text{gas}) + 5O\,(\text{gas}) = 2CO_2\,(\text{gas}) + H_2O\,(\text{liquid}) + 315 \text{ Cal.},$$

$$2C,\, O_2 = 188{\cdot}6, \qquad H_2,\, O\,(\text{liquid}) = 68{\cdot}4;$$

whence $C_2,\, H_2 = -58$ Cal.

Heat of formation of bodies composed of carbon, hydrogen, and oxygen. The heat of formation of these compounds is derived from their heat of combustion, the latter being measured by burning or exploding with oxygen. The difficulty mentioned above shows itself here too.

For the heat of combustion of vapour of methyl alcohol, Thomsen found

$$CH_4O\,(\text{vapour}) + 3O\,(\text{gas}) = CO_2\,(\text{gas}) + 2H_2O\,(\text{liquid}) + 182{\cdot}2 \text{ Cal.},$$

therefore

$$C,\, H_4,\, O\,(\text{vapour}) = -182{\cdot}2 + 94{\cdot}3 + 136{\cdot}8 = 48{\cdot}9 \text{ Cal.}$$

(*c*) *Application of the rule to predict heat of reaction.* In the preceding cases the heat of reaction was used to determine the heat of formation; conversely, the former can be calculated when the heat of formation of all the substances occurring in the reaction is known. And even if it is not known whether the reaction can be realized, it is possible to predict what the production of heat would be when reaction takes place according to a definite equation.

It being known that

$$H_2, S, O_4, Aq = 210{\cdot}9 \text{ Cal.},$$

and

$$Zn, S, O_4, Aq = 248{\cdot}5 \text{ Cal.},$$

it follows that in the reaction

$$Zn\,(\text{solid}) + H_2SO_4Aq = ZnSO_4Aq + H_2\,(\text{gas})$$

there must be an evolution of 37·6 calories.

Again, it has been found that

$$K, Cl\,(\text{solid}) = 105{\cdot}6 \text{ Cal.},$$

$$K, I\,(\text{solid}) = 80{\cdot}1 \text{ Cal.};$$

hence, when reaction occurs according to the equation

$$KCl\,(\text{solid}) + I\,(\text{solid}) = KI\,(\text{solid}) + Cl\,(\text{gas}),$$

an *absorption* of heat of 25·5 Cal. must take place.

NOTE. The following point must be considered in determining the heat of formation of gaseous substances. If the volume of the products of reaction is not the same as that of the reagents, as e. g. in the reactions

$$2NH_3\,(2 \text{ litres}) = N_2 + 3H_2\,(4 \text{ litres}),$$

$$2C_2H_2 + 5O_2\,(7 \text{ litres}) = 4CO_2 + 2H_2O\,(6 \text{ litres}),$$

$$2H_2 + O_2\,(3 \text{ litres}) = 2H_2O\,(2 \text{ litres}),$$

the experimentally found quantity of heat is produced not only by the chemical action, but by the pressure of the atmosphere during the change of volume: comparing the initial and final states of the system, we see that external as well as internal work has been done in the process. It is therefore common to speak of the heat of formation *at constant pressure*, in which the equivalent of the external work is included, and the heat of formation *at constant volume*, which is corrected for the external work. Usually, however, this correction is very small compared with the heat of formation itself, and it will be left out of consideration in what follows.

§ 32. Some general results of researches on heats of formation. *Stable and unstable compounds.* In general compounds are stable towards heat and collision when their heat of formation is positive, and the stability is the greater the greater the heat of formation. A negative heat of formation, on the contrary, usually accompanies instability. Steam and gaseous hydrochloric acid, whose heats of formation are + 58 calories and + 22 calories, are only very slightly dissociated at very high temperatures, and are not at all influenced by pressure or shock. Chloride of nitrogen, on the other hand, whose heat of formation is − 38 calories, is extremely unstable, and decomposes into chlorine and nitrogen on the least incitement. Still, many compounds with negative heats of formation behave under most circumstances as stable. Acetylene, for instance, though its heat of formation is − 58 calories, can suffer many manipulations without being decomposed. It has, however, been shown that this compound is unstable when it is exposed simultaneously to a sudden high pressure and a high temperature.

Substances with positive heat of formation, which decompose partially at high temperatures, possess the property of reforming out of their products of decomposition when the temperature falls again—they show the phenomenon of *dissociation*; the change which they suffer in consequence of rise of temperature is a *reversible* one, i. e. one which proceeds with rise of temperature, and is reversed with fall of temperature, so that when the original temperature is again reached, the state of the material system is the same as at first. In the case of compounds with a negative heat of formation, on the other hand, the decomposition when it once sets in is *complete* and *irreversible*; in this case the term dissociation is not used.

NOTE. The heat of formation of dissociable substances may be regarded as a latent heat, comparable with the internal latent heat of evaporation of water. Although it is measured as an actual quantity of heat, it appears theoretically as latent—as the quantity of energy which must be given to the system to carry out *isothermally* a certain change of state.

In the study of phenomena of dissociation one is obliged to use the heat of formation as measured at low temperatures, and which is equal to the heat of dissociation, in treating reactions which occur at high temperatures; for the phenomena of dissociation can usually be observed and studied only at high temperatures. It is, however, probable that the magnitude of the heat of formation depends on the temperature at which the formation or dissociation occurs.

Magnitude of heats of reaction. Compounds of a halogen with different metals follow the rule that the heat of formation is great for compounds of the so-called strongly positive metals, and the greater the more positive the metal is. In general, chlorides have a higher heat of formation than bromides, and bromides than iodides. Oxygen comes between chlorine and bromine; sulphur is exceeded by both oxygen and iodine.

Strong acids with strong bases in dilute solution all give the same heat of neutralization, 13·7 calories.

Mixtures of dilute solutions of neutral salts which do not yield a precipitate cause as a rule no change of heat (law of thermo-neutrality).

The heats of combustion of saturated hydrocarbons differ for two adjacent members of the same series by + 158 calories. The same phenomenon is observed in the case of many homologous unsaturated hydrocarbons and homologous alcohols; further, in the case of homologous fatty acids, a uniform increase of the heat of combustion for each CH_2 is observed.

Tables are given below containing specific results of thermo-chemical researches.

With regard to heats of combustion of organic substances, it must be expressly noted that the results of Thomsen's measurements frequently differ much from Berthelot's.

It should be noted further that the elements are assumed in that state of aggregation in which they occur under ordinary circumstances. Thus in

$$H, Br = 8{\cdot}4 \text{ Cal.}$$

the hydrogen is gaseous, the bromine liquid, and the hydrobromic acid gaseous. In H_2S the sulphur is assumed octahedral. In the carbon compounds the carbon is always taken as solid and in the form of diamond. Thus $C, H_3, Br, = 11{\cdot}6$ Cal. is to be interpreted

$$\mathrm{C\,(diamond) + Br\,(liquid) + 3H\,(gas)} \\ = \mathrm{CH_3Br\,(gas)} + 11{\cdot}6\ \mathrm{Cal.}$$

HEAT OF FORMATION OF SOME COMPOUNDS OF THE METALLOIDS AT ORDINARY TEMPERATURES.

Substance.	Mode of formation.	Heat produced.			
		Gaseous.	Liquid.	Solid.	Dissolved.
HCl	H, Cl	+ 22	—	—	+ 39·3
HBr	H, Br	+ 8·4	—	—	+ 28·4
HI	H, I	− 6·1	—	—	+ 13·1
H_2O	H_2, O	+ 58	+ 68·4	+ 69·8	—
H_2O_2	H_2, O_2	—	—	—	+ 45·3
H_2O_2	H_2O, O	—	—	—	− 23·1
H_2S	H_2, S	+ 2·7	—	—	+ 7·3
H_2Se	H_2, Se	− 25·4	—	—	− 16·1
H_2Te	H_2, Te	− 35	—	—	—
NH_3	N, H_3	+ 12	—	—	+ 20·4
NH_2OH	N, H_3, O	—	—	—	+ 19·4
H_3P	H_3, P	+ 4·3	—	—	—
H_3As	H_3, As	− 44·1	—	—	—
N_2O	N_2, O	− 17·4	—	—	—
NO	N, O	− 21·5	—	—	—
N_2O_3	N_2, O_3	—	—	—	− 6·8
NO_2	N, O_2	− 7·7	—	—	—
N_2O_4	N_2, O_4	− 2·6	—	—	—
N_2O_5	N_2, O_5	0	—	+ 13·1	+ 29·8
HNO_3	H, N, O_3	—	+ 41·9	—	+ 49·1
HNO_3	$\frac{1}{2}(N_2, O_5, H_2O)$	—	+ 7·7	—	+ 14·9
$H_2S_2O_3$	H_2, S_2, O_3	—	—	—	+ 145·3
SO_2	S, O_2	+ 71	—	—	+ 78·8
SO_3	S, O_3	—	—	+ 103·3	+ 142·5
H_2SO_4	S, O_4, H_2	—	+ 189·9	—	+ 210·9
SeO_2	Se, O_2	—	—	+ 57·2	+ 56·3

Substance.	Mode of formation.	Heat produced.			
		Gaseous.	Liquid.	Solid.	Dissolved.
H_2SeO_4 . .	Se, O_4, H_2 . .	—	—	—	+ 145·2
TeO_2 . . .	Te, O_2 . . .	—	—	—	+ 77·3
H_2TeO_4 . .	Te, O_3, H_2O .	—	—	—	+ 98·5
H_3PO_2 . .	$\frac{1}{2}$(P_2, O, $3H_2O$)	—	—	+ 37·5	+ 37·3
H_3PO_3 . .	$\frac{1}{2}$(P_2, O_3, $3H_2O$)	—	—	+ 125·3	+ 125·2
P_2O_5 . . .	P_2, O_5 . . .	—	—	+ 370	+ 406
CO_2. . . .	C, O_2 . . . (C diamond)	+ 94·3	—	—	+ 98·2
CO_2. . . .	C, O_2. . . . (C amorph.)	+ 97·6	—	—	+ 101·5
CO	C, O . . . . (C diamond)	+ 26·3	—	—	—
CO_2 . . .	CO, O . . .	+ 68	—	—	—
H_3PO_4 . .	H_3, P, O_4 . .	—	—	+ 302·9	+ 305·6
As_2O_3 . . .	As_2, O_3 . . .	—	—	+ 154·7	+ 147
As_2O_5 . . .	As_2, O_5 . . .	—	—	+ 219·4	+ 225·4
B_2O_3 . . .	B_2, O_3 . . .	—	—	+ 317·2	+ 335·2
Cl_2O . . .	Cl_2, O . . .	− 17·8	—	—	− 8·4
$HClO_3$ . .	H, Cl, O_3 . .	—	—	—	+ 24
$HClO_4$ . .	H, Cl, O_4 . .	—	+ 18·3	—	+ 38·6
Br_2O . . .	Br_2, O . . .	—	—	—	− 16·2
$HBrO_3$ . .	H, Br, O_3 . .	—	—	—	+ 12·3
I_2O_5 . . .	I_2, O_5 . . .	—	—	+ 45·3	+ 43·5
HIO_3 . . .	H, I, O_3 . .	—	—	+ 57·9	+ 55·7
HIO_4 . . .	H, I, O_4 . .	—	—	—	+ 47·6
CS_2. . . .	C, S_2. . . . (C diamond)	− 28·7	− 22·3	—	—
ClI. . . .	Cl, I. . . .	—	+ 5·8	—	—
Cl_3I . . .	ICl, Cl_2. . .	—	—	+ 15·7	—
S_2Cl_2 . . .	S_2, Cl_2 . . .	—	+ 14·3	—	—
$SOCl_2$ . . .	S, O, Cl_2 . .	—	+ 49·8	—	—
SO_2Cl_2 . .	S, O_2, Cl_2 . .	—	+ 89·8	—	—
Se_2Cl_2. . .	Se, Cl_2 . . .	—	+ 22·2	—	—
$SeCl_4$ . . .	Se, Cl_4 . . .	—	—	+ 46·2	—
$TeCl_4$ . . .	Te, Cl_4 . . .	—	—	+ 77·4	—
PCl_3 . . .	P, Cl_3 . . .	—	+ 75·5	—	—
PCl_5 . . .	P, Cl_5 . . .	—	—	+ 105	—
PCl_5 . . .	PCl_3, Cl_2 . .	—	—	+ 29·7	—
PCl_3O . . .	P, Cl_3, O . .	—	+ 146	—	—

Substance.	Mode of formation.	Heat produced.			
		Gaseous.	Liquid.	Solid.	Dissolved.
$AsCl_3$ . . .	As, Cl_3 . . .	—	+ 71·5	—	—
BCl_3 . . .	B, Cl_3 . . . (B amorph.)	—	+ 104	—	+ 183·2
$COCl_2$ . . .	C, O, Cl_2 . . (C diamond)	+ 52·9	—	—	—
IBr	I, Br . . .	—	+ 2·5	—	—
S_2Br_2 . . .	S_2, Br_2 . . .	—	+ 1	—	—
PBr_3 . . .	P, Br_3 . . .	—	+ 44·8	—	—
PBr_5 . . .	P, Br_5 . . .	+ 59·1	—	—	—
$AsBr_3$ . . .	As, Br_3 . . .	—	—	+ 44·9	—
S_2I_2 . . .	S_2, I_2 . . .	—	—	0·0	—
P_2I_4 . . .	P_2, I_4 . . .	—	—	+ 19·8	—
PI_3	P, I_3	—	—	+ 10·9	—
AsI_3 . . .	As, I_3 . . .	—	—	+ 12·7	—

The heat of solution of a substance is the difference between its heats of formation in the water-free and in the dissolved state.

HEAT OF FORMATION OF SOME METALLIC COMPOUNDS.

A. Oxides and Haloids.

Substance.	Heat of formation.		Substance.	Heat of formation.	
	Solid.	Dissolved.		Solid.	Dissolved.
K, H, O . . .	+ 103·2	+ 116·5	Sr, O_2, H_2 .	+ 214·5	+ 226·1
K_2, O . . .	—	+ 164·6	Ba, O_2, H_2 .	+ 214·9	+ 227·1
Na, H, O . .	+ 101·9	+ 111·8	Mg, O_2, H_2 .	+ 217·3	—
Na_2, O . . .	+ 100·2	+ 155·2	Al_2, O_6, H_6 .	+ 594	—
Li, H, O . .	—	+ 117·4	Mn, O, H_2O .	+ 94·8	—
N, H_3, Aq .	—	+ 20·3	Zn, O . . .	+ 85·3	—
Mg, O . . .	+ 144	—	Zn, O, H_2O .	+ 82·7	—
Ca, O . . .	+ 131	+ 149·5	Cd, O, H_2O .	+ 65·7	—
Sr, O	+ 128·4	+ 157·7	Fe, O, H_2O .	+ 68·3	—
Ba, O . . .	+ 124·2	+ 158·7	Fe_2, O_6, H_6 .	+ 396·4	—
Ca, O_2, H_2 . .	+ 214·9	+ 217·9	Ni, O, H_2O .	+ 60·8	—

Substance.	Heat of formation.	
	Solid.	Dissolved.
Co, O, H_2O	+ 63·4	—
Pb, O	+ 50·3	—
Cu, O	+ 37·2	—
Cu_2, O	+ 40·8	—
Ag_2, O	+ 5·9	—
Hg_2, O	+ 22	—
Hg, O	+ 20·1	—
Sn, O, H_2O	+ 68·1	—
$Au_2, O_3, (H_2O)_3$	− 13·2	—
Pt, O, H_2O	+ 17·9	—
K, Cl	+ 105·6	+ 101·2
K, Br	+ 95·3	+ 90·2
K, I	+ 80·1	+ 75
K, F	+ 109·5	+ 113·1
Na, Cl	+ 97·6	+ 96·4
Na, Br	+ 85·8	+ 83·9
Na, I	+ 69·1	+ 70·3
Na, F	+ 109	+ 108·4
N, H_4, Cl	+ 75·8	+ 71·9
N, H_4, Br	+ 65·4	+ 61
N, H_4, I	+ 49·3	+ 45·8
Li, Cl	+ 93·8	+ 102·2
Ca, Cl_2	+ 169·8	+ 187·2
Ca, Br_2	+ 140·9	+ 165·4
Ca, I_2	+ 107·3	+ 135
Ba, Cl_2	+ 194·7	+ 196·8
Ba, Br_2	+ 170	+ 175
Sr, Cl_2	+ 184·6	+ 195·7
Sr, Br_2	+ 157·7	+ 173·8
Mg, Cl_2	+ 151	+ 186·9
Zn, Cl_2	+ 97·2	+ 112·8
Zn, Br_2	+ 76	+ 91
Zn, I_2	+ 49·2	+ 60·5
Mn, Cl_2	+ 112	+ 128
Fe, Cl_2	+ 82·1	+ 100
Fe, Br_2	—	+ 78·2
Fe, I_2	—	+ 46·4
Fe, Cl_3	+ 96·1	+ 126·1
Al, Cl_3	+ 161	+ 237·8
Al, Br_3	+ 119·7	+ 205
Al, I_3	+ 70·4	+ 159·4
Co, Cl_2	+ 76·5	+ 94·8
Ni, Cl_2	+ 74·5	+ 93·7
Hg, Cl	+ 31·4	—
Hg, Br	+ 24·1	—
Hg, I	+ 14·1	—
Hg, Cl_2	+ 53·3	+ 50
Hg, Br_2	+ 40·5	—
Hg, I_2	+ 24·2	—
Cu, Cl	+ 32·9	—
Cu, Br	+ 25	—
Cu, I	+ 16·3	—
Cu, Cl_2	+ 51·6	+ 62·7
Cu, Br_2	+ 32·6	+ 40·8
Cd, Cl_2	+ 93·2	+ 96·2
Cd, Br_2	+ 75·2	+ 75·6
Cd, I_2	+ 48·8	+ 47·9
Pb, Cl_2	+ 82·8	+ 76
Pb, Br_2	+ 64·5	+ 54·5
Pb, I_2	+ 39·8	—
Ag, Cl	+ 29·4	—
Ag, Br	+ 22·7	—
Ag, I	+ 13·8	—
Au, Cl	+ 5·8	—
Au, Br	− 0·1	—
Au, I	− 5·5	—
Au, Cl_3	+ 22·8	+ 27·3
Au, Br_3	—	+ 5·1
Sn, Cl_2	+ 80·8	+ 81·1
Sn, Cl_4	+ 127·3	+ 157·2
Pt, Cl_4	+ 59·8	+ 79·4
Pt, Br_4	+ 42·4	+ 52·3

B. Sulphides.

Substance.	Heat of formation.		Substance.	Heat of formation.	
	Solid.	Dissolved.		Solid.	Dissolved.
K_2, S	+101·2	+111·2	Fe, S, nH_2O	+ 23·8	—
K, H, S	+ 62·3	+ 63·1	Co, S, nH_2O	+ 19·7	—
Na_2, S	+ 87	+102	Ni, S, H_2O	+ 17·4	—
Na, H, S	+ 54	+ 58·4	Zn, S, nH_2O	+ 39·6	—
Ba, S	+ 98·3	—	Cd, S, nH_2O	+ 32·4	—
Sr, S	+ 97·4	—	Cu, S	(+8·1)[1]	—
Ca, S	+ 89·6	—	Cu_2, S	+ 18·3	—
Mg, S	+ 77·6	—	Hg, S	(+4·8)[1]	—
Al_2, S_3	+122·4	—	Ag_2, S	(+3·3)[1]	—
Mn, S, nH_2O	+ 44·4	—	Pb, S	+ 18·4	—

C. Oxy-salts.

Carbonates ($C=diamond$).		
K_2, C, O_3	+278·4	+284·9
Na_2, C, O_3	+269·9	+275·4
Ba, C, O_3	+280·5	—
Sr, C, O_3	+277·5	—
Ca, C, O_3	+267·7	—
Mn, C, O_3	+210·8	—
Cd, C, O_3	+179·2	—
Ag_2, C, O_3	+120·2	—
Pb, C, O_3	+166·9	—
K, H, C, O_3	+232·9	+227·6
Na, H, C, O_3	+227	+223·7
Sulphates.		
K_2, S, O_4	+344·6	+338·2
K, H, S, O_4	+277·5	+273·7
Na_2, S, O_4	+328·4	+329
Na_2, H, S, O_4	+267·8	+266·6
N_2, H_8, S, O_4	+282·2	+279·7
Mg, S, O_4	+302·3	+322·6
Ba, S, O_4	+338·1	—
Ca, S, O_4	+318·4	+318·4
Sr, S, O_4	+331	—
Zn, S, O_4	+230	+248·5
Mn, S, O_4	+249·9	+263·7
Co, S, O_4	—	+230·5
Ni, S, O_4	—	+229·7
Fe, S, O_4	—	+235·6
Cu, S, O_4	+182·8	+198·4
Cd, S, O_4	+221·2	+231·9
Ag_2, S, O_4	+167·3	+162·8
Pb, S, O_4	+216·2	—
Nitrates.		
K, N, O_3	+119·5	+111
Na, N, O_3	+111·3	+106·3
N, H_4, N, O_3	+ 88	+ 81·8
Ba, N_2, O_6	+226·2	+216·8
Sr_2, N_2, O_6	+219·8	+215·2
Ca, N_2, O_6	+202·6	+206·6
$Mg, N_2, O_6, 6H_2O$	+210·5	+206·3
$Sr, N_2, O_6, 4H_2O$	+227·7	+215·2

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[1] Not certain.

Substance.	Heat of formation.		Substance.	Heat of formation.	
	Solid.	Dissolved.		Solid.	Dissolved.
Ca, N_2, O_6, $4H_2O$	+ 213·8	+ 206·6	Na, Cl, O_3	+ 86·8	+ 81·2
Zn, N_2, O_6, $6H_2O$	+ 138·1	+ 132·3	Na_2, S, O_3	+ 260·5	+ 262·9
Cu, N_2, O_6, $6H_2O$	+ 93	+ 82·3	Na_2, S_2, O_6	+ 398·9	+ 393·5
Cd, N_2, O_6, $4H_2O$	+ 121·1	+ 116·1	Na_2, H, P, O_4	+ 413·9	+ 419·5
Pb, N_2, O_6	+ 105·5	+ 97·9	N, H_4, N, O_2	+ 64·9	+ 60·2
Ag, N, O_3	+ 28·7	+ 23·3	K, Mn, O_4	+ 195	+ 184·8
			Bi, Cl_3	+ 90·6	—
			Bi, O, Cl	+ 88·2	—
Other Salts.			Na_2, Pt, Cl_6, $6H_2O$	+ 288·3	+ 277·7
K, O, Cl	—	+ 88·8	K, C, N	+ 29·8	+ 26·8
K, Cl, O_3	+ 95	+ 85	Na, C, N	+ 25·5	+ 25
K, Cl, O_4	+ 113·1	+ 101	Hg, C_2, N_2	− 52	− 55
K, Br, O_3	+ 84·1	+ 74·3	Ag, C, N	− 31·2	—
K, I, O_3	+ 124·5	+ 117·4	AgCN, KCNAq	—	+ 6·5
Na, O, Cl	—	+ 83·4	K, O, C, N	+ 34·3	+ 29·1

HEAT OF COMBUSTION AND HEAT OF FORMATION OF SOME ORGANIC SUBSTANCES.

Saturated Hydrocarbons.

C = Diamond.

Substance.	Formula.	Heat of combustion.	Heat of formation (constant volume).	Observer.
Methane	CH_4	+ 213·8	+ 16·5	Thomsen
Ethane	C_2H_6	+ 370·5	+ 22·1	,,
Propane	C_3H_8	+ 529·2	+ 25·4	,,
Butane	$(CH_3)_3CH$	+ 687·2	+ 29·1	,,
Pentane	$(CH_3)_4C$	+ 847·1	+ 31·5	,,
Hexane (liquid)	C_6H_{14} (normal)	+ 989·2	+ 53·2	Stohmann
Heptane (liquid)	C_7H_{16} (normal)	+ 1137·5	—	Luginin

Unsaturated Hydrocarbons.

Substance.	Formula.	Heat of combustion.	Heat of formation (constant volume).	Observer.
Ethylene	C_2H_4	+333·4	− 12·8	Thomsen
Propylene	C_3H_6	+492·7	− 6·0	"
Isobutylene	C_4H_8	+650·6	− 1·9	"
Amylene (gaseous)	C_5H_{10}	+807·6	+ 3·1	"
Diallyl	C_6H_{10}	+932·8	− 27·8	"
Acetylene	C_2H_2	+315·0	− 58	Berthelot
Allylene	C_3H_4	+467·6	− 48·9	Thomsen
Halogen Derivatives.				
Methyl chloride	CH_3Cl	+164·8	+ 19·2	Thomsen
Ethyl chloride	C_2H_5Cl	+321·9	+ 24·2	"
Propyl chloride	C_3H_7Cl	+480·2	+ 27·8	"
Isobutyl chloride	C_4H_9Cl	+637·9	+ 32·2	"
Vinyl chloride	C_2H_3Cl	+286·2	− 7·9	"
Chloroform	$CHCl_3$	+ 70·5	+ 20·9	"
Carbon tetrachloride	CCl_4	—	+ 18·4	"
Methyl bromide	CH_3Br	+184·7	+ 11·6	"
Ethyl bromide	C_2H_5Br	+341·8	+ 16·6	"
Propyl bromide	C_3H_7Br	+499·3	+ 21·1	"
Amyl bromide	$C_5H_{11}Br$	—	+ 27·1	Berthelot
Allyl bromide	C_3H_5Br	+462·1	− 9·6	Thomsen
Ethylene dibromide (gaseous)	$C_2H_4Br_2$	—	+ 15	Berthelot
Methyl iodide	CH_3I	+201·5	− 4·7	Thomsen
Ethyl iodide	C_2H_5I	+359·2	− 0·6	"
Alcohols (gaseous).				
Methyl alcohol	CH_3OH	+182·2	+ 47·9	Thomsen
Ethyl alcohol	C_2H_5OH	+340·5	+ 51·5	"
Propyl alcohol	C_3H_7OH	+498·6	+ 56	"
Isobutyl alcohol	C_4H_9OH	+658·5	+ 57·5	"
Isoamyl alcohol	$C_5H_{11}OH$	+820·1	+ 58	"
Allyl alcohol	C_3H_5OH	+464·8	+ 21·6	"
Propargyl alcohol	C_3H_3OH	+431·1	− 12·7	"

Acids.

Substance.	Formula.	Heat of combustion.	Heat of formation (constant volume).	Observer.
Formic acid (gaseous)	CH_2O_2	+ 69·4	+ 92·8	Thomsen
Acetic acid (gaseous)	$C_2H_4O_2$	+ 225·4	+ 98·6	”
Propionic acid (gaseous)	$C_3H_6O_2$	+ 386·5	+ 99·1	”
Capric acid	$C_{10}H_{20}O_2$	+ 1455·6	—	Stohmann
Lauric acid	$C_{12}H_{24}O_2$	+ 1747·6	—	”
Myristic acid	$C_{14}H_{28}O_2$	+ 2052·9	—	”
Palmitic acid	$C_{16}H_{32}O_2$	+ 2361·9	—	”
Stearic acid	$C_{18}H_{36}O_2$	+ 2677·8	—	”
Oxalic acid	$C_2H_2O_4$	+ 60·2	+ 196·7	”
Malonic acid	$C_3H_4O_4$	+ 207·3	—	”
Succinic acid	$C_4H_6O_4$	+ 356·8	—	”
Tartaric acid	$C_4H_6O_6$	+ 261·8	—	”
Other Substances.				
Dimethyl ether (gas.)	$(CH_3)_2O$	+ 349·4	+ 42·7	Thomsen
Diethyl ether (gaseous)	$(C_2H_5)_2O$	+ 659·6	+ 56·5	”
Glycerine	$C_3H_5(OH)_3$	+ 396·8	—	Stohmann
Acetaldehyde (gaseous)	C_2H_4O	+ 281·9	+ 42·5	Thomsen
Hydrocyanic acid (gas.)	HCN	+ 158·6	− 30·2	”
Cyanogen (gaseous)	$(CN)_2$	+ 259·6	− 71	”
Acetonitril (gaseous)	CH_3CN	+ 312·1	− 21·6	”
Methylamine (gaseous)	CH_3NH_2	+ 258·3	+ 5·7	”
Dimethylamine (gas.)	$(CH_3)_2NH$	+ 420·5	+ 5·6	”
Urea	$CO(NH_2)_2$	+ 152·2	+ 77·5	Stohmann
Mercaptan (gaseous)	CH_3SH	+ 298·8	+ 5·4	Thomsen
Benzene	C_6H_6	+ 787·8	−17·1 (gas.) − 9·1 (liquid)	Stohmann
Phenol (solid)	C_6H_5OH	+ 731·9	—	”
Benzoic acid	$C_7H_6O_2$	+ 770·5	—	”
Phthalic acid	$C_8H_6O_4$	+ 771·9	—	”
Salicylic acid	$C_7H_6O_3$	+ 729·5	—	”
Thiophene (gaseous)	C_4H_4S	+ 610·6	− 26·2	Thomsen
Dextrose	$C_6H_{12}O_6$	+ 673·7	—	Stohmann
Cane sugar	$C_{12}H_{22}O_{11}$	+ 1352·7	—	”
Cellulose	$C_6H_{10}O_5$	+ 678·0	—	”
Starch	$C_6H_{10}O_5$	+ 677·5	—	”

MOLECULAR HEAT OF EVAPORATION OF SOME ORGANIC COMPOUNDS.

Carbon disulphide . .	6·4	Methyl iodide . . .	6·5
Ethyl alcohol	9·8	Chloroform	7·3
Amyl alcohol	10·7	Carbon tetrachloride .	7·2
Aldehyde	6·0	Ethyl chloride . . .	6·45
Acetone	7·5	Ethyl bromide . . .	7·5
Chloral	8·0	Ethyl iodide	9·2
Chloral hydrate . . .	21·9	Ethylene dibromide .	8·2
Formic acid	5·6	Methyl alcohol . . .	8·45
Acetic acid	7·25	Butyric acid	10·1
Hydrocyanic acid . .	5·7	Valerianic acid . . .	10·6
Benzene	7·2	Ether	6·7

HEAT OF NEUTRALIZATION OF BASES.

Solutions containing two equivalents of acid or base dissolved in 400 mol. water. (But many bases are insoluble.)

Base.	H_2SO_4, Aq	2ClH, Aq	$2NO_3H$, Aq	$2C_2H_4O_2$, Aq
2NaOH, Aq . . .	31·4	27·5	27·4	26·8
2KOH, Aq . . .	31·3	27·5	27·5	26·6
2LiOH, Aq . . .	31·3	27·7	27·8	—
$2NH_3$, Aq	28·2	24·4	24·6	23·8
$Ba(OH)_2$, Aq . .	(36·9)	27·8	28·2	26·8
$Sr(OH)_2$, Aq . .	30·7	27·6	27·8	26·6
$Ca(OH)_2$, Aq . .	31·1	27·6	—	26·8
$Mg(OH)_2$	31·1	27·7	27·6	—
$Mn(OH)_2$	26·5	23·0	23·0	22·6
$Ni(OH)_2$	26·3	22·6	—	—
$Co(OH)_2$	24·7	21·1	—	—
$Fe(OH)_2$	24·9	21·4	—	—
$Zn(OH)_2$	23·5	19·9	19·9	18·0
$Cd(OH)_2$	23·8	20·3	20·6	—
$Cu(OH)_2$	18·4	14·9	14·9	12·8
PbO	(23·4)	(16·8)	17·8	15·5
HgO	—	18·9	6·4	—

Base.	H_2SO_4, Aq	$2ClH$, Aq	$2NO_3H$, Aq	$2C_2H_4O_2$, Aq
Ag_2O	14.5	(42.5)	10.9	—
$\frac{2}{3}Al(OH)_3$	21.0	18.6	—	—
$\frac{2}{3}Cr(OH)_3$	16.4	13.7	—	—
$\frac{2}{3}Fe(OH)_3$	11.2	11.2	11.3	8.0
SnO	—	2.8	—	—

The numbers in brackets refer to the formation of insoluble salts. In such cases of neutralization, the evolution of heat = heat of neutralization + heat of precipitation.

Heat of Neutralization of Acids by Soda.

1 mol. of the acid mixed with *a* equivalents soda, both in dilute solution.

Acid.	$a=\frac{1}{2}$	$a=1$	$a=2$	$a=3$	$a=4$	$a=6$
HCl	6.87	13.74	13.74	—	—	—
HBr	6.87	13.75	13.75	—	—	—
HI	6.84	13.68	13.68	—	—	—
HNO_3	6.84	13.68	13.68	—	—	—
$HClO_3$	6.88	13.76	13.76	—	—	—
$HBrO_3$	6.89	13.78	13.78	—	—	—
HIO_3	6.9	13.81	13.81	—	—	—
$HClO_4$	7.18	14.35	14.35	—	—	—
HF	—	16.27	16.27	—	—	—
H_3PO_2	7.60	15.20	15.40	—	—	—
$C_2H_4O_2$	—	13.40	—	—	—	—
CH_2O_2	—	13.45	—	—	—	—
$C_3H_6O_2$	—	13.48	—	—	—	—
HCN	1.37	2.77	2.77	—	—	—
H_2SO_4	—	14.6	31.0	31.0	—	—
H_2SO_3	—	15.9	29.0	—	—	—
H_2CrO_4	—	13.13	24.7	—	25.2	—
H_3PO_3	7.43	14.8	28.4	28.9	—	—
H_3PO_4	7.3	14.8	27.1	34.0	—	—
H_3AsO_4	7.36	15.0	27.6	35.9	—	—
H_2CO_3	—	11.0	20.2	20.6	—	—

Acid.	$a=\frac{1}{2}$	$a=1$	$a=2$	$a=3$	$a=4$	$a=6$
$(COOH)_2$	6·9	13·8	28·3	—	28·5	—
$C_2H_4(COOH)_2$	—	12·4	24	24·1	—	—
Malic acid	—	13	26·17	—	—	—
Tartaric acid	—	12·4	25·3	25·8	—	—
Citric acid	—	12·67	25·4	38·9	—	41·7
H_2SiO_3	3·2	4·3	5·2	—	5·4	—
H_2BO_4	6·4	11·1	20·0	—	—	20·6

HEAT OF SOLUTION.

When one gram-molecule of the substance dissolves in the given quantity of water at 18°, the given number of calories is evolved.

Dissolved substance.	Gram-molecules of water.	Evolution of heat.	Dissolved substance.	Gram-molecules of water.	Evolution of heat.
$NaCl$	200	− 1·18	$FeCl_3$	400	+ 63·3
KCl	200	− 4·4	$CoCl_2 + 6H_2O$	,,	− 2·9
NH_4Cl	200	− 3·9	$CoCl_2$	,,	+ 18·3
$BaCl_2 + 2H_2O$	400	− 4·8	$NiCl_2 + 6H_2O$	,,	− 1·1
$BaCl_2$	400	+ 2·1	$NiCl_2$	,,	+ 19·2
KBr	200	− 5·08	$ZnCl_2$	,,	+ 15·6
$NaBr + 2H_2O$	200	− 4·7	$ZnBr_2$	,,	+ 15
$NaBr$	200	− 0·19	ZnI_2	,,	+ 11·3
KI	200	− 5·1	$CuCl_2 + 2H_2O$	,,	+ 4·2
$NaI + 2H_2O$	200	− 4·0	$CuCl_2$	,,	+ 11·1
NaI	200	+ 1·2	$HgCl_2$	,,	− 3·3
$CaCl_2 + 6H_2O$	400	− 4·34	$PbCl_2$	,,	− 6·8
$CaCl_2$	,,	+ 17·4	$SnCl_2 + 2H_2O$	,,	− 5·4
$CaBr_2$	,,	+ 24·5	$SnCl_2$	,,	+ 0·3
CaI_2	,,	+ 27·7	$SnCl_4$	300	+ 29·9
$MgCl_2 + 6H_2O$	,,	+ 2·9	$AuCl_3 + 2H_2O$	,,	− 1·7
$MgCl_2$	,,	+ 35·9	$AuCl_3$	,,	+ 4·5
$MnCl_2 + 4H_2O$	,,	+ 1·5	$PtCl_4 + 4H_2O$	,,	− 1·7
$MnCl_2$	,,	+ 16·0	$PtCl_4$	,,	+ 19·6
$FeCl_2 + 4H_2O$	,,	+ 2·7			
$FeCl_2$	,,	+ 17·9	$NaNO_3$	200	− 5·0
$FeCl_3 + 12H_2O$	,,	+ 11·3	KNO_3	200	− 8·5

Dissolved substance.	Gram-molecules of water.	Evolution of heat.
NH_4NO_3	200	− 6·3
$Ba(NO_3)_2$ . . .	400	− 9·4
$Sr(NO_3)_2 + 4H_2O$.	„	−12·5
$Sr(NO_3)_2$ . . .	„	− 4·6
$Ca(NO_3)_2 + 4H_2O$.	„	− 7·2
$Ca(NO_3)_2$ . . .	„	+ 4·0
$Mg(NO_3)_2 + 6H_2O$.	„	− 4·2
$Mn(NO_3)_2 + 6H_2O$	„	− 6·2
$Zn(NO_3)_2 + 6H_2O$.	„	− 5·8
$Cd(NO_3)_2 + 4H_2O$.	„	− 5·0
$Cu(NO_3)_2 + 6H_2O$.	„	−10·7
$AgNO_3$	200	− 5·4
$Pb(NO_3)_2$ . . .	400	− 7·6
$Na_2SO_4 + 10H_2O$.	400	−18·76
Na_2SO_4	„	+ 0·46
K_2SO_4	„	− 6·4
$(NH_4)_2SO_4$ . . .	„	− 2·4
$CaSO_4 + 2H_2O$ . .	„	0·0[1]
$CaSO_4$	„	+ 4·7
$MgSO_4 + 7H_2O$ . .	„	− 3·8
$MgSO_4$	„	+ 20·3
$MnSO_4 + 5H_2O$.	„	+ 0·04
$MnSO_4$	„	+ 13·8
$FeSO_4 + 7H_2O$ . .	„	− 4·5
$CoSO_4 + 7H_2O$ . .	„	− 3·6
$NiSO_4 + 7H_2O$ . .	„	− 4·3
$ZnSO_4 + 7H_2O$ . .	„	− 4·24
$ZnSO_4$	„	+ 18·5
$CdSO_4 + \frac{8}{3}H_2O$.	400	+ 6·0
$CdSO_4$	„	+ 10·7
$CuSO_4 + 5H_2O$.	„	− 2·7
$CuSO_4$	„	+ 15·8
Ag_2SO_4	„	− 4·5
$K_2SO_4, Al_2(SO_4)_3 + 24H_2O$	2400	− 20·2
$K_2SO_4, Cr_2(SO_4)_3 + 24H_2O$	1600	− 22·3
K_2CO_3	400	+ 6·5
$K_2CO_3 + 3H_2O$.	„	− 3·8
$KHCO_3$	„	− 5·3
Na_2CO_3	„	+ 5·6
$Na_2CO_3 + 10H_2O$.	„	− 16·1
$NaHCO_3$ . . .	„	− 4·3
Heat of solution in almost saturated solution.		
NH_4Cl	—	− 3·88
KCl	—	− 3·5
$NaCl$	—	− 0·2
$(NH_4)_2SO_4$ . . .	—	− 1·4
$NaNO_3$	—	− 2·5
NH_4NO_3 . . .	—	− 3·5
$MgSO_4 + 7H_2O$.	—	− 4·4
$CuCl_2 + 2H_2O$ . .	—	− 3·0
$CaCl_2 + 6H_2O$ . .	—	− 8·4

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[1] Slightly positive.

Problems. 1. What is the quantity of heat developed in mixing 100 grams Na_2CO_3 with so much water as to form the hydrate $Na_2CO_3 10H_2O$?

2. Calculate the heat of reaction in the process

$$Pb(NO_3)_2Aq + H_2SO_4Aq = PbSO_4 + 2HNO_3Aq.$$

3. And in the reaction

$$AgNO_3Aq + HClAq = AgCl + HNO_3Aq.$$

4. How much heat is evolved in the combination of C_2H_4 with gaseous bromine, the volume being kept constant?

5. Calculate the evolution of heat accompanying the solution of zinc in dilute sulphuric acid.

6. What is the heat of formation of dipropargyl at constant pressure, the heat of combustion being $+882 \cdot 9$ Cal.?

7. Berthelot burnt C_2Cl_6 in presence of water, according to the equation

$$C_2Cl_6 + O + Aq = 2CO_2 + 6HClAq,$$

and found an evolution of heat of $+131 \cdot 2$ Cal. What is the heat of formation of C_2Cl_6?

8. 20 c.c. of 10 per cent. cupric chloride solution were shaken with excess of iron filings till the copper was completely deposited. Calculate the rise of temperature of the liquid approximately, by assuming that its density and specific heat are both unity, and the thermal capacity of the iron and copper may be neglected.

9. A calorimeter contains 350 c.c. of tenth-normal HCl solution. It is mixed with 250 c.c. of a solution of NaOH sufficient to neutralize; what is the rise of temperature?

10. 350 c.c. of tenth-normal H_2SO_4 solution are mixed with 250 c.c. of fifth-normal NaOH solution of the same temperature. What is the rise of temperature?

§ 33. **Principle of maximum work.** Substances which can act chemically on one another tend, when left freely to their mutual action, to produce that system which is formed with the greatest evolution of heat.

Another mode of expression. Of the various reactions of which a material system is capable, that one will occur which gives the greatest evolution of heat.

Examples. If a system be composed of potassium chlorine and iodine, then KCl will be formed, and not KI, because

$$K + I = KI + 80{\cdot}1 \text{ Cal.},$$
$$K + Cl = KCl + 105{\cdot}6 \text{ Cal.}$$

The system (KI + Cl) will change into the system (KCl + I), for

$$KI + Cl = KCl + I + 25{\cdot}5 \text{ Cal.}$$

Acids and bases act on one another, for the formation of salts is accompanied by evolution of heat. E. g.

$$KOH\,Aq + HCl\,Aq = KCl\,Aq + H_2O + 13{\cdot}7 \text{ Cal.}$$

Gaseous chlorine does not decompose *steam*, for at 100°

$$H_2O \text{ (gas)} + 2Cl \text{ (gas)} = 2HCl \text{ (gas)} + O \text{ (gas)} - 14 \text{ Cal.},$$

since H_2, O (gas at 100°) $= +58$ Cal.,

while H, Cl (gas) $= +22$ Cal.

On the other hand, *liquid water* at atmospheric temperature is decomposed by chlorine, although very slowly, because

$$H_2O \text{ (liquid)} + 2Cl \text{ (gas)} + Aq = 2HCl\,Aq + O \text{ (gas)} + 10 \text{ Cal.},$$

for $H, Cl \text{ (gas)} = +22$ Cal., $HCl, Aq = +17{\cdot}2$ Cal.,
and $H_2, O \text{ (liquid)} = +68{\cdot}4$ Cal.

Copper does not displace iron from a solution of ferrous chloride, but the reverse reaction occurs easily, for

$$Fe \text{ (solid)} + CuCl_2 Aq = FeCl_2 Aq + Cu \text{ (solid)} + 37{\cdot}3 \text{ Cal.}$$

NOTE. The application of this principle—which was first stated by J. Thomsen, but soon given up, afterwards adopted by Berthelot and for thirty years defended by him—is extraordinarily wide and important, notwithstanding the serious errors involved in it. The underlying idea of it is that chemical actions only take place when heat is evolved by them. This idea is really only of value in considering reactions that take place at low temperatures; van 't Hoff has shown that the principle gains in applicability the nearer one approaches to the absolute zero.

The formulation of the principle involves a difficulty, because of the condition that the bodies are to be left to their *free* mutual action, without the interference of any outside influence, any outside energy. Outside influences, however, exist in the customary conditions, if only in the temperature and pressure of the surroundings. It must be noted here that the universality of the principle has for some years past been given up by Berthelot himself.

§ 34. **Applications of the principle of maximum work.** (*a*) *Law of simultaneous reactions.* A reaction occurs the more readily if its products can effect a second reaction.

NOTE. This law includes the phenomena of the action of the elements in the so-called *statu nascendi*, as well as those which were formerly ascribed to *predisposing affinities*. The law may be deduced from the principle of maximum work, since the second reaction involves an evolution of heat which is added to that of the first reaction. In consequence of this the heat of reaction is raised: it may be converted from a negative to a positive value, or from a small positive value to a considerable one, so that the entire heat of reaction rises to a large number of calories.

First Example. It has already been remarked that chlorine acts on liquid water, but not on steam. In the latter case the HCl formed is at once dissolved in water, a process which is accompanied by a large evolution of heat.

The action, however, is very slow. But if opportunity is afforded for the HCl or the oxygen formed to effect some chemical action, the decomposition of the water takes place rapidly. Thus the reaction

$$H_2O\,(\text{liquid}) + 2Cl + Aq = 2HClAq + O + 10\text{ Cal.}$$

goes slowly, but the reaction

$$H_2O\,(\text{liquid}) + SO_2Aq + 2Cl\,(\text{gas}) = H_2SO_4Aq + 2HClAq + 73{\cdot}7\text{ Cal.}$$

takes place at once.

The latter reaction is an instance of the action of oxygen *in statu nascendi*, and perhaps is to be explained by the evolution of that element in the atomic condition; it acts as such before the reunion into molecules can take place. This explanation may be correct, but at any rate it is certain that the small heat of reaction in

$$H_2O + Cl_2 = 2HClAq + O + 10 \text{ Cal.}$$

is increased by the considerable evolution due to the reaction

$$SO_2Aq + O = H_2SO_4Aq + 63{\cdot}7 \text{ Cal.}$$

In the latter case the second reaction is produced by the oxygen; but the hydrochloric acid also may be made use of for a second reaction. If KOH be dissolved in the water, the following second reaction may take place:

$$KOHAq + HClAq = KClAq + H_2O + 13{\cdot}7 \text{ Cal.};$$

the two together will accordingly give

$$2KOHAq + Cl_2 = 2KClAq + H_2O + O + 37{\cdot}4 \text{ Cal.}$$

The action is, however, not yet complete. The oxygen combines with KCl to form KClO,

$$KClAq + O = KClOAq - 12 \text{ Cal.},$$

and finally we have for the whole reaction

$$\begin{aligned} &2KOHAq + Cl_2 \text{ (gas)} \\ &\qquad = KClAq + KClOAq + H_2O + 25{\cdot}4 \text{ Cal.} \end{aligned}$$

The formation of KClO thus leads to a *diminution* of the heat of reaction. This is in fact still appreciably greater than that due to the action of chlorine on water; it must, however, be regarded as a want of logical strictness in the principle of maximum work, that such a bye-reaction as the formation of KClO can occur, even if such reactions can be regarded as coming under the rule at all.

Second example. Manganese dioxide and dilute sulphuric acid do not act according to the equation

$$MnO_2\,(\text{solid}) + H_2SO_4Aq = MnSO_4Aq + H_2O + O,$$

but if oxalic acid is added, the reaction takes place, with oxidation of the oxalic acid. The first reaction is presumably accompanied by an *absorption* of heat; the second, however, adds to that the very considerable (positive) heat of combustion of oxalic acid.

In the same way the action of sulphuric acid on potassium permanganate is rendered possible by oxalic acid.

Third example. The reaction

$$H_2O + Aq + 2I = 2HIAq + O$$

involves an *absorption* of 42 Cal. Consequently water is not decomposed by iodine according to the above equation; the reaction occurs, however, when the oxygen can effect an oxidation, whether of SO_2 to H_2SO_4 or of $Na_2S_2O_3$ to $Na_2S_4O_6$, with formation of NaI, or of arsenious acid with formation of As_2O_5.

(*b*) *Prediction of reactions.* The following rules are often satisfied:—

(*a*) A and B will combine when $A, B = +q$ Cal.

For if $A, B = +q$ Cal.,

$$A + B = AB + q \text{ Cal.},$$

and the system will tend from the form $(A + B)$ to that (AB), the form $(A + B)$ being unstable.

Example. KCl is formed by direct combination of K and Cl for $K, Cl = +105{\cdot}6$ Cal.

(β) A and B will not enter into combination when A, B $= -q$ Cal., for in this case

$$A + B = AB - q \text{ Cal.},$$

and the system (A + B) will retain that form.

Example. Chlorine and nitrogen will not unite directly, $NCl_3 = -38{\cdot}5$ Cal.

(γ) A will displace B from combination with C if (A, C − B, C) $= +q$ Cal., for in this case

$$A + BC = AC + B + q \text{ Cal.},$$

and the system (A + B + C) tends to the form (AC + B), the form (AB + C) being unstable.

Example. KI (solid) + Cl (gas)

$$= \text{KCl (solid)} + \text{I (solid)} + 25{\cdot}5 \text{ Cal.},$$

$$\text{K, Cl} = 105{\cdot}6 \text{ Cal.,} \qquad \text{K, I} = 80{\cdot}1 \text{ Cal.}$$

The reverse reaction only occurs under special conditions.

(δ) AB and CD effect a double decomposition

$$AB + CD = AC + BD$$

if

$$(A, C + B, D) > (A, B + C, D),$$

and therefore

$$(A, C + B, D) - (A, B + C, D) = +\ q \text{ Cal.},$$

for in this case the system (A + B + C + D) takes more readily the form (AC + BD) than the form (AB + CD).

(c) *Proof of the above rules by experience.* When only reactions occurring at atmospheric temperature, or at temperatures not very far removed from that, are considered, the above rules are fairly well confirmed by experience. The heat of formation of chlorides is greater than for the corresponding bromides and iodides; and, as a matter of fact, bromine and iodine are commonly expelled from their compounds by chlorine. The heat of combination of the metals with halogens follows the rule that it is large for strongly positive metals, and less and less according to the feebler positive character of the metal; this is in agreement with the rule that the more feebly positive metals are displaced from their compounds by the more strongly positive. The processes of salt-formation from acids and bases are double decompositions, in which the sum of heats of formation of the products is greater than that of the original substances, and actually, such salt-formation usually occurs without difficulty.

(*d*) *Production of compounds with negative heat of formation.* The production of such compounds is possible when they are bye-products in a reaction of which the other products possess a larger heat of reaction. It is true that in this case the heat of reaction is not the greatest possible—it would be greater if these bye-products were not formed—still it may be positive.

Examples. Formation of potassium hypochlorite (p. 82). *Formation of nitrogen trichloride.*

$$\text{N, Cl}_3 = -38 \text{ Cal.}$$

This substance is formed when chlorine is led into a solution of ammonium chloride.

$$\text{NH}_4\text{ClAq} + 6\text{Cl} = 4\text{HClAq} + \text{NCl}_3,$$

$$\text{N, H}_4\text{, Cl, Aq} = +71{\cdot}9 \text{ Cal.}, \quad 4\text{H, Cl, Aq} = +156{\cdot}8 \text{ Cal.}$$

The total heat of reaction is thus $+46{\cdot}9$ Cal.

(*e*) *Explosive substances and mixtures.* Systems whose heat of reaction is great usually suffer conversion. Usually, too, when in such a system the reaction is started at *one* point, so much heat is evolved there that neighbouring points are raised to the temperature required to initiate the reaction; consequently the reaction is propagated from one point, throughout the mass. When this propagation takes place with great velocity and production of high pressures, it is called an explosion. The commencement of a reaction at one point is frequently brought about by a violent pressure or shock.

Explosive substances (compounds) are such as are formed with a large absorption of heat, and give gaseous products on explosion. Such are, e. g., NCl_3, acetylene, nitroglycerine. These substances decompose on the application of a local pressure because this pressure brings about the reaction at that place, and in consequence is propagated through the whole mass, just as sound is. The pressure required to generate the explosion is not the same in all cases. NCl_3 and nitroglycerine decompose on the application of a very slight blow; acetylene, on the contrary, requires a violent shock.

Explosive mixtures contain components by whose reaction much heat is liberated, and at the same time gaseous products are evolved.

Examples. Gunpowder, detonating mixture (of oxygen and hydrogen).

The force of an explosion depends on the velocity of propagation of the reaction, on the production of heat, and on the fact that all or a part of the products are gaseous. For the heat evolved causes, in a very short time, a great expansion of the gas. The explosion is, however, very much more violent when not only gaseous products result, but ones formed from liquid or solid material. For in this case the pressure is due not only to rise of temperature, but also, and chiefly, to the conversion from solid or liquid state to the gaseous: for a definite mass of the substance, occupying a certain space, first as solid or liquid, after the reaction suddenly comes to occupy the same space as a gas. This change of state causes a pressure in the substance of the order of magnitude of a thousand atmospheres, and the latter quantity is commonly multiplied by a considerable factor due to rise of temperature.

Examples. NCl_3, nitroglycerine, gunpowder.

Theoretical determinations of the pressure and temperature in an explosion give higher values than experiment. This depends on the fact that the reaction is not complete, and further, that in the calculation it is unavoidable to use numbers for the heat of reaction and the specific heat of the products, which are determined at altogether different temperatures and pressures than those occurring in the explosion.

§ 35. Causes of the commencement of a reaction. Substances which are capable of reaction can frequently be mixed for a long time without the reaction setting in; the beginning of the reaction has to be brought about by special causes. The same thing is observed in the case of substances with negative heats of reaction; without special occasion they remain as they are.

Examples. Mixture of oxygen and hydrogen at atmospheric temperatures, gunpowder, acetylene, mixture of iron and sulphur.

The cause is not always the same: sometimes it is a blow or a local heating, as in explosive substances, fulminate of mercury, nitroglycerine, NCl_3, and in explosive mixtures such as gunpowder and oxyhydrogen mixture; sometimes illumination with magnesium light, as in the case of a mixture of chlorine and hydrogen. Sometimes the substance or mixture must be heated throughout its mass; the reaction proceeds, without further heating from outside, when once started in this way.

Example. Formation of chloroform from calcium chloride, calcium hydroxide, alcohol, and water.

§ **36. Criticism of the principle of maximum work.** This principle has a very wide applicability to reactions which take place under normal conditions of temperature and pressure, and especially to reactions of substances which are very stable towards rise of temperature.

A difficulty, however, soon shows itself: viz. the existence of *endothermic* reactions as part of a complex action, which as a whole is *exothermic* (cf. § 34, *a* and *d*).

The generality of the rule is, however, much restricted by other important considerations, which we will now mention.

§ **37. Endothermic reactions at ordinary temperatures.** The following is a purely chemical endothermic reaction:

$$\mathrm{NaFAq + HCl\,Aq = NaCl\,Aq + HFAq - 2{\cdot}3\ Cal.},$$

and in many other cases heat is absorbed when solutions of a salt and an acid are mixed. But it is not necessary to take only purely chemical processes into account, for the distinction between chemical and physical processes cannot always be made, and, what is more important, the theory on which the principle of maximum work rests implies the validity of the principle for physical processes as well. And the existence of many physical actions which are endothermic, and take place of their own accord, can easily be shown.

Freezing mixtures. Snow and salt at 0° mixed give a liquid—a salt solution—whose temperature is many degrees below 0°. Solid Glauber salt and concentrated hydrochloric acid, when mixed, absorb a large amount of heat.

In both these cases we have *strongly endothermic processes which take place of their own accord.*

Solution of salts in water. Salts mostly dissolve in water with absorption of heat: this process, too, is self-acting.

NOTE. Salts which form crystallized compounds with water mostly only dissolve with absorption of heat when they are brought into the same quantity of water as goes to form the crystalline hydrates which exist at ordinary temperatures.

Evaporation of liquids. Many liquids evaporate at ordinary temperatures, and in doing so absorb the considerable *latent heat of evaporation*: water, alcohol, ether. This change of state is also endothermic and self-acting.

§ 38. **Influence of chemical mass.** An element C can frequently decompose a compound AB, even when $A, B > A, C$, if only the quantity of C in comparison with AB is sufficiently great. The same is true of double decompositions.

Examples. A small quantity of potassium chloride is decomposed by a large quantity of bromine, with formation of potassium bromide, although

$$K, Cl = +105{\cdot}5, \qquad K, Br = +95{\cdot}8 \text{ Cal.}$$

Ethyl alcohol and acetic acid mixed in molecular proportions are only two-thirds converted into water and ethyl acetate, one-third remaining as acid and alcohol. If the quantity of acid or of alcohol is increased then the quantity converted becomes greater. The heat of reaction is in this case almost zero.

Dilute HCl mixed with a solution of Glauber salt decomposes the salt with an endothermic reaction, and the reaction goes further the greater the quantity of acid employed.

§ **39. Dissociation.** Compounds which are formed at ordinary temperatures, with an exothermic reaction, are commonly decomposed at very high temperatures (cf. § 32). The decomposition is, however, an *endothermic* reaction.

NOTE. The investigation of dissociation phenomena was first undertaken by Henri Saint Claire Déville in 1857.

Examples. Water, hydrochloric acid, carbon dioxide, are partly decomposed at high temperatures. Ammonium chloride and many other ammonium salts split into ammonia gas and acid. Calcium carbonate, on heating, gives carbon dioxide gas. The so-called *efflorescence*, or loss of water by salts with water of crystallization, may be reckoned amongst phenomena of dissociation.

§ **40. Principle of mobile equilibrium.** This principle is the combination of many of the above deviations from the principle of maximum work.

When a chemical system of definite form changes reversibly into another form at any temperature, both forms exist with definite concentration[1].

If the passage from the form A *to the form* B *is accompanied by an evolution of heat, rise of temperature causes an increase in the quantity in the form* A.

If A *is changed into* B *with absorption of heat, rise of temperature increases the amount of* B.

If the change from A *into* B *is unaccompanied by thermal effect, rise of temperature does not alter the distribution of the system between the two forms which exists at ordinary temperature.*

NOTE. This principle was introduced into chemistry by van 't Hoff in 1884.

Examples. Phenomena of Dissociation. The dissociation phenomena mentioned above are instances of exothermic reactions, which, on rise of temperature, are partly replaced by endothermic. Water is formed from oxygen and hydrogen with large evolution of heat; but at high temperatures it is partially decomposed; part therefore reacts according to the equation

$$2H_2O \text{ (vapour)} = 2H_2 \text{ (gas)} + O_2 \text{ (gas)} - 58 \text{ Cal.}$$

The reaction

$$CaO + CO_2 = CaCO_3$$

is exothermic, but at high temperatures the reverse reaction

$$CaCO_3 = CaO + CO_2$$

takes place, which is endothermic $= -30{\cdot}8$ Cal.

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[1] For *condensed* equilibrium another rule holds (cf. § 45 *c*).

Salt solutions. Good examples are to be found in the phenomena of solution of salts.

When a saturated solution of a salt (cf. § 52) is in contact with the solid salt, the system (salt + water) exists in two forms: solid salt and solution.

On heating, the concentration of the solution changes: it either increases or decreases, only in exceptional cases remaining the same.

In most cases the concentration of the solution increases, e.g. KNO_3, $Na_2SO_4 10Aq$, $CuSO_4 5Aq$. The salts dissolve with evolution of heat, i.e. with an *endothermic* reaction, and so the reaction produces that form which on rise of temperature gains in quantity (cf. § 53, Note 1).

Concentration diminishes, for example, with ethyl acetate, and with gypsum. These substances, dissolved with evolution of heat, separate from the water of solution on rise of temperature; that is, the form produced by exothermic action decreases in amount with rise of temperature.

The concentration of a saturated solution of sodium chloride is hardly altered by temperature; and, in fact, the heat of solution of that salt is almost zero.

Esterification. An instance of a purely chemical reaction which occurs without heat-effect is the formation of ethyl acetate and water from alcohol and acetic acid. At normal temperature only two-thirds of the substances mixed in molecular proportions are converted into the second form; at higher temperatures the transformation takes place more rapidly, but the quantity formed is neither more nor less than at normal temperature.

NOTE. The criticism of the principle of maximum work implied in the principle of mobile equilibrium may be put briefly as follows, according to van 't Hoff: The principle of maximum work is the more nearly correct the nearer the temperature of reaction is to the absolute zero; at the absolute zero that principle would be absolutely correct. That the principle is often confirmed at ordinary temperatures is explained by the fact that such temperatures are not far removed from the absolute zero by comparison with the highest attainable temperatures.

It may be put: There is no dissociation at the absolute zero.

§ 41. **Chemical equilibrium.** The principle of maximum work would involve the complete transformation of the reagents, and therefore the existence of only one form of the chemical system—that which is produced with the greatest evolution of heat.

It has been mentioned that this conclusion is contradicted by many facts; these facts are: Self-acting endothermic reactions at ordinary temperatures, effect of chemical mass, phenomenon of mobile equilibrium.

These facts may be brought together into a general theory, which is called the *theory of chemical equilibrium.* The fundamental idea of it is this:

Reacting substances are not completely transformed, and the amount transformed depends on the relative masses of the reagents, the pressure, and the temperature.

This fundamental idea may be formulated in other ways. A chemical system can assume more than one form; in general these forms exist side by side, and the system divides itself between them in parts which depend on the mass of the substances, the pressure, and temperature.

The term *equilibrium* of the forms does not imply a condition of rest, but rather one of movement; transformation to and fro takes place simultaneously, but in the end the same amount of each form is composed and decomposed. When this condition has set in the masses of the different forms bear a constant relation.

§ 42. **Schematic expression.** If AB and CD enter into a double decomposition, in the final state a certain amount of AC and BD exists together with AB and CD. This final state may be expressed by the equation

$$AB + CD = x(AC + BD) + (1 - x)(AB + CD).$$

In this way the quantitative as well as qualitative relation may be expressed, but to bring out the formation and decomposition it may be written

$$AB + CD \rightleftarrows AC + BD.$$

It is clear that in the same way simple decompositions and substitutions may be expressed:

$$AB \rightleftarrows A + B, \qquad AB + C \rightleftarrows AC + B.$$

Examples. The elements oxygen and hydrogen can take the form of water, but they can also exist in the form (hydrogen + oxygen). At high temperatures both forms exist in measurable quantities together.

That is $$2H_2 + O_2 \rightleftarrows 2H_2O,$$

$$2H_2 + O_2 = 2xH_2O + (1 - x)(2H_2 + O_2).$$

2. Action of nitric acid on sodium sulphate:

$$NaSO_4Aq + 2HNO_3Aq \rightleftarrows 2NaNO_3Aq + H_2SO_4Aq,$$

or $$Na_2SO_4Aq + 2HNO_3Aq = \tfrac{2}{3}(H_2SO_4Aq + 2NaNO_3Aq) + \tfrac{1}{3}(Na_2SO_4Aq + 2HNO_3Aq).$$

3. Colourless nitrogen tetroxide decomposes with rise of temperature and reduction of pressure, with formation of the coloured modification

$$N_2O_4 \rightleftarrows 2NO_2.$$

4. Calcium carbonate is decomposed on heating into calcium oxide and carbon dioxide

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

§ **43. Proof of the existence of equilibrium between simultaneous reactions.** That, eventually, there is equilibrium between the two reactions

Form A = Form B and Form B = Form A

follows from the fact which is characteristic of the reaction: the final state is the same whichever form is chosen for initial state.

If ethyl alcohol and acetic acid are mixed in molecular proportions, the final state is

$$\tfrac{1}{3}(C_2H_6O + C_2H_4O_2) + \tfrac{2}{3}(C_2H_5OOC_2H_3 + H_2O).$$

The same result is reached, however, if water and ethyl acetate are mixed in molecular proportions.

From this fact it is clear that not only the molecules C_2H_6O and $C_2H_4O_2$ act on one another, but also the molecules of the ester and of water. And there is no reason to suppose that this action ceases when the stationary state is arrived at.

For this reason such reactions are called *reversible* by contrast with those which proceed in one direction only. For though it is supposable that all reactions are reversible under certain conditions, these conditions are not known for all reactions. It should be remembered, moreover, that in many cases the existence of a reversible reaction at *all* temperatures may be concluded from the observed existence of such a reaction at some temperature. At high temperatures an appreciable decomposition of steam has been observed, but at lower temperatures decomposition cannot be detected. Still it may be assumed that it exists, although the products of decomposition are vanishingly small in amount.

§ 44. The three kinds of chemical equilibrium. (*a*) *Homogeneous equilibrium.* That is, equilibrium between substances which form a physical mixture, e.g. steam, oxygen, and hydrogen; N_2O_4 and $2NO_2$; $Na_2SO_4Aq + HNO_3Aq + HNaSO_4Aq + NaNO_3Aq$.

(*b*) *Heterogeneous equilibrium.* That is, equilibrium between substances which are not in the same state of aggregation. E. g.

$$CaCO_3\,(\text{solid}) \rightleftarrows CaO\,(\text{solid}) + CO_2\,(\text{gas}),$$

$$KNO_3\,(\text{solid}) \rightleftarrows KNO_3\,(\text{dissolved}),$$

$$Na_2SO_4.10H_2O\,(\text{solid}) \rightleftarrows Na_2SO_4.9H_2O\,(\text{solid}) + H_2O\,(\text{vapour}).$$

(*c*) *Condensed equilibrium.* That is, equilibrium between substances which are all solid, or all liquid, or partly solid and partly liquid, but not forming a homogeneous mixture.

§ 45. Influence of temperature on equilibrium. (*a*) *On homogeneous equilibrium.* The condition of a system of two substances in equilibrium is, at definite pressure and temperature, given by the ratio of the masses of the two forms.

This ratio depends on the temperature of the system, and stands in a definite relation to the evolution of heat which accompanies the passage of the one form into the other.

The laws connecting the quantity transformed, the temperature, and the heat of transformation, are those of mobile equilibrium explained in § 40.

Note. In homogeneous equilibrium the specific gravity frequently suffices to determine the ratio of mass of the two forms. When in a specimen of nitrogen tetroxide, at definite temperature and pressure, the weight of a litre has been determined, and it is known what would be the weight if the space were filled with N_2O_4 only or NO_2 only, the composition of the mixture that is in agreement with the observed specific gravity can be calculated.

In reactions between solutions of salts and acids the mass transformed, and therefore the equilibrium state, can be reckoned from the results of calorimetric, volumetric, or optical observations. J. Thomsen determined the evolution of heat with which the mixture of solutions of salts and acids is accompanied, and by comparison with the evolution that would take place if the decomposition were complete, calculated the quantity transformed. W. Ostwald determined the specific volume and the refractive index of the mixed solutions, as well as those of the separate acid and salt and their products of reaction, and used these data to calculate the amount transformed.

There are also several special methods.

(*b*) *Influence of temperature on heterogeneous equilibrium.* When a condensed system is in contact with a dilute one—a solid or liquid body in contact with a gas, a vapour, or a solution—the equilibrium is not described by the *partition* of the system between the two forms, but by the *concentration* of the dilute form. If the latter is a gas or vapour the concentration is defined by a definite pressure—the *dissociation pressure*, which is independent of the mass of the condensed substance.

The concentration rises with the temperature when the evolution of heat or passage of the condensed form into the dilute is negative; if the latter is positive the concentration diminishes, in accordance with the principle of mobile equilibrium (§ 40).

An example is the case of calcium carbonate, which, heated in a closed space, dissociates into calcium oxide and carbon dioxide till the gas attains a certain pressure. Other examples are to be found in salts with water of crystallization, each of which possesses a definite vapour pressure, dependent on the temperature; and also saturated salt solutions (§ 40).

(*c*) *Influence of temperature on condensed equilibrium.* This equilibrium occurs, under definite pressure, only at one temperature, and the mass of the co-existing forms of the substances occurring is indeterminate: rhombic and monosymmetric sulphur at 96° are in equilibrium in any proportions together. On rise of temperature equilibrium ceases, and the transformation takes place according to the rules of § 40: that form appears which is formed from the other with absorption of heat.

In condensed systems, therefore, the condition is that the forms can only coexist at one temperature: above that, only the one form is stable; below it, only the other. The temperature which separates these two states is called the *transformation temperature* or *point of transformation.*

§ 46. Influence of pressure on equilibrium. (*a*) *Influence on homogeneous equilibrium.* When a homogeneous gaseous mixture of reagents is in equilibrium, and the temperature remains constant, rise of pressure upsets the equilibrium, and favours that form which is produced from the other with *a diminution in the number of molecules.*

More briefly put: The system tends, in consequence of rise of pressure, towards the more condensed form.

Example. $N_2O_4 \rightleftarrows 2NO_2$

compression of the mixture increases the quantity of N_2O_4.

Equimolecular reactions constitute a special case, e. g.

$$2HI \rightleftarrows H_2 + I_2,$$

in such cases the equilibrium state is not altered by pressure, provided the latter is not too great.

(*b*) *Influence of pressure on heterogeneous equilibrium.* When the dilute form is a gas, increase of pressure at constant temperature is of no permanent influence on the equilibrium :

$$CaCO_3\,(\text{solid}) \rightleftarrows CaO\,(\text{solid}) + CO_2\,(\text{gas}).$$

At constant temperature, increase of pressure of the carbon dioxide, i. e. increase of concentration of the carbon dioxide, causes formation of $CaCO_3$ until the original pressure is restored.

The same is observed in the case of salts with water of crystallization : compression of the vapour causes it to recombine with the dehydrated salt.

For salts in contact with their saturated solution, rise of pressure increases the amount dissolved when that increase is attended with contraction; i.e. when the total volume of the salt and the water required to dissolve it is greater than that of the solution formed.

For these cases, too, the rule holds that the system tends to the more condensed form, when the pressure is increased.

(*c*) *Influence of pressure on condensed equilibrium.* The mass ratio of the two forms in this kind of equilibrium does not bear a fixed relation to the pressure when the temperature is constant, for at the temperature of transformation the forms can coexist in any proportion. The transformation point itself is affected by increase of pressure, and commonly lowered.

§ **47. Influence of chemical mass on equilibrium.** This influence only presents novelty in the case of homogeneous equilibrium. Increase in the quantity of a reagent increases the extent of that reaction which the substance in question can effect.

In the reaction

$$\text{alcohol} + \text{acid} \rightleftarrows \text{ester} + \text{water},$$

esterification is favoured by increase in the quantity of either alcohol or acid; addition of water, on the other hand, reduces the amount of ester formed.

NOTE I. When a substance is hindered in its action its mass is practically lessened. Thus, the formation of ester is facilitated by leading a stream of hydrochloric acid gas through the solution, for that combines with the water, and takes it out of the reaction.

NOTE 2. The conception of chemical mass was introduced as early as the beginning of this century by Berthollet. In more recent chemistry, important applications of it were first made by Guldberg and Waage (1867).

§ 48. **Analogy between physical and chemical changes of state.** The laws of chemical equilibrium are elucidated by comparison with the physical changes of state of a substance.

Water may be solid, liquid, or gaseous, and the passage from one state to another is accompanied by a thermal effect. Each transformation is influenced by temperature and pressure, and is reversible with respect to them: a change of state, which is produced by a change of pressure or temperature, is reversed when the pressure of temperature returns to its former value.

There is equilibrium between the physical states: at 0° ice is in equilibrium with water, below 0° ice with vapour, above 0° water with vapour.

Rise of temperature favours that state of aggregation which is formed from the other with absorption of heat (principle of mobile equilibrium, § 40). Ice, on heating, is converted into water. This transformation absorbs a considerable amount of heat—*the latent heat of fusion.*

Water, on heating, gives off steam of increasing density and increasing pressure, and the steam is formed with absorption of heat—*the latent heat of evaporation.*

The system water + steam

is in equilibrium according to the equation

$$\text{water} \rightleftarrows \text{steam},$$

and is analogous to heterogeneous equilibrium. The equilibrium is such that at a definite temperature, the density, and consequently the pressure, of the steam has a definite value. Compression does not permanently alter this value, for it converts the vapour into liquid water, till the pressure resumes its former value.

Condensed equilibrium exists at 0° in the system

$$\text{ice} \rightleftarrows \text{water};$$

by increase of pressure the temperature of conversion (in this case the *freezing point*) is lowered.

§ **49. Laws of Berthollet.** *Principles.*

1. When two substances, A and B, each of which can react with a third, C, are both present with C in a homogeneous mixture, in the final state neither AC nor BC will exist alone, but a mixture of AC and BC in *equilibrium*, in proportions depending on the relative affinities, and on the *chemical masses* of A and B.

2. When the substances AC and BC are not soluble, or only slightly soluble, in the liquid, they will separate from it, and the remaining dissolved substances will tend to a new equilibrium by forming new quantities of AC or BC. From these principles certain laws may be deduced:

First law of Berthollet. When dissolved substances give rise to an *insoluble* compound by their mutual action, the reaction proceeds to complete transformation of the reagents.

Example. Silver nitrate and hydrochloric acid are completely converted into silver chloride and nitric acid.

Second law of Berthollet. When reacting substances give rise to a *volatile* compound by their mutual action, the reaction becomes complete by continuous formation of the volatile substance.

Example. Calcium carbonate is completely decomposed by dilute hydrochloric acid, with formation of carbon dioxide; sodium chloride by sulphuric acid, with formation of hydrochloric acid.

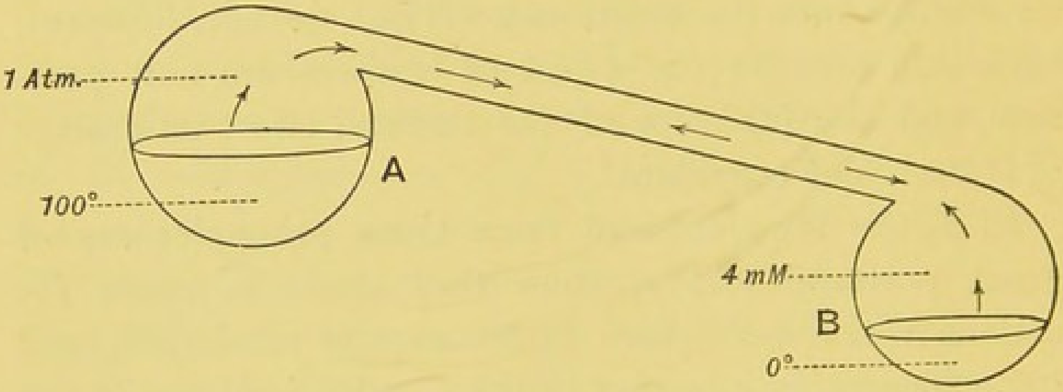
NOTE. These laws were stated in the *Essai de Statique Chimique* in 1804.

Explanation. Berthollet's principles are in agreement with modern theories, for they specify a state of equilibrium between two forms, and introduce the notion of *mass-action* into the treatment. They do not, however, take into account the effect of temperature and pressure, and the influence of the thermal effect on change of state is not considered.

Still, the laws deduced from these principles are of great practical utility, since they apply to many reactions which take place under normal conditions, and come frequently into play in the usual operations in the laboratory. They are wanting in logical strictness, however, because the conditions of insolubility and volatility with regard to the liquid are not accurately defined. It could not be predicted from the first law that $AgCN$ would dissolve in KCN, and $AgCl$ be decomposed by KCN. The second law does not explain why sulphide of iron is attacked by hydrochloric acid, but not sulphide of copper; the first leaves unexplained why sulphureted hydrogen deposits copper sulphide from an acid solution of ferrous and cupric chlorides, but not ferrous sulphides. Such problems may, however, often be explained by aid of the law of maximum work.

§ 50. **Watt's principle.** If a space includes two points of different but constant temperature, and contains liquid at these points, the vapour of the liquid will move towards the colder point; it will condense there, until liquid exists only at the colder spot, and the rest of the space is filled with vapour of pressure equal to the saturation pressure corresponding to the lower temperature.

Example. Water heated to boiling, in a still whose condenser is kept at 0°, sends its vapour into the condenser; there the vapour is mostly condensed, till all the water has passed from the boiler into the condenser, and the apparatus is filled with vapour at 4 mm. pressure.



Explanation. Water at 100° is in equilibrium with vapour of such density that its pressure is one atmosphere; water at 0°, on the other hand, is in equilibrium with vapour whose density corresponds to 4 mm. pressure.

In A the vapour pressure is therefore steadily one atmosphere, in B it cannot rise above 4 mm. Since the vapour spreads out from both points throughout the space, the colder vapour will be driven back by the hotter, since the pressure of the latter is the greater.

The hot vapour thus comes into B, where it must mostly be transformed into liquid water, since in B vapour can only exist of a density corresponding to 4 mm. This distillation will obviously only come to an end when all the liquid has vanished from A, and a pressure of 4 mm. holds throughout the space.

Applications. Distillation. A liquid is separated from non-volatile substances dissolved in it by heating in a vessel provided with a receiver kept constantly cool. The vapour of the liquid passes into the receiver and condenses there while the non-volatile substance remains in the vessel.

In this way water, e. g., may be separated from salts dissolved in it. So, too, nitric acid is separated from the mixture that results from adding sulphuric acid to $NaNO_3$, the separation leading at the same time to the complete transformation of the mixture : for the equilibrium is upset, and to *restore it new quantities of nitric acid are continually formed.* Sulphuric acid may be separated by distillation from lead sulphate, which absorbs it in the leaden chambers.

Fractional distillation. A mixture of liquids gives off, on heating in distillation apparatus, vapour which at first consists principally of the most volatile constituent. Consequently the distillate contains this substance purer than in the original liquid. When the liquid obtained by condensing is redistilled, the first part of the distillate is again purer than the liquid obtained by the previous operation. No perfectly pure product can be obtained by repeated distillation; first, because in each distillation the quantity of impurity is diminished, but never altogether removed, and secondly, because the liquid remaining undistilled often becomes a mixture capable of evaporation and condensation without further change of composition. That happens because the boiling point of such a mixture is *lower* than that of either constituent, or of mixtures of any other composition; for in that case the mixture boils first, and any other mixture goes over afterwards. But also, if the boiling point of a certain mixture is higher than that of either constituent, or of mixtures of other composition, it distils without change of composition; for in that case the more volatile mixtures go over first, while the least volatile remain in the still.

Fractional distillation has an important application in the purification of rock oil.

The existence of such mixtures of constant composition is the reason that, e. g., ethyl alcohol cannot be obtained absolutely pure by distillation from its aqueous solution, for a mixture of 94 per cent. C_2H_6O and 6 per cent. of H_2O passes over unchanged. So, too, aqueous hydrochloric acid cannot be indefinitely concentrated by continued distillation, for the composition of the vapour continually approaches that of the liquid remaining in the retort, so that finally vapour and liquid have just that composition which is not altered by boiling.

The composition of the mixture that passes over unchanged depends on the pressure, so that the mixture cannot be regarded as a chemical compound.

Liquefaction of gases under their own pressure. If in a closed knee-shaped tube, one limb contains crystals of chlorine hydrate $Cl_2 10H_2O$, and the other limb is immersed in snow, or in a freezing mixture, free chlorine can be evolved by cautious heating of the hydrate, and passes over to the cooler spot. If the gas is in excess its pressure eventually rises to the maximum pressure of liquid chlorine at the temperature of the freezing mixture, and chlorine condenses in the cold limb; thenceforward distillation occurs, as might be anticipated from the principle of Watt.

Ammonia gas can be liquefied in the same way, by heating its solid compound with silver chloride in a closed tube, of which one limb is placed in a freezing mixture.

Of course the temperature of the freezing mixture must be below the critical temperature of the gas.

Application to the theory of the transformation point. A substance in contact with its vapour in a space which is not all at the same temperature tends to assume that form for which the vapour pressure is least. So when at the lowest temperature more than one form can exist, the substance will assume that form which possesses the lowest vapour pressure. Liquid water can, under certain circumstances, exist below 0° in contact with vapour of definite density and definite pressure. But ice, too, is in equilibrium with vapour of water below 0°. But at any given temperature below 0° the pressure of water vapour is greater than the pressure of the vapour of ice. Consequently, if ice and liquid water coexist at any temperature below 0°, the vapour of water will distil over towards the ice and be converted into ice. Ice and water cannot, therefore, form a stable system below 0° (cf. § 48).

At 0°, on the contrary, the vapour from water and that from ice have the same density and pressure, so that at that temperature the existence of both forms is possible, while at higher temperatures only one form is stable.

The *freezing point* of water is therefore the transformation point for the condensed equilibrium

$$\text{ice} (+\text{vapour}) \rightleftarrows \text{water} (+\text{vapour}).$$

By similar reasoning it can be shown that at a definite temperature rhombic and monosymmetric sulphur can exist together, while above it only one, below it only the other, form is stable.

§ 51. **The principle of Watt applied to the transference of bodies at normal temperature.** The validity of Watt's principle is explained by two facts. *Firstly*: A condensed substance forms a stable system with its vapour, which at a definite temperature possesses a definite density and pressure. *Secondly*: There is not equilibrium between two systems having vapour of different densities and pressures when present in the same space, but the vapour moves from the place of high to the place of low pressure.

In the preceding section cases were considered in which the difference of pressures was due to difference of temperature. It is, however, plain that the movement of vapour must take place when there is a difference of vapour pressure due to any cause. Watt's principle may, therefore, be extended and formulated as follows:—If there are two points in a given space whose properties cause a difference of pressure for the vapour of a substance in contact with a condensed form, the vapour will flow from the point of high to the point of low pressure.

The system consisting of the two points tends, therefore, towards equality of pressure.

Example. Water placed in a closed space beside a salt solution sends vapour to the solution.

Applications. Hygroscopic salts and acids. By hygroscopic acids and salts is meant those that are very soluble in water; their saturated solution is in equilibrium with vapour whose pressure is much less than that of water at the same temperature. Water, when present in a closed space by the side of such a substance, sends vapour to it, since a small quantity of water brought into contact with the substance forms a very concentrated solution on its surface; this solution has a very small vapour pressure, and so forms a *point of low pressure* to which the vapour of the pure water constantly moves, and consequently *distils over* at normal temperature.

Since the vapour pressure of all salt solutions is lower than that of water, they all attract vapour of pure water. The pressure of saturated solutions of slightly soluble substances is, however, but little less than that of water, so the distillation is excessively slow.

The atmosphere always contains water vapour, whose density and pressure vary much in different places and at different times. If there is anywhere a concentrated salt solution whose vapour pressure is less than the actual pressure of vapour in the atmosphere, it will absorb vapour from the atmosphere; the solution then exercises a *hygroscopic* action. The hygroscopic action of very soluble salts is therefore still more intense.

Damp air forms on the surface of such bodies a layer of very concentrated, saturated solution, which acts as a point of low vapour pressure. As soon as it is formed, the vapour of the atmosphere, which usually exceeds the salt solution in pressure, moves towards it. There is thus formed more solution, which remains saturated and of very low pressure so long as the solid salt is not all dissolved. When the salt is all dissolved, the solution continually absorbs moisture till it reaches a degree of dilution at which its vapour pressure is equal to that of the atmospheric vapour.

NOTE 1. This treatment is not unconditionally true for hygroscopic action of purely chemical character, such as that of P_2O_5. P_2O_5 is not in equilibrium with water vapour of a definite pressure, but forms with it a compound H_3PO_4. One may, however, say that P_2O_5 constitutes a point of vapour pressure zero. The same holds for anhydrous calcium chloride. The first hygroscopic action of this salt consists in the formation of the hydrated salt, and it acts as a point of vapour pressure zero; afterwards a saturated solution is formed.

Saturated solutions of slightly soluble substances exercise no hygroscopic action because their vapour pressure is greater than that of the vapour in the atmosphere. Such a solution gives off water vapour till all the water has disappeared.

Deliquescence of solids in the air. It can now be easily seen what solids deliquesce in the air. It is those bodies whose saturated solutions possess at ordinary temperatures a pressure *less* than the pressure of the atmospheric water vapour; if the pressure is *greater* than that of atmospheric water vapour, the solid does not deliquesce, but, on the contrary, if it be damp, becomes dry in the air.

In general, therefore, deliquescence is a property of very soluble substances only.

Potassium carbonate deliquesces, because a trace of water forms with it a trace of saturated and very concentrated solution, possessing a very small vapour pressure, so that water vapour steadily distils into this solution.

Potassium sulphate does not deliquesce, for if it gets accidentally wet it forms only a dilute solution whose pressure is greater than that of atmospheric moisture, so that the sulphate gives up its water again to the air.

Pure sodium chloride is moderately soluble and not deliquescent. But the common salt of commerce contains some very soluble chloride of magnesium, and as that deliquesces, the common salt itself appears hygroscopic.

Sodium nitrate (Chili saltpetre) is very soluble at ordinary temperatures, potassium nitrate (saltpetre) only slightly so. Consequently Chili saltpetre is too hygroscopic to employ in making gunpowder, but potassium nitrate is well adapted to that purpose. The difference of solubilities is the reason why saltpetre can be made from the sodium salt according to the reaction

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

Hot solutions of $NaNO_3$ and KCl are mixed and boiled, and the KNO_3 formed, remains dissolved, being highly soluble in hot water. On cooling, it crystallizes out, being but slightly soluble in cold water. The solubility of sodium chloride, however, is about the same in hot and cold water, so the sodium chloride remains in solution. The same causes which render saltpetre applicable to the preparation of gunpowder make possible the preparation of saltpetre from sodium nitrate and potassium chloride.

Efflorescence of aqueous salts. It has already been remarked that a salt containing water of crystallization is, at a definite temperature, in equilibrium with water vapour of definite density and pressure. There is, therefore, for each salt, as for pure water, a characteristic *table of vapour pressures.* An aqueous salt is, therefore, at a definite temperature, a point of definite vapour pressure.

If, at normal temperature, the density and pressure of the vapour from the salt exceeds that of the atmospheric water vapour, the crystal will give off water to the air, and *effloresce.* If the vapour pressure of the crystal is exceeded by that of the air, the crystal does not lose water, or more correctly, what it does give off is continuously replaced by atmospheric vapour, and the crystal does not effloresce.

Example. Sodium sulphate effloresces, magnesium sulphate does not.

If fresh crystals of the two salts are placed side by side in the air, it is easy to tell one from the other after a time, for the first effloresces, but not the latter.

NOTE 2. It is assumed in the above treatment that the vapour pressure of the atmosphere is more or less constant. It is, however, clear that if the pressure is low substances may effloresce instead of deliquescing, whilst if it be high they may deliquesce instead of efflorescing.

CHAPTER V

SOLUTIONS

§ **52.** Many substances make, with water, a homogeneous liquid mixture, which is called a *solution.*

NOTE. It is not water only that is capable of dissolving substances: but in this book aqueous solutions will be considered chiefly.

A solution is *saturated,* at a given temperature, when, on contact with a substance of which it already contains some, it will not take up any more. If from any cause it contains more than the quantity required to saturate, it is called *supersaturated.* Supersaturation only occurs when the solution is not in contact with the substance it contains dissolved; for contact at once causes separation of a part of the dissolved substance, however little there may be of the solid.

A saturated solution of a substance in contact with that substance in the undissolved state forms—at a given temperature—a system in stable equilibrium. As a rule the quantity of dissolved substance increases with rise of temperature; there are, however, bodies whose solubility decreases with rise of temperature.

Examples. Nitre, Chili saltpetre, Glauber salt, and many others are more soluble hot than cold. Gypsum and ethyl acetate, on the other hand, are more soluble cold than hot. Sodium chloride dissolves to about the same extent in hot and cold water.

§ **53.** The solubility of a substance at a given temperature is the number of grams of it which dissolve in 100 grams of water.

On the relation between solubility, temperature, and heat of solution, see § 40.

NOTE 1. It must be remembered that the heat of solution occurring in § 40 means the heat evolved when the substance is dissolved in a solution already nearly saturated, i.e. *the heat of solution in an almost saturated solution.*

The solubility of solids and liquids is only appreciably affected by pressure when the latter is very great. Cf. § 46.

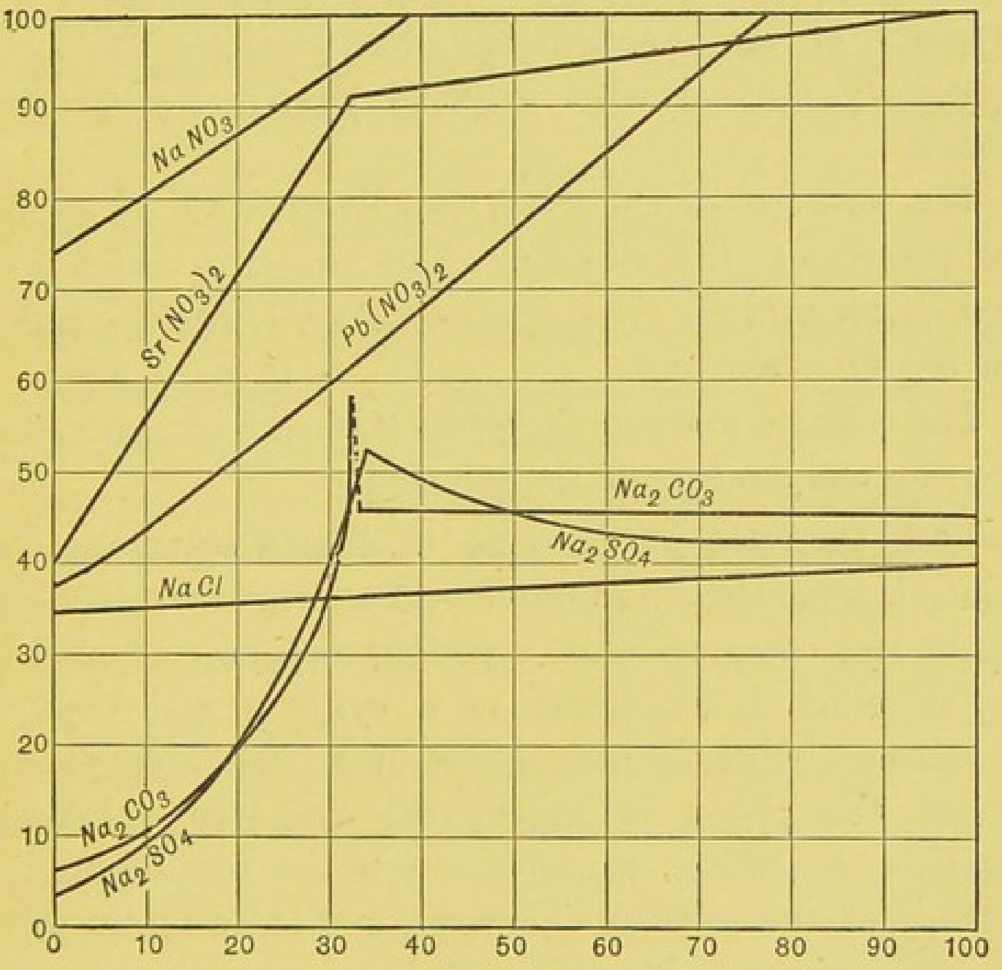
NOTE 2. The relations between solubility and pressure, solubility and temperature, are only valid when water and the dissolved substance do not mix in all proportions. For alcohol, e. g., which mixes in all proportions with water, there is no coefficient of solubility.

Gases which are little soluble in water follow the *law of Henry*; their solubility at a given temperature is proportional to the pressure.

§ **54.** For salts containing water of crystallization, each hydrate has its own solubility. It is thus possible for a solution to be supersaturated for various substances, viz. for various hydrates. A concentrated solution of sodium sulphate prepared at 40°, and then cooled to atmospheric temperature, is not only supersaturated with (i.e. crystallizes on contact with) $Na_2SO_4 10H_2O$, but also with $Na_2SO_4 7H_2O$.

This fact makes it difficult to decide in what condition a dissolved salt is present in solution. It is at any rate certain that a hydrate in contact with the solution forms a system in stable equilibrium.

NOTE. The relation between solubility of a salt and temperature is frequently expressed graphically, the temperatures being taken as abscissae, solubilities as ordinates. The solubility should be, not that of a hydrate, but the mass of anhydrous salt in 100 parts of water. Or frequently it is expressed as the mass of anhydrous salt in 100 parts of the *solution*. In the curves above, the former meaning is adopted.



§ 55. **Osmosis.** If a solution be surrounded by an envelope which allows water to pass through it, but not the dissolved substance, and the envelope, with the solution in it, be placed in water, the water will pass into the solution through the envelope from outside (osmosis).

Many animal and vegetable membranes possess this property of semi-permeability, but Osmosis has been accurately studied with artificial *semi-permeable membranes.*

The passage of the water can be stopped by applying pressure to the solution. The pressure, which is *in equilibrium with the force of the penetrating water,* is called the *osmotic pressure.*

The osmotic pressure increases with the concentration and the temperature of the solution.

§ 56. **Osmotic phenomena in dilute solution.** A solution, separated from water by a semi-permeable membrane and compressed by a piston, may be compared to a gas which is contained in a cylinder and kept in equilibrium with the atmosphere by a frictionless piston. When the piston is raised, the dissolved substance expands, i. e. water passes through the membrane, the volume of the solution increases, and the osmotic pressure decreases. If the piston is lowered into the cylinder, water is forced out through the membrane, the solution becomes more concentrated, and the osmotic pressure increases. If the system is heated, and the piston is to remain in place, the pressure on it must be increased, i. e. the osmotic pressure is greater.

Both dilute and concentrated solutions are in this way analogous to gases. But in the case of dilute solutions, a *complete quantitative agreement* with gases occurs, which was first shown by Van 't Hoff in 1886. When a dilute solution is contained in a cell with a semi-permeable membrane, and the cell is placed in water, the solution *follows the laws of Boyle and Gay-Lussac* and the *law of Avogadro.*

So, for solutions of the same substance, at constant temperature, the osmotic pressure is proportional to the density; at constant volume, the osmotic pressure is proportional to the absolute temperature.

For solutions of different substances, at equal temperature and equal concentration, the osmotic pressure is inversely as the molecular weight; or, solutions of the same molecular concentration[1] have, at the same temperature, equal osmotic pressures.

Finally, the osmotic pressure of a dissolved substance, at any temperature and concentration, is equal to the gas pressure of the same substance imagined in the gaseous state with the same temperature and concentration.

Example. Cane sugar gives at about 14°:
in one per cent. solution, an osmotic pressure of 535 mm.
„ two „ „ „ „ 1016 „
„ four „ „ „ „ 2082 „
„ six „ „ „ „ 3075 „

If cane sugar could exist as a gas a concentration of 10 grams per litre at 14° would exert a pressure of

$$760 \times 22\cdot32 \times \tfrac{10}{342} \times \tfrac{287}{273} = 521 \text{ mm.}$$

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[1] The molecular concentration is the number of gram-molecules per litre.

NOTE. It is obvious that the *molecular quantity* of a dissolved substance can be found from the osmotic pressure of a solution of known concentration (cf. § 21, note 1).

§ 57. **Experimental data.** These are partly from measurements of osmotic pressure. There are, however, considerable difficulties in the way of such measurements; it is, moreover, almost impossible to prepare a membrane that is quite impermeable for the dissolved substance.

Valuable data are, however, to be obtained from other phenomena, whose connexion with the osmotic pressure has been demonstrated also by Van 't Hoff. These phenomena are the *lowering of the freezing point*, the *raising of the boiling point*, and the *lowering of the vapour pressure.*

(*a*) *Lowering of the freezing point.* It has long been known that the freezing point of water is lowered by the addition of soluble substances. The lowering is, within certain limits, proportional to the concentration of the solution. According to the theory, the osmotic pressure is proportional to the number of molecules dissolved in a litre, and so is, for the same substance, proportional to the lowering of the freezing point, while for solutions of different substances of the same concentration, the lowering is inversely proportional to the molecular weight.

NOTE 1. When the lowering of the freezing point has been determined for a one per cent. solution, that for a solution containing the molecular quantity may be calculated, assuming that the latter can be treated as dilute. This *molecular lowering of the freezing point* depends on the nature of the liquid, and is the same for all dissolved substances (cf. § 58).

Note 2. The constant of the lowering of freezing point has a different value for each solvent. Van 't Hoff proved that the molecular lowering, and the *latent heat of fusion*, bear a definite quantitative relation to each other, so that one of the two quantities can be calculated from the other.

(*b*) *Rise of boiling point.* For a given dissolved substance the rise of boiling point is proportional to the concentration.

For equally concentrated solutions of different substances the rise of boiling point is *inversely proportional* to the molecular weight.

(*c*) *Lowering of vapour pressure.* For this phenomenon the same rules hold.

Note 3. The above rules may be summarized as follows: osmotic pressure, change of freezing point, of boiling point, and of vapour pressure are equally great for solutions which contain, in the same solvent, the same number of molecules per litre.

Note 4. From each of the three rules the molecular mass of the dissolved substance may be found. The method of the lowering of the freezing point is that most in use.

Many substances whose molecular weight was known previously have given the same values by the new methods. But sometimes the molecular weight depends on the nature of the solvent.

NOTE 5. Important osmotic phenomena are observed in living organized cells.

When a plant cell is placed in a salt solution osmosis occurs. For the protoplasm which surrounds a liquid—the cell-sap—and normally adheres to the stiff cell-wall, acts as a semi-permeable membrane, since it allows water to pass through it, but not the substances dissolved in water. According as the solution employed is more or less concentrated, it will withdraw water from the cell-sap, or allow water to pass into the sap through the protoplasm. Of course there exists a concentration of the salt solution which is in equilibrium with the cell-sap, so that neither the solution nor the sap withdraws water from the other. In that case the solution and the cell-sap have the same osmotic pressure : they are isosmotic or *isotonic.* Solutions of different salts are isotonic, or of the same osmotic pressure as one another, if they are each in equilibrium with the sap of the same cell. Solutions of greater concentration than those which are isotonic with the cell extract water from it. The elastic protoplasm contracts and separates from the cell-wall. This phenomenon—known as *plasmolysis*—may be observed under the microscope.

The isotonic coefficient of a substance is the osmotic pressure of an aqueous solution of it, of the same molecular concentration as a KNO_3 solution whose osmotic pressure is taken as 3. The isotonic coefficient for cane sugar is 1·88 ; therefore a cane sugar solution is isotonic with a solution of KNO_3 when the molecular concentration of the former is to that of the latter as 3 : 1·88 (H. de Vries).

Isotony or equal osmotic pressure exists between equimolecular solutions of different neutral organic substances and organic acids. Phenomena very similar to those observed with plant cells can be observed also with blood-corpuscles ; the latter were first studied by Donders and Hamburger, and the last named worked out the investigation to form a method for determining molecular weights.

§ 58. **Exceptions.** The methods described in this chapter for measuring molecular weights lead, in the case of a large group of substances, to results which are not in agreement with prevalent chemical views. The group includes the strong acids, strong bases, and salts. Arrhenius first, in 1887, pointed out that the exceptions occur in all substances which conduct electricity in the dissolved state—which are *electrolytes* ; the better the solution conducts, the greater the exception.

In general, organic substances conduct badly, mineral substances well. Strong acids conduct better than weak; organic acids only begin to conduct notably when in very dilute solution. Organic salts are good conductors.

All this refers to substances dissolved in water. Other solutions do not yield exceptions, or only to a very slight extent, and, in agreement with that, salts, acids, and bases dissolved in other liquids have far less conductivity. E. g. potassium acetate gives in aqueous solution an abnormally great lowering of the freezing point; in alcoholic solution it produces a lowering of vapour pressure of the magnitude which the theory of osmotic pressure requires.

§ 59. **Principle of electrolytic dissociation.** When salts dissolve in water their molecules break up, partially, into ions.

NOTE. Ions are atoms or groups of atoms of the same composition as the substances which separate from the electrolyte under the action of the current, and are *charged with electricity*. They give up their electric charges when the current conveys them to the poles. The action of the current on the electrolyte is, therefore, not a decomposition, since the salt is already decomposed into ions on solution, but the carrying of the ions to the poles. Just because the ions are charged with electricity they can exist in water without acting on it. A normal potassium atom would at once decompose water; a charged potassium ion behaves neutrally towards water until its charge is removed, as happens when it comes into contact with the negative electrode. Strong acids and bases also dissociate into ions for the most part.

Examples. KCl in aqueous solution breaks up partly into ions $(K+)$ and $(Cl-)$; KNO_3 into $(K+)$ and (NO_3-); H_2SO_4, according to dilution, into $(H+)$ and (HSO_4-), or into $(H+)$ $(H+)$ and (SO_4-); potassium acetate into $(K+)$ and $(C_2H_3O_2-)$.

§ 60. **Some laws of electrolytic dissociation.** (*a*) The dissociation increases with the dilution, and on progressive dilution approaches a maximum.

Examples. In moderately concentrated solution KCl is partly dissociated into K and Cl. The condition is therefore

$$xKCl+(1-x)(K+)+(1-x)(Cl-).$$

The degree of dissociation is definite for definite temperature and concentration. On progressive dilution x decreases, $1-x$ increases, till finally, on infinite dilution, all the molecules of KCl are broken up into ions.

(*b*) The dissociation is, for moderate concentrations, the greatest for *strong* acids and bases and their salts, especially for strongly reactive substances.

The reactions of analytical chemistry are mostly reactions between ions. E. g. formation of silver chloride from silver nitrate and sodium chloride is according to the equation

$$\mathrm{Na} \mid \mathrm{ClAq} + \mathrm{Ag} \mid \mathrm{NO_3Aq} = \mathrm{AgCl\,(solid)} + \mathrm{Na} \mid \mathrm{NO_3Aq}.$$

NOTE 1. The dissociated condition is frequently expressed by a vertical line between the ions in the molecule.

NOTE 2. At first sight it may appear strange that such bodies as HCl, NaOH, and KCl should be the most dissociated. It should, however, be remembered that these substances are the most capable of reaction, and that readiness to react is caused by the ease with which substances exchange their components.

NOTE 3. The existence of electrolytic dissociation explains why, e. g., chlorine does not always show the same reaction. For the reactions are, according to the theory of Arrhenius, not actions of atoms, but of ions. Thus, $\mathrm{K} \mid \mathrm{ClO_3}$ will not form AgCl with $\mathrm{Ag} \mid \mathrm{NO_3}$, for it is not the atom Cl that reacts, but the ion $\mathrm{ClO_3}$.

NOTE 4. The part played by phenolphthalëin in titration is explained by the theory of Arrhenius.

Phenolphthalëin is a body of very complicated constitution containing two phenol residues—the group C_6H_4OH. These groups give to the substance the properties of an acid to some extent, so that phenolphthalëin may be regarded as an organic acid RH. Like other organic acids, it is hardly dissociated at all in aqueous solutions, but its salts are. On neutralization with a base it forms a salt RK, and this dissociates into ions (R –) and (K +). *The red colour is due* to the formation of ions (R –) from the undissociated substance RH.

That this explanation is correct follows first from the fact that *all soluble bases* give the same red colour with phenolphthalëin, and secondly from the fact that the red colour is *extremely faint in* alcoholic solution—alcohol prevents electrolytic dissociation almost completely (cf. § 58)—but becomes stronger as the alcoholic solution is diluted with water.

(*c*) In respect of osmotic pressure and the phenomena connected with it, each ion has the same value as a molecule.

This law holds because each ion moves in the liquid as an independent whole.

The law explains the existence of exceptions to the theory of osmotic pressure as put forward by Van 't Hoff. We will elucidate this by means of an example.

The condition of potassium chloride in solution, it has been remarked, is

$$(1-x)\ \mathrm{KCl} + x(\mathrm{Cl}-) + x(\mathrm{K}+);$$

if n molecules have been dissolved there exist in solution

$$n[(1-x)\ \mathrm{KCl} + x(\mathrm{Cl}-) + x(\mathrm{K}+)];$$

the number of independent moving particles is therefore not n, but

$$n\left[(1-x)+2x)\right] = n(1+x).$$

Since the osmotic pressure is proportional to the number of molecules in the solution, and each ion acts as an independent particle, the pressure will not be that due to n molecules per litre, but $n(1+x)$.

The magnitude of x increases with increase of dilution and has a maximum of 1, so that on extreme dilution the osmotic pressure would have double the theoretical value.

The same reasoning applies to the phenomena of lowering of freezing point, &c.

§ 61. Verification of the theory of electrolytic dissociation. (*a*) Exceptions to the theory of osmotic pressure occur in the case of electrolytes. We have already discussed that fact.

(*b*) The exceptions are more marked with increase of dilution.

(*c*) The degree of dissociation reckoned from the lowering of the freezing point is the same as that derived from the conductivity of the solution.

According to the theory of Arrhenius, electricity is conducted through solutions only by the ions, not by undissociated molecules. To determine the degree of dissociation for a given concentration the conductivity of the solution of that concentration is compared with the conductivity of an extremely dilute solution: in the latter case the conductivity has its maximum value. From those data the number of free ions and the degree of dissociation can be calculated for the given concentration.

NOTE. The conductivity must be always expressed by reference to a definite concentration of the solution. For though the dissociation increases with dilution, the concentration of the dissolved substance of course diminishes.

The degree of dissociation determined in that way from the conductivity of the liquid agrees with that calculated from the lowering of the freezing point.

(*d*) When dissociation is prevented the exceptions disappear.

Alcoholic solutions conduct very badly, and dissociation hardly occurs in them. They behave too normally with regard to lowering of the vapour pressure.

(*e*) The law of thermo-neutrality (cf. § 32).

Mixing dilute salt solutions gives rise to no thermal effect. That fact is easily explained on the dissociation theory; for in dilute solution the salts are nearly completely dissociated, and on mixing *no change of state occurs.*

$Na \mid ClAq + K \mid NO_3Aq$ is, both before and after mixture, a solution in water of the ions

$$(Na+)(K+)(Cl-)(NO_3-).$$

(*f*) Neutralization of a strong base by a strong acid yields always the same evolution of heat.

Hydrochloric, nitric, hydrobromic, hydriodic acids in dilute solution give the same amount of heat for the molecular quantity, viz. 13·7 Cal.; e. g.

$$HClAq + KOHAq = KClAq + H_2O + 13{\cdot}7 \text{ Cal.}$$

According to the theory of electrolytic dissociation, that reaction may be expressed thus:

$$H \mid ClAq + K \mid OHAq = K \mid ClAq + H_2O + 13{\cdot}7 \text{ Cal.}$$

The mixture therefore has no other result than *the formation of water from its ions*. The heat of formation of water from its ions is accordingly 13·7 Cal.

Since the strong acids and strong bases are all nearly completely dissociated into ions by water, the only result of mixing is in all cases the formation of water from its ions, and the evolution of heat is therefore the same in all cases.

CHAPTER VI

PHOTO-CHEMISTRY

§ 62. **Coloured flames.** Many substances placed in a non-luminous gas flame communicate to it a colour which is usually characteristic for the metal of the salt. Sodium salts colour the flame yellow, potassium violet, barium green. These colours are employed in analytical chemistry to identify certain metals.

Often, however, the coloration does not suffice to characterize the element, as the colour of it is obscured by that of another: the intense yellow of sodium is rarely absent. For that reason it is necessary to analyze the phenomenon observed and decompose the light into its constituents. A rough means of doing so is cobalt glass, or an indigo prism; they allow the potassium light to pass through, but not the sodium; they consequently allow of the observation of potassium light in a mixture of the two.

§ 63. A far more accurate means of analysis, however, is the spectroscope. A small strip of flame is observed with the apparatus, and the light from that strip meets a prism which deviates each constituent of the light according to its refractive index, so that the constituents can be observed side by side in the emergent light.

The coloration imparted to the flame by any metal in the state of vapour, consists of a definite number of kinds of light, of definite refrangibility; observation of the kinds, and measurement of their refractive index, constitute an exact proof of the presence of the metal in the flame.

NOTE 1. Whilst luminous vapours give out only a few rays, the *spectrum* (i. e. the totality of the refracted rays) of an incandescent solid or liquid body consists of an unbroken succession of kinds of light.

As a rule, on introducing a salt into the flame, only the spectrum of the free metal is obtained, because the substances of the flame decompose and reduce the compound, so that the metal itself is observed free. When salts and oxides can be made incandescent in the flame, without decomposition, other spectra are produced.

NOTE 2. According to a research by Pringsheim the light given out by metals in the flame is not due to temperature, but only to the chemical action of the flame on the salt or oxide, i. e. to the reduction.

The temperature of a gas flame is insufficient to convert many metals into glowing vapours. In such cases, electrodes of the metal are prepared, and electric sparks passed between them; the latter carry traces of metal with them, which they volatilize.

The spectrum of a gaseous substance is obtained by introducing it, very highly rarefied, into a tube, and passing a current from an induction coil through it: the gas is made to glow, and the colour analyzed with the spectroscope.

Since the light of each gaseous element consists of a system of rays of definite refrangibility, the presence of certain lines in the spectrum is proof of the presence of certain elements; observation of new lines may therefore lead to the discovery of a new element. In fact, several elements have been discovered by spectrum analysis, e. g. caesium, indium, gallium, germanium.

NOTE 3. Peculiar phenomena are observed in the spectranalytical study of salts of the so-called *rare earths*—earths of the didymium group, the erbium group, and the yttrium group. A well-founded theory of the nature of these earths has not yet been arrived at, but it is probable that they are mixtures of various oxides, instead of consisting of single oxides.

§ **64.** Whilst luminous vapours give out light of definite refrangibility and show a bright line spectrum in the spectroscope, they absorb from white light (i. e. a mixture of light of all refrangibilities, consequently giving a continuous spectrum) those *same kinds of light which they themselves give out*; the spectrum of the transmitted light accordingly shows dark lines where that of the vapour itself would show bright ones. Non-luminous vapours, too, can absorb light.

This fact plays an important part in the explanation of the dark lines that occur in the solar spectrum. Each dark line occurs in the spectrum at a place where a bright line can be produced by a glowing metal. Kirchoff arrived in consequence at the following hypothesis :—The sun consists of a solid or liquid core which is surrounded by an atmosphere of incandescent vapour. The core sends out white light, but before reaching the earth the light has been deprived of those rays which are absorbed by the sun's atmosphere. The dark lines in the sun's spectrum thus indicate what are the elements constituting the sun's atmosphere, and which must also exist in its core. Since, however, the dark lines of the solar spectrum correspond to bright lines given out by the glowing vapour of terrestrial elements, it must be concluded that the sun and the earth consist, at least to a large extent, of the same elements. The fixed stars also give a spectrum with dark lines.

§ 65. **Photo-chemical action.** In the luminous phenomena just described, no chemical change is assumed to take place in the substance which receives and absorbs the light. There is, however, a series of actions due to light in which the substance illuminated suffers a chemical change. The following generalizations have been made with regard to such actions :—

(*a*) All kinds of light from infra-red to ultra-violet are capable of exercising *photo-chemical* action.

NOTE 1. It is, therefore, not correct to suppose that violet light alone is chemically active. The most frequent effect in nature of an obviously chemical character —the decomposition of the carbon dioxide of the air by the green parts of plants—is produced chiefly by the yellow component of sunlight. It is, therefore, not correct to speak of a source of light as especially rich in chemically active rays; for every kind of light can effect definite chemical actions according to its nature.

(*b*) Photo-chemical action is only produced by such rays as the illuminated body absorbs.

NOTE 2. The converse statement that absorption is necessarily coupled with chemical action is incorrect.

(*c*) The nature of the illuminated substance conditions the chemical action produced. However, red light acts mostly as an oxidizing agent on metallic compounds, violet light as a reducing agent. Mutual action of metalloids is commonly favoured by violet light.

(*d*) The sensitiveness of a body towards rays of a definite refrangibility is increased by the admixture of other substances which absorb the same rays.

(*e*) A substance is usually decomposed faster by a given colour when it is mixed with other substances which unite with its products of decomposition.

NOTE 3. The explanation of this fact is that the combination of the products of decomposition in other ways makes it impossible for them to recombine to form the original substance.

§ 66. Photo-chemical extinction means the phenomenon that rays which have passed through a medium sensitive to light are weakened in their chemical activity when they pass through a second layer of the same medium, in so far as the weakening cannot be accounted for by purely optical absorption.

Example. Light which has passed through a column of mixed chlorine and hydrogen has suffered the same degree of weakening in its chemical activity as if it had passed through a column half as long of pure chlorine[1]. Here the purely optical absorption is the same in the two cases.

The fact that the chemical activity of light commonly does not reach its greatest intensity immediately after absorption, but only after a certain time, is called photochemical induction.

NOTE. Induction in the case of hydrogen and chlorine may be explained on the assumption that the two gases do not act immediately on one another, but by means of water vapour, which forms an intermediate compound. Perhaps the process is the following:

$$H_2O + Cl_2 = Cl_2O + H_2,$$

and

$$2H_2 + Cl_2O = H_2O + 2HCl.$$

It would require a certain time before enough Cl_2O had been formed to initiate the second reaction.

This hypothesis is supported by the fact that damp chlorine and hydrogen are much more sensitive to light than dry.

§ 67. Formation and fixation of a photographic image. In all photographic processes the light acts

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[1] Half as long a column because one volume of the mixture only contains half a volume of chlorine.

for a short time on the sensitive plate, and in that time no visible image is produced. When the plate, however, immediately after exposure is submitted to the action of a *developer*, the image gradually appears. This developer is, in modern processes, a reducing agent which reduces the silver salts on the sensitive plate at the spots where the light has acted, and a latent image therefore exists.

Note. The explanation of the process of development is almost entirely hypothetical, and is based on the long-disused Daguerrotype. Daguerre (1838) exposed a silver plate, slightly iodized on its surface, to the light for some seconds. No visible image was produced, but Daguerre then brought the plate in contact with mercury vapour. The mercury deposits most quickly on places where the light has formed traces of silver, and the surface is in consequence somewhat rough.

That procedure seems to suggest that, in the newer chemical methods of development, the developer first attacks places where the sensitive film is already slightly decomposed. The silver bromide, in silver bromide-gelatine plates, slightly decomposed by the action of the light, concentrates the effect of the developer on the parts where reduction has already commenced, and at those points rapid reduction takes place, and rapid separation of silver.

It should be repeated that this explanation is of a very hypothetical character.

When the image is developed it is rendered permanent or *fixed*. The plate is dipped into a solution of a substance which dissolves and so removes the undecomposed part of the sensitive film.

In that way, however, only a so-called *negative* is obtained; the light parts of the object photographed having sent out much radiation have caused a considerable separation of silver and produced a dark image; the dark parts, on the other hand, have produced a light image. The positive is obtained by laying the negative plate on sensitive paper and exposing it to the light; then obviously the arrangement of light and dark will be reversed.

§ 68. **Colour photography.** In 1891 Lippmann succeeded in photographing the solar spectrum in its natural colours. He placed a layer of mercury under the sensitive plate and exposed the arrangement to the light. The vibrations of the ether penetrate the glass, strike the mercury, and are reflected; the reflected vibrations interfere with fresh vibrations and set up stationary waves. The wave-length of these waves is extremely small, so that numerous nodes and loops occur in the thickness of the sensitive film, while the decomposition of the silver salt is a maximum at the loops and nil at the nodes. Consequently layers of silver form in the sensitive film, and the layers are, for each colour, separated by a distance of half a wave-length from one another; they cause interference phenomena in white light falling on the plate and reflect the same colour as produced them.

CHAPTER VII

THE PERIODIC SYSTEM

§ **69.** The periodic system is an arrangement of the elements resting on the fact that the *properties of the elements,* so far as they are expressible by numbers, *are periodic functions of their atomic weights.*

Note 1. A quantity A is a function of a quantity B when they vary together, and each value of B corresponds to one or more values of A. Thus A is a function of B in the equations

$$\begin{aligned} A &= 3B, \\ A &= B^n, \\ A &= B^n + p, \\ A &= \sqrt{B^n + p}, \\ A &= \text{arc} . \sin B. \end{aligned}$$

A is a *periodic* function of B when A repeats its values at regular intervals, on continuous increase of B. Thus in the equation

$$A = \sin B$$

A is a periodic function of B, since for any given value of B, A has a definite value; but A has the same value when B becomes greater by 360°, 720°, or n times 360°, so A repeats its values at intervals of 360°.

The interval is called a *period,* but the word period may also be taken to imply all the values of A occurring while B has passed through that interval.

Note 2. The fundamental idea of the periodic system is the periodic function. Still the periodicity is not associated, with mathematical accuracy, with a definite interval. For that reason it is more in agreement with the facts to say: if the elements are arranged in order of atomic weight they may be divided into several groups, and the properties of one group are repeated by another in corresponding positions.

NOTE 3. For a long time past it has been sought to find relations between the properties of the elements and their atomic weights; it was early noticed that mathematical relations exist between the atomic weights of elements which form a natural family, on account of their active properties. Thus the atomic weight of strontium is nearly the mean between the atomic weights of calcium and barium; the atomic weight of sodium nearly the mean between those of lithium and potassium. Zeuner (1857) arranged all the elements then known in *triads*.

In the years 1862 and 1863 Chancourtois and Newlands attempted a systematic treatment of the elements according to their atomic weight; the latter stated that in general the same properties recur at every eighth element, *the law of octaves*.

In the year 1869 the periodicity of the properties of the elements with regard to atomic weight was put forward by Mendeléef and Lothar Meyer; they founded a system which endeavoured to carry out strictly the conception of periodicity, and their system is still in use.

§ 70. **Graphical representation.** If points in a plane be defined by reference to two axes, so that abscissae represent atomic weight, and ordinates numbers expressing some property of the element, and the points thus defined be joined by straight lines, a broken curve consisting of several waves is obtained. The peculiarities of the property studied, occurring in one wave, recur in the others at corresponding points. The periodic variation of the properties of the elements is most clearly shown by graphical representation of the atomic volume.

Such a wave-curve is then a graphical expression of the periodic system.

§ 71. **Tabular expression.** If the groups of associated elements are arranged in horizontal rows one below another a table of the periodic system is obtained. Here, too, the elements succeed one another, from left to right, in order of atomic weight, and the properties which appear in one horizontal series are found again at corresponding points of the other series. Consequently elements with analogous properties are arranged in vertical rows [1].

§ 72. **Small and large periods.** In the first two periods, which each contain seven elements, the agreement between corresponding terms is close. The third period begins with potassium, which corresponds to sodium ; but between potassium and rubidium, which begins the fourth group, there are sixteen elements ; and after rubidium, again, sixteen elements [2] must be passed

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[1] In this book a table of the series, chiefly according to Lothar Meyer's arrangement, is given ; that of Mendeléef does not differ essentially from it.

[2] The existence of an unknown element of atomic weight about 100 is assumed.

to reach caesium, an element possessing a great similarity to potassium and rubidium. Here, then, two periods of seventeen elements must be assumed, and in fact these two groups of seventeen elements may be considered as independent periods, so far as most of their properties are concerned. They are called *large* periods, as opposed to the *small* ones formed by the groups Li—F and Na—Cl.

The large periods may, however, be divided into two groups of *seven* elements in considering certain of their properties, as a slight analogy exists between them and the small periods; the remaining three elements show no such analogy, and are therefore placed in a separate series. In L. Meyer's table the first large period constitutes the third and fourth horizontal rows, the seven later elements the second group. The chief analogies with the small periods come out when the large period is treated as a whole; the secondary analogies, especially that of valency, appear in each group.

§ 73. Not only does this regularity exist with regard to the recurrence of the properties of the elements, but the variation of properties within one period may be brought under certain rules. In general, other physical properties, expressed by numbers, show either a maximum or a minimum in the middle of each period.

The *specific gravity* (in the solid state) increases to the middle of the period, reaches a maximum there, and diminishes again.

The *atomic volume* (quotient of the atomic weight by the specific gravity in the solid state) diminishes to the middle of the period, reaches a minimum there, and increases again.

When the relation of atomic volume to atomic weight is expressed by a curve (cf. § 70) a group of waves is obtained which brings out very clearly the notion of periodicity of properties. Other properties, too, are expressed by the position of the elements on the curve. The *falling* part of the curve, including the lowest point, includes the difficultly fusible and non-volatile elements, the *rising* part the easily fusible and volatile.

The atomic heat, which for most solid elements is nearly constant (cf. § 24), can also be treated as a quantity subject to the law of periodicity, of which the variation is almost nothing. If, like the atomic volume, the atomic heat be expressed graphically as a function of the atomic weight, a straight line is obtained.

The elements which differ appreciably from Dulong and Petit's law occur in the first and second periods, and show a certain regularity in their deviation ; the atomic heat decreases towards the middle of the period, and then increases again. The valency increases in the first two horizontal rows from 1 to 4, and then falls again to 1. (The valency is here derived from hydrogen and hydrocarbon compounds, or if such do not exist, from chlorine compounds.) On the right-hand side of the system the elements with more than one valency occur, and whilst the lowest valency falls from 4 to 1 the highest increases from 4 to 7, as may be seen from the oxygen compounds.

In the large periods, *double periodicity* with regard to valency may be noted. From potassium to manganese the valency in salt-forming oxides rises from 1 to 7 (K_2O to Mn_2O_7); in the second period a second group is formed from copper to bromine (Cn_2O to Br_2O_7). The two groups thus show a secondary analogy with the two small principal periods, and on that L. Meyer based his arrangement of the large periods, putting in a special position the three elements which do not show any analogy with the small principal periods as regards change of valency.

Other properties of the elements can also be expressed with more or less accuracy on the periodic system. But the most important are those mentioned above.

§ **74. Applications of the periodic law.** (*a*) *Correction of atomic weights.* Since the totality of the properties of an element depends on its atomic weight, one may use them instead of the atomic weight to determine its position in the system. The introduction of the natural system has in this way led to a change in the value attributed to the atomic weight of several elements. Indium, for which an atomic weight 75·6 was assumed, must, according to all its properties, lie between tin and cadmium; accordingly, the atomic weight has been increased by one-half to 113·4. The metals of the platinum group, too, have been subjected to a new investigation, and that has yielded values for their atomic weights in agreement with the place which the other properties of those elements indicate for them.

Note 1. However, the latest investigations on nickel and cobalt and on tellurium do not agree with the position of those elements in the periodic system.

(*b*) *Prediction of undiscovered elements.* Many gaps are noticed in the table; it is to be expected that they will be filled up by elements yet undiscovered, which by their atomic weight and other properties will claim them. It is possible to tell beforehand the approximate atomic weights and the principal properties of such elements. These anticipations have several times been fulfilled, as by gallium, scandium, and germanium (but see § 75).

(*c*) *Determination of atomic weight.* It appears from (*a*) that determination of the place of an element leads to determination of the order of magnitude of the atomic weight, and the magnitude can then be corrected by the help of analytical data.

(*d*) *The unit of the elements.* The fact that many properties of the elements are associated with a purely mathematical property—the atomic weight—gives new support to the notion, early thought of, that all the elements are formed by condensation of one original substance. Prout (1817) assumed that all the atomic weights are multiples of the atomic weight of hydrogen. More exact analyses by later investigators have, however, shown that the atomic weights are not integral numbers, and no common factor for them has been found.

Still it is remarkable that the atomic weights of many elements are close to whole numbers.

NOTE 2. The methods for determining atomic weights are:

1. Analysis of the molecular quantity of compounds of the element.

The molecular quantity, or mass, of a gram-molecule is determined—

(*a*) From the gas-density, on Avogadro's hypothesis.

(*b*) From the osmotic pressure of solutions of the compound, and other associated quantities.

(*c*) From special considerations on the constitution of compounds.

Method (*a*) is the most important.

2. Application of the laws of Dulong and Petit, and of Joule.

3. Application of the periodic system.

Each of the three methods only gives an approximate value for the atomic weight, which must be corrected by analysis of the compounds.

§ 75. Concluding remark on the meaning of the periodic system. The element argon, recently discovered by Rayleigh and Ramsay, has apparently the atomic weight 39·9, and cannot be put into the periodic system as above described. A new arrangement of the system is therefore to be expected, for it cannot be supposed that it will lose all validity through the discovery of argon.

The position of helium, newly discovered by Ramsay, in the periodic system has not yet been studied.

[Note. Ramsay has since announced the existence of crypton, metargon, and neon, which, like argon and helium, appear to differ from the other elements in forming no compounds. Ramsay places them in a new vertical series of the periodic system.—Translator.]

NATURAL SYSTEM OF THE ELEMENTS

Hydrogen, H = 1·0076.

I	II	III	IV	V	VI	VII	VIII		
Lithium Li = 7·03	Beryllium Be = 9·1	Boron B = 11·0	Carbon C = 12·00	Nitrogen N = 14·04	Oxygen O = 16·00	Fluorine F = 19·0	—	—	—
Sodium Na = 23·05	Magnesium Mg = 24·3	Aluminium Al = 27·1	Silicon Si = 28·4	Phosphorus P = 31·0	Sulphur S = 32·06	Chlorine Cl = 35·45	—	—	—
Potassium K = 39·15	Calcium Ca = 40·0	Scandium Sc = 44·1	Titanium Ti = 48·1	Vanadium V = 51·2	Chromium Cr = 52·1	Manganese Mn = 55·0	Iron Fe = 56·0	Cobalt Co = 59·5	Nickel Ni = 58·9
Copper Cu = 63·6	Zinc Zn = 65·4	Gallium Ga = 70	Germanium Ge = 72·3	Arsenic As = 75·0	Selenium Se = 79·1	Bromine Br = 79·95		—	—
Rubidium Rb = 85·4	Strontium Sr = 87·7	Yttrium Y = 89·0	Zirconium Zr = 90·6	Niobium Nb = 94	Molybdenum Mo = 96·1	—	Ruthenium Ru = 101·7	Rhodium Rh = 103·1	Palladium Pd = 106·4
Silver Ag = 107·93	Cadmium Cd = 111·9	Indium In = 113·7	Tin Sn = 119·1	Antimony Sb = 120·4	Tellurium Te = 127·6	Iodine I = 126·86	—	—	—
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Helium, He. Gas-density = 2·15. Argon, A. Gas-density = 19·94.

In this table the atomic weights are referred to oxygen = 16. Several metals of the rare earths are not mentioned because their atomic weights have not been determined with sufficient accuracy. The atomic weights of Co and Ni, according to recent researches, do not agree with their position in the periodic system : the same is true of tellurium and iodine.

INDEX

A.

Abnormal gas-densities, 23, 26, 40.
Absolute zero, principle of maximum work true at, 80, 93.
Absorption spectrum, 130.
Ampère, 24.
Analogy between solutions and gases, 117.
Analysis by coloured flames, 127.
— of a reaction, 10.
Argon, 142.
Arrhenius, 121, 125.
Association of liquids, 40.
Asymmetric carbon atom, 37.
Atom, 24.
Atomic heat, 46, 138.
— volume, 138.
— weight, 26, 141.
— — correction of, 140.
— — regularities, 136.
— weights are whole numbers, 141.
Atomicity of elements, 29, 31.
Avogadro, 24.

B.

Berthelot, 61, 65, 72, 80.
Berthollet, 101, 102.
Berzelius, 6.
Blood corpuscles, osmotic pressure of, 121.
Boiling point, elevation of, 119.
Boyle, 17.

C.

Calorimeters, 54, 55.
Chancourtois, 136.
Chemically active rays, 130.
Chemistry, definition of, 1.
Chlorine and hydrogen, combinations in light, 132.
Colour photography, 134
Combination in gaseous state, law of, 15, 17, 44.
Compound and mixture, 2.
Coefficients in chemical equations, to determine, 7.
Concentration, 98, 117.
Conservation of mass, 3.
Constant boiling point, mixtures with, 106.
— proportions, law of, 12.
— volume, heat of formation at, 63.
Crystals, structure of, 2.

D.

Daguerre, 133.
Dalton, 5.
Deliquescence, 110.
Democritus, 24.
Development of photograph, 133.
Déville, H. St. C., 90.
Diatomic elements, 30.
Dissociation, 64, 90, 91.
— electrolytic, 122.
— pressure, 98.
Distillation, 104.
Donders, 121.
Double bond, 44.
— periodicity, 139.
Dulong and Petit, 45, 139.
Dumas, 19.

E.

Efflorescence, 90, 112.
Electrolyte, 121.

Elements, 1.
— discovered by spectra, 129.
— prediction of, 140.
Endothermic reactions, 85, 88, 92.
Equation, 6.
Equilibrium, chemical, 93.
— condensed, 98, 100.
— heterogeneous, 97, 99.
— homogeneous, 96, 99.
Equimolecular reaction, 99.
Equivalent, 13.
Esterification, 92, 95, 100.
Explosion, 86.

F.

Favre and Silbermann, 55.
Fictitious reaction, 10.
Fixing photographs, 133.
Flames, coloured, 127.
Formulae, chemical, 5.
Fractional distillation, 105.
Freezing mixture, 89.
— point, lowering of, 118.
Function, meaning of, 135.
— periodic, 135.

G.

Gases, density of, 18, 23.
— laws of, 16.
— liquefaction of, 106.
— solubility of, 114.
Gay-Lussac, 15, 17, 20.
Gram-molecules, 26.
Green part of plants, action of, 131.
Guldberg and Waage, 101.

H.

Hamburger, 121.
Heat of formation, 52.
Henry, 114.
Hess, 56.
van 't Hoff, 36, 80, 91, 117, 118, 124.
Hofmann, 20.
Humboldt, 17.
Hydrates, 114.
Hydrocarbons, heat of formation, 60.
Hygroscopic substances, 109.

I.

Indigo prism, 127.
Ions, 122.
Isomerism, 34.
Isotonic solutions, 120.

J.

Joule, 48.

K.

Kirchoff, 130.
Kundt, 31.

L.

Laplace, 31, 56.
Laurent, 24.
Lavoisier, 2, 3, 56.
Lebel, 36.
Lippmann, 134.
Liquefaction of gases, 106.

M.

Mass, influence of chemical, 89, 100.
Maximum work, principal of, 79, 88, 93.
Mendeléef, 136, 137.
Meyer, L., 136, 137.
Meyer, V., 20.
Mobile equilibrium, 91.
Molecular formula, determination of, 32.
— quantity, 26.
— weight, 25.
Molecule, 24.
Multiple proportions, law of, 4.

N.

Neumann, 49.
Newlands, 136.
Nitric acid prepared by distillation, 105.

O.

Osmosis, 116, 120.
Ostwald, 97.

P.

Perfect gases, 17.
Periodic system, 135.
Phenolphthaleïn, 123.
Photo-chemical extinction, 131.
— induction, 132.
Physical state, change of, 101, 108.

Plasmolysis, 120.
Polarized light, rotation of, 36.
Predisposing affinities, 81.
Pressure, influence on equilibrium, 99, 114.
Pringsheim, 128.
Prout, 4, 141.

R.

Ramsay, 142.
Rare earths, spectra of, 129.
Rayleigh, 142.
Reaction, exo- and endothermic, 53.
— heat of, 53, 56.
— reversible, 95.
Refractive index, use of, 97.
Regnault, 19.
Relative element, 2.

S.

Saturated compounds, 41.
— solutions, 113.
Semi-permeable membrane, 116.
Simultaneous reactions, 81.
Sodium nitrate not used for gunpowder, 111.
Solar spectrum, 130.
Solubility, measure of, 114, 115.
Solution, 113.
— heat of, 114.
Sound, velocity of, in gases, 31.
Specific gravity and atomic weight, 138.
— heats, abnormal, 47.
— — of compounds, 49.
Specific volumes, use of, 97.
Spectrum analysis, 128.
Stability and heat of formation, 63.
Status nascendi, 81.
Stohmann, 72.
Structural formula, 34.
Substitution, 14.
Sugar, osmotic pressure of, 117.
Sulphur, vapour density of, 23.
Supersaturation, 113.
Symmetry, planes of, 3.

T.

Tartaric acid, 37.
Temperature, influence of, 97, 98, 113.
Thermo-neutrality, law of, 65, 126.
Thomsen, J., 61, 65, 72, 80, 97.
Transformation point, 107.

V.

Valency, 41, 139.
Vapour density, measurement of, 19.
— pressure, lowering of, 119.
de Vries, 120.

W.

Water formed from its ions, 127.
Watt, 104, 108.

Z.

Zeuner, 136.

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