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PHYSICAL CHEMISTRY
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BY

DR. CH. VAN DEVENTER

WITH AN INTRODUCTION

BY

PROF. J. H. VAN'T HOFF

AUTHORIZED AMERICAN EDITION FROM THE SECOND GERMAN EDITION

TRANSLATED BY

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INTRODUCTION

In delivering in Amsterdam my lectures on Chemistry, chiefly to students of medicine, I was confronted by a double task: on the one hand to present the systematic side of the subject with relative completeness and entirely on an experimental basis, on the other hand to show how the fundamental laws of chemistry might be deduced from these facts. The scheme of presentation which I adopted therefore comprised two topics: the first included the consideration of certain elements, the second was confined to a general summary.

I began with "Matter from a Qualitative Standpoint," water, oxygen, hydrogen, air, and nitrogen supplying me with the necessary material; then came the concepts, compound, mixture, element, and the whole table of atoms; the halogens furnished the material for the second topic, in the course of which the laws governing weight were introduced, and in this manner I continued until the vacation.

This was all very well, but nevertheless a book was required. For the systematic side I indeed recom-

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mended many, but for the theoretical side this was difficult, until as a welcome assistance this little book by Van Deventer appeared. The author had attended my lectures, had worked under me in the laboratory, had pursued his studies still further, and had devoted considerable time to the instruction of medical students.

But from a broader point of view it is indeed a commendable task which the author has set himself in presenting in his own way the subject of physical or general chemistry to the students of medicine, pharmacy and chemistry, without placing too great stress on the physical and mathematical side of the subject. A realm of science is concerned which in recent years has proved extremely fruitful, a journal especially devoted to physical chemistry having just appeared in the New World, and from the corresponding journal of the Old World a good word from the pen of an eminent scientist will be quoted:

"The prospective development of all sciences in which chemistry plays a part, from geology to physiology, including the whole of chemical technology, can be more readily appreciated at the present moment than perhaps at any time previously; they will all undergo a fundamental reform through the application of the facts recently acquired through the agency of general chemistry."

J. H. VAN'T HOFF.

AMSTERDAM, 1897.

AUTHOR'S PREFACE TO GERMAN EDITION.

IN the book at hand the author has endeavored to collect the most important results of physical chemistry in such a manner that this important branch of modern chemistry may be accessible to those who have not made an exhaustive study of physics and mathematics. The requirements of students of medicine and pharmacy, as well as of elementary chemistry, have been especially considered in the preparation of this work.

The author desires to express his sincere thanks to Dr. Ernst Cohen, who has prepared the present edition.

CH. M. VAN DEVENTER.

BATAVIA, June, 1901.

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Table of the Elements arranged according to the Natural System.

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CHAPTER I.

DEFINITIONS.

§ 1. **Chemistry** is the science which treats of the conditions under which one substance of itself, or several substances by reciprocal action, give rise to the appearance of new substances. The province of chemistry also includes the description of the substances, as well as of the phenomena which accompany the formation of new substances.

§ 2. **Substance or Matter** is the name given in chemistry to every homogeneous body, without reference 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; of the properties of the elements, the weight only is retained in the properties of the compound.

A mixture is a combination of substances in which the essential properties of the substances are retained.

REMARK 1. The substances which are now called *elements* are *relative elements*—i.e., non-decomposable by any known forces. For the introduction of the conception *relative element* we are indebted to Lavoisier.

---

* A table of elements will be found at the end of this book.

REMARK 2. It is often difficult to plainly distinguish the limits between compounds and mixtures. The difference may be most clearly stated as follows : in a compound the elements are indeed present as such, but are so influenced by one another that the properties of the whole, with the exception of the weight, are not equal to the sum of the properties of the components ; also the behavior of the compound towards other substances is in no way similar to that of the free elements. In a mixture, however, the mingled components may be considered as side by side, each part retaining its characteristic properties, these properties being so little influenced by one another that the components act upon other substances in the same manner that they would act if entirely separate.

REMARK 3. Solid bodies often form from liquids and produce solid figures enclosed by planes. Bodies of this sort are called *crystals*. They show certain regularities upon which the systems of the crystals depend. They are so divided into six groups that every crystalline chemical compound is included in one of these groups.

Crystals grow by the addition of new layers of material to the faces already existing. As a result of this process the forms of crystals are not materially influenced by their dimensions, but are dependent upon the angles between their faces; since, by the *parallel extension* of the plane faces of the crystals, these angles remain unaltered. It is always possible, by shifting the faces of a crystal, to reduce it to an ideal form in which a certain symmetry can be detected. The *degree* of symmetry is dependent upon the number of symmetry planes.

The position of the crystal faces is often expressed by their intersections with certain *axes* taken in the crystal ; these axes being chosen with direct reference to the planes of symmetry.

Each group of crystal forms in which an equal number of symmetry planes can be detected is called a *crystal system.* There are six of these: with nine, with seven, with five, with three, with one, and with no symmetry planes.

Solid substances which are not crystalline are called *amorphous.*

Some compounds can, however, crystallize in more than one crystal system; such cases are usually dependent on the temperature.

CHAPTER II.

FUNDAMENTAL LAWS OF COMPOSITION.

§ 3. **The Law of Constant Weight** (Lavoisier's Law). A system of matter on changing into another system does not alter in mass (weight).

Differently formulated. On chemical action no mass is either lost or gained.—The weight of a system of matter is independent of the chemical *form.*—On chemical action the total weight of matter before and after the reaction is the same.

REMARK 1. This principle was dogmatically employed by Lavoisier as a fundamental doctrine in experimental chemical investigation. But only after his death, and chiefly as a result of his efforts, was it introduced as a fundamental law of all chemical teaching.

REMARK 2. From the law of Lavoisier, in connection with the conception element, it follows directly that not only the entire system, by a change in the chemical form, does not alter in weight, but also *each element* before and after the reaction is present in exactly the same quantity.

§ 4. **The Law of Constant Composition.** The composition of a compound is independent of the method by which it is prepared.

Differently formulated. A compound, characterized by a definite number of physical and chemical properties, has an invariable qualitative and quantitative composition.

Example. Alcohol is obtained by the fermentation of sugar in water. The same substance is formed also from the oxidation of ethane, by the action of ethyl iodide on an aqueous solution of potassium hydroxide, and by other reactions. The product, which has a specific gravity of 0.792 and a boiling-point of 78°, is always of the same composition: 46 grams of the substance contains 24 grams of carbon, 6 grams of hydrogen, and 16 grams of oxygen.

REMARK. This law was introduced by Proust at the beginning of the present century.

§ 5. **The Law of Multiple Proportions.** When two elements occur together in more than one compound, then the *different* quantities of the one element which are associated with the same quantity of the other element, stand with respect to their weights in proportions which can be expressed by *rational* numbers.

Differently formulated. A fixed quantity of one element so combines with *different* quantities of another element that the ratio between the latter may be expressed by rational numbers.

Example. In the compounds methane, ethane, ethylene, acetylene, benzene there are to every 12 grams of carbon respectively 4, 3, 2, 1, and 1 grams of hydrogen. In the substances ammonia, ammonium chloride, nitric acid, methyl-amine, amido-benzene, nitrotoluene, hydrazoic acid there are to every 14 grams of nitrogen respectively 3, 4, 1, 5, 7, 7, and $\frac{1}{3}$ grams of hydrogen.

Remark 1. This law was discovered by Dalton in 1802. The law of constant weight permits, following Lavoisier's example, of the expression of chemical reactions by means of *equations*, in which the substances in the initial state stand on the left of the equality sign, and the products of the reaction on the right.

Thus: Sodium hydroxide + Hydrochloric acid = Sodium chloride + Water.

Remark 2. Since each separate substance has a fixed composition, a substance is often named from its composition. Substances are also denoted by a symbol, a *formula*, which expresses their qualitative and quantitative composition. These formulas consist of letters which represent the element and *a characteristic number belonging to it;* coefficients at the rear of the letters denote how many times this characteristic number shall be taken. How these numbers, the so-called *atomic weights*, are determined will be explained later.

The substance potassium chloride is represented by the formula KCl; it contains for every 39 grams of potassium 35.5 grams of chlorine. HNO_3 is nitric acid, a substance which in 63 grams contains 1 gram of hydrogen, 14 grams of nitrogen, and 48 grams of oxygen.

When the formulas—frequently multiplied by a coefficient—of the substances which enter into a reaction are assembled in an equation, an accurate idea is obtained of the substances and the relative quantities in which they enter into the reaction, and an exact expression for *the qualitative and quantitative course of the reaction* is secured.

The equation

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$$

states that by the action of sulphuric acid on potassium nitrate each 101 grams of potassium nitrate requires for its decomposition 98 grams of sulphuric acid, and as a result of this process 136 grams of hydrogen potassium sulphate and 63 grams of nitric acid are formed.

From the equation

$$2H_2 + O_2 = 2H_2O$$

it is seen that 4 grams of hydrogen combine with 32 grams of oxygen to form 36 grams of water.

When the substances exist in the form of gas or vapor, the formulæ have a special significance which will be explained later (compare § 17, Rem. 3 and § 23).

REMARK 3. Berzelius was the first to represent elements by letters, and compounds by combinations of letters, and it was he who gave a quantitative significance to the latter.

The characteristic numbers now associated with the letters by all chemists were first used about thirty years ago.

REMARK 4. A chemical equation, according to the law of Lavoisier and the definition of an element, shall have the same elements, and of each element the same quantity on both sides of the equality sign. If the formulas of the substances in the initial and final state are known, correct results are not always attained by writing the formulas on both sides of the equality sign. Hydrogen and oxygen react to form water, but the equation

$$H_2 + O_2 = H_2O\ *$$

is *incorrect.* What shall be done in this case is quite evident ; since by writing

$$2H_2 + O_2 = 2H_2O$$

the equation is made to conform with Lavoisier's law.

But it is not always so simple to determine the correct coefficients, and in some cases careful consideration is required. Since the coefficients determine the conformity of the equation with Lavoisier's law, the law prescribing only the equality of two quantities but not their absolute values, it is evident that only the relative values of the coefficients must be determined.

---

* Hydrogen and oxygen, as will be explained later, are not denoted by H and O, but by H_2 and O_2.

For explaining the method a special case will be considered.

When potassium manganate (K_2MnO_4) is added to a considerable volume of water, potassium permanganate ($KMnO_4$), manganese dioxide (MnO_2), and potassium hydroxide (KOH) are produced. The equation expressing this reaction must have the following form :

$$p\mathrm{K_2MnO_4} + q\mathrm{H_2O} = x\mathrm{KMnO_4} + y\mathrm{MnO_2} + z\mathrm{KOH}.$$

From the definition of an element and Lavoisier's law the following equations must be true :

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

As is evident, there are five unknown quantities and only four equations. But since, as already stated, the *relation* only of the coefficients is required, the number of equations is sufficient, and it is only necessary to choose some rational value for one of the unknown quantities. If on carrying out the calculation the values found for other unknown quantities are fractions, the whole must be multiplied by some suitable factor in order to reduce the coefficients to whole numbers. *Irrational quantities must not appear in the results ;* the equations must therefore be of the first degree and the coefficients of the unknown quantities must be rational.

If we now take $z = 1$, then from (d) . . . . $q = \frac{1}{2}$.

By the combination of (*c*) and (*b*) we obtain

$$-q = 2y - z \quad \text{and} \quad y = \tfrac{1}{4}.$$

From (*b*) and (*a*) $p = z - y$, that is $p = \tfrac{3}{4}$.

Finally: from (*a*) $\tfrac{3}{2} = x + 1$, which gives $x = \tfrac{1}{2}$.

If now all the results of the calculation be multiplied by 4, and be inserted in the equation of the reaction, we obtain

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

More equations than unknown quantities cannot be obtained; but the case is not excluded where the number of equations may differ by more than one from the number of unknown quantities. For example, the reaction by which potassium chlorate, on heating, forms oxygen, potassium perchlorate, and potassium chloride:

$$pKClO_3 = qKCl + rKClO_4 + sO_2.$$

This gives for 2 independent relations 4 unknown quantities, with which more than one system of values can be determined. Experience has shown that the temperature determines which system makes its appearance. The equations, however, are of the first degree and their unknown quantities have whole numbers for coefficients, so that in this case, also, only rational values can be obtained for the unknown quantities.

It is therefore always possible to represent a chemical reaction by an equation in which the coefficients are ***whole numbers.***

An important application of this rule will be given later in § 23.

REMARK 5. The fact must not be overlooked that the quantities of the substances which appear in the equation are only the portions which actually take part in the transformation. In the equation

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

but a relatively small quantity of water appears. It must not be assumed, however, that this small quantity of water is sufficient to cause the transformation ; since the equation merely states that in the reaction referred to—and this occurs only in the presence of much water—the given quantity of water has changed into another form.

REMARK 6. The methods which have been given for the determination of the proper coefficients usually lead to the desired results. Nevertheless it is often simpler to refer the chemical change to an imaginary reaction, the coefficients of which can be immediately determined ; when the latter are known it is not difficult to write the actual equation with the proper coefficients.

The action of water on potassium manganate will be again considered. K_2MnO_4 is a derivative of MnO_3 ; with water it gives $KMnO_4$, a derivative of Mn_2O_7, and the peroxide MnO_2. The imaginary change of the oxide is the formation of Mn_2O_7 and MnO_2 from MnO_3.

For this imaginary reaction the equation can be immediately found :

$$3MnO_3 = Mn_2O_7 + MnO_2.$$

$3MnO_3$ requires $3K_2MnO_4$; Mn_2O_7 assumes $2KMnO_4$; 4K remains, appearing as 4KOH, and therefore $4H_2O$ is required.

Finally : The action may be divided into a series of phases ; each phase can be represented by a simple reaction, the equation for each phase written, and then it is only necessary to combine the separate phases in order to arrive at an equation which represents the initial and final states of the reaction.

It is known, for example, that by the action of potassium bichromate on alcohol there are formed aldehyde, potassium sulphate, and chromic sulphate. It is accordingly assumed : that sulphuric acid and potassium bichromate give potassium sulphate and chromic acid ; that chromic acid splits up into water and anhydride; that the anhydride oxidizes alcohol with the formation of aldehyde and water, and is itself reduced to chromium trioxide. These changes are expressed in the following equations:

$$K_2Cr_2O_7 + H_2SO_4 + H_2O = K_2SO_4 + 2H_2CrO_4;$$
$$2H_2CrO_4 = 2H_2O + 2CrO_3;$$
$$2CrO_3 = Cr_2O_3 + 3O;$$
$$3C_2H_6O + 3O = 3C_2H_4O + 3H_2O;$$
$$Cr_2O_3 + 3H_2SO_4 = Cr_2(SO)_4 + 3H_2O.$$

By addition, similar members being cancelled on both sides, we obtain

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_6O$$
$$= K_2SO_4 + Cr_2(SO_4)_3 + 3C_2H_4O + 7H_2O.$$

The disappearance—in the above addition—of so many substances has not only a mathematical but also a chemical significance. The division of the whole change into phases is a purely mental operation, and the substances which occur in this operation, but do not actually come into existence, are not found in the final equation. The members of the equation which disappear are all formulas of substances, the existence of which is assumed in order to connect the equations with one another, and only those substances appear in the final equation which can be identified in the initial and final stages of the reaction.

Problems. The equations should be found which represent the following reactions:

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

2. The action of concentrated sulphuric acid (H_2SO_4) on copper (Cu) gives copper sulphate ($CuSO_4$), sulphur dioxide (SO_2), and water (H_2O).

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

4. Potassium bichromate ($K_2Cr_2O_7$) on heating with concentrated hydrochloric acid (HCl) is decomposed, with the formation of chromic chloride (Cr_2Cl_6), potassium chloride (KCl), and water (H_2O).

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

§ 6. **Law of Constant Proportions.** The elements combine with one another in fixed relations by weight and these relations are often retained when the same elements appear together in combination with other elements.

Example. Ethylene is composed of 6 parts carbon and 1 part hydrogen. Carbon and hydrogen occur in the same relation by weight in all other hydrocarbon compounds of the ethylene series, also in all fatty-acid, aldehyde, and dihalogen compounds of ethylene; the latter containing in addition both oxygen and halogen.

200 grams of mercury combine with 32 grams sulphur, forming mercuric sulphide. The same quantities are found in mercuric sulphate combined with 64 grams of oxygen.

39 parts of potassium by combination with 35.5 parts chlorine form potassium chloride. In potassium chlorate the same quantity of potassium is found combined with the same quantity of chlorine and 48 parts of oxygen.

In connection with this law the following rules will be given:

The same relation by weight existing between two elements, combined with a third, is often observed when the two elements combine with another element.

Example. 48 parts oxygen and 14 parts nitrogen, form a compound with 108 parts silver: 48 parts oxygen and 14 parts nitrogen are also found in combination with 31.75 parts copper, with 103 parts lead, with 100 parts mercury, with 32.5 parts zinc, with 68.5 parts barium, with 20 parts calcium, with 39 parts potassium, with 23 parts sodium, with 1 part hydrogen.

32 parts sulphur and 64 parts oxygen combine with 216 parts silver; an equal quantity of sulphur and oxgen is found combined with 206 parts lead, 63.5 parts copper, 200 parts mercury, 65 parts zinc, 137 parts barium, 40 parts calcium, 78 parts sodium, and 2 parts hydrogen.

§ 7. **Law of Equivalence of the Elements.** In many cases the elements can enter into combination with one another according to fixed relations by weight. The number of grams of an element which can replace one gram of hydrogen is called the *equivalent* of the element.

Example. 1 gram of hydrogen combines with 8 grams of oxygen. But the hydrogen in combination with 8 grams of oxygen can be replaced by 23 grams 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 mercury.

REMARK. The equivalence of an element can therefore be determined from the quantity of it which combines with 8 grams of oxygen, or with such quantity of another element as forms a saturated compound with 1 gram of hydrogen.

§ 8. **Explanation of the Fundamental Laws.** Only the first three of the six laws given are independent laws, stating something which is in itself unrestricted. The law of constant proportion and the law of equivalence can be considered as special cases of the law of multiple proportion. Nevertheless the formulation of these special cases is necessary, since they make clear the existence of important phenomena: and without this formulation the important special cases would perhaps be overlooked.

In order to express the fact "that an element *takes the placc of* another in a compound," the word *substitute* is often employed. It is said "that copper chloride is hydrochloric acid in which the hydrogen has been substituted by copper." Relative to this it is to be remarked that the substitution is not always directly practicable. Although it is possible without difficulty to substitute the copper in copper sulphate by zinc, by introducing a rod of zinc in the solution of the copper sulphate, the reverse substitution does not take place so easily and is attained only by a relatively complicated chemical process.

It is possible, under certain conditions, to effect the substitution with quantities of the elements other than the so-called equivalents. For example, a chlorine compound may be obtained from hydrochloric acid which in place of 1 gram of hydrogen contains, not 31.75 grams copper, but double that quantity. Especially in organic chemistry this circumstance has made the determination of the equivalents very difficult,—since here the question: which substitution quantity shall be called *the* equivalent ? often arose,—and the complex substitutions increased the difficulty of representing the substances by universally valid formulæ at a time when the significance of equivalence was attributed to the letters representing the elements. The subsequently developed atomic theory saves us the trouble of deciding on the proper equivalent, and furnishes us with a method of formulation which is not affected by the uncertainty of the notation previously used. It is true that atomic weight and the equivalence do bear a certain relation to one another, but in each stage of experimental chemistry there is for each element a fixed atomic weight, while the significance of the correct equivalent may always vary.

§ 9. **Gay-Lussac's Law on the Combination of Elements in a Gaseous State.** When a gaseous compound is formed from gaseous elements, the volume of a fixed quantity of the compound stands to the volumes of the combining elements in a ratio which can be expressed by whole numbers.

Example. *Two* liters of gaseous hydrogen chloride result from the combination of *one* liter of chlorine and *one* liter of hydrogen. *Two* liters of water-vapor can be decomposed into *two* liters of hydrogen and *one* liter of oxygen, and can be formed from the same quantities. *Two* liters of ammonia-gas give on decomposition *three* liters of hydrogen and *one* liter of nitrogen.

REMARK I. This law is a special case of a more general law discovered by Gay Lussac in 1808, which will be given later in § 11.

REMARK 2. When substances in a gaseous condition are compared with respect to their volumes, it is always assumed that the pressure and temperature are the same in all cases.

CHAPTER III.

THE PROPERTIES OF GASES.

§ 10. **Law of Boyle-Gay-Lussac.** Many substances, by heating or by a decrease of pressure, are transformed into gaseous bodies; many others are gaseous at *normal* temperature and *normal* pressure, i.e., at 15° C. and 760 millimeters of mercury. For most gaseous bodies there exist certain limits, within which for a certain quantity of substance the relation between pressure, volume, and temperature is governed with great exactitude by the following equation:

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

In this formula V is the volume of a certain quantity of the substance at the *absolute* temperature T, and P the corresponding pressure.

Example. 1 gram of hydrogen at 0° C. and 760 mm occupies a volume of 11.16 liters; 1 gram of chlorine a volume of 0.324 liters.

---

* t = temperature in centigrade degrees.
C = a constant.

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

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

with the law of Gay-Lussac (also called law of Charles),

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

or

$$V_t = V_0 \left(1 + \frac{t}{273}\right). \quad . \; . \; . \quad (P \text{ constant}).$$

REMARK 2. The gases which conform to the above law are called *ideal* gases. *Vapors* can be considered as ideal gases when they are at temperatures relatively far above their condensation-points. If gases show a considerable deviation in their behavior from the Boyle-Gay-Lussac law, their closer investigation belongs to the field of physics. In this book only the case of the so-called *abnormal gas densities* will be considered. (Compare § 14.)

§ 11. **Gay-Lussac's Law on the Reactions of Substances in a Gaseous Condition.** When gaseous substances appear in a reaction, their volumes stand to one another in most simple relations, which may be expressed by whole numbers.

Example. *Two* liters of hydrogen combine with *one* liter of oxygen to form *two* liters of water-vapor (see Remark to § 12).—*One* liter of chlorine combines with *one* liter of hydrogen to form *two* liters of hydrogen chloride.—*One* liter of methane with *two* liters of oxygen gives *one* liter of carbon dioxide and *two* liters of water-vapor.—1 gram of diamond combines with 1.9 liters of oxygen to form 1.9 liters of carbon dioxide.

REMARK. This law was deduced by Gay Lussac from investigations carried out in 1808 and was proved by Humboldt. It includes the law given in § 9.

§ 12. **Gas Density.** In chemistry the density of a gas is compared with that of *air* or, more generally, with that of *hydrogen* at the same temperature and pressure. The relation between the weights of equal volumes of a gas and hydrogen under the same conditions shall, according to the law of Boyle–Gay-Lussac, be the same for all temperatures and pressures. If the volume occupied by a definite weight of a substance in a gaseous condition at a definite temperature and pressure is known, then the weight of one liter of the gas under *normal* conditions (0° and 760 mm) can be calculated by applying the Boyle–Gay-Lussac law. This weight, expressed in grams, divided by 0.0896 gram (the weight of 1 liter of hydrogen at 0° and 760 mm) gives the *gas density* of the substance.

REMARK 1. The weight of a substance in a gaseous condition at 0° and 760 mm is often only a *mathematical fiction*, and this is true of those substances whose maximum vapor pressure at 0° is less than 760 mm. When it is stated that one liter of water-vapor at 0° and 760 mm has a weight of 0.8 gram, this is not an actually true statement, since water-vapor at a temperature of 0° has a vapor pressure of only 4 mm. The weight *would*, however, be 0.8 gram if water-vapor could be compressed at 0° without condensing until a pressure of 760 mm was reached and obeyed the Boyle-Gay Lussac law at this pressure. This imaginary value is used since it allows all gases and vapors to be compared directly with hydrogen, of which the weight of one liter at 0° and 760 mm has been very accurately determined, and since by this comparison the vapor density of different substances may be readily obtained.

REMARK 2. The *specific volume* of a gas is the volume of 1 gram of the gas, at 0° and 760 mm, expressed in liters. For hydrogen, for example, this value is

$$\frac{1}{0.0896} \text{ liters} = 11.16 \text{ liters.}$$

REMARK 3. The knowledge of the gas densities is of great importance in chemistry, not only because this is a property of substances, but also because it has been shown that relations exist between the gas densities and the weights of substances which take part in reactions; also relations exist between the vapor densities and the laws of composition, and their most striking application is found in the atomic theory, which will presently be considered. (See § 14 ff.)

§ 13. **Some Methods for Determining the Gas Density.**—*General Principle.* In order to calculate the gas density of any substance—the weight of 1 liter of hydrogen at 0° and 760 mm being accepted as already determined—there must be known: the weight of the quantity of substance taken, its volume in the gaseous condition, and the pressure and temperature at which the volume has been measured. From these data the weight of 1 liter at 0° and 760 mm can be calculated. This principle is the foundation of the following methods:

a. Regnault's Method. A glass globe, the capacity of which is known, is weighed first evacuated and then filled with the gas, at the temperature and pressure of the surroundings. This method is especially suitable for substances which are gases at ordinary temperatures, and gives very accurate results.

b. Dumas' Method. This is much used for liquids

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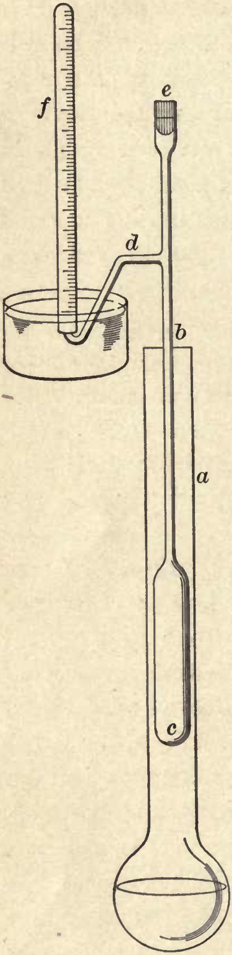
which do not have a high boiling-point. A small quantity of the liquid to be examined is introduced into a glass globe of known weight and capacity; this is then heated in a bath, the temperature of which is several degrees above the boiling-point of the substance. The liquid boils, the vapor escapes through the narrow neck, and the air is driven out. Finally the globe is filled with the vapor at the temperature of the bath and at the atmospheric pressure. The neck of the globe is sealed by fusion, the globe is removed from the bath and again weighed.

REMARK. By certain alterations, this method may be used also for very high temperatures, the glass globe being replaced by one of porcelain. The Dumas method has the disadvantage that liquids are often mixed with small quantities of substances having higher boiling-points ; as a result the impurities play an important part in the final state.

c. Gay Lussac's Method, modified by Hoffmann. This is used for liquids having a low boiling-point. A little flask, weighed first empty, then filled with liquid, fused shut, and again weighed, is introduced into the Torricellian vacuum of a graduated barometer. The latter is surrounded by a jacket into which is led the vapor of a boiling liquid. The substance is thus transformed into vapor, the flask bursts, and the mercury falls in the tube. The volume is then read off by the graduations on the tube; the pressure of the vapor is the atmospheric pressure minus the column of mercury remaining in the tube; the weight is already determined, and the temperature is that of the vapor in the jacket.

d. Victor Meyer's Method. (Air-displacement Method.) In this method the volume of the vapor is not measured directly, but the volume of air displaced by the vapor is determined.



A long glass tube *ec*, having an elongated bulb on its lower end, is provided with a side tube *d*. The jacket *a*, which surrounds the greater part of the tube, contains a liquid, the vapor of which on boiling heats the part *c* to a constant temperature. The opening *e* is closed with a stopper, while *d* extends into a vessel filled with water, in which stands the graduated tube *f*, likewise filled with water. The liquid in *a* is heated to boiling; the vapor surrounds the bulb *c*; the air in the latter expands and escapes through *d* until the expansion ceases. The end of *d* is now brought under the opening of *f* and, by removing the stopper, there is quickly dropped into the tube through *e* a little bottle containing a known quantity of the substance the gas density of which is to be determined, and the stopper is replaced immediately. The substance is now vaporized in the lower part of the apparatus and a volume of air corresponding to the volume of vapor is displaced; this volume of air escapes through the connecting tube *d* into *f*. When the substance is completely vaporized the escape of air-bubbles ceases. Now since the gas has displaced an equal volume of air, the volume of the air is exactly equal to the volume of the gas if this were to be cooled under atmospheric pressure to the temperature of the room. The volume of the air is suitably measured, the pressure and temperature are noted, and the former is decreased by the vapor pressure of water at the temperature of observation. After the weight, pressure, temperature, and volume have been determined in this manner, the weight of one liter of the vapor at 0° and 760 mm can be readily calculated.

Example. In a gas-density determination by Victor Meyer's method 0.184 gram of a liquid was vaporized and at the end of the operation 37.5 cc of moist air were obtained. The height of the barometer was 752 mm, the temperature of the room 14° C.

What is the gas density of the substance?

The total pressure of air and water-vapor is 752 mm. But since the vapor pressure of water at 14° is 12 mm, the pressure of the air must be equal to 740 mm. At 0° and 760 mm the volume of the air is accordingly

$$37.5 \times \frac{740}{760} \times \frac{273}{273 + 14} = 35 \text{ cc},$$

and this is equal to the volume of 0.184 gram of the vaporized substance at 0° and 760 mm. Therefore one liter of this substance at 0° and 760 mm has the weight

$$1000 \times \frac{0.184}{35} \text{ gram} = 5.3 \text{ grams}.$$

The gas density accordingly is $\frac{5.3}{0.0896} = 59$.

REMARK 1. When it is desired to determine the gas density with only relative accuracy the Victor Meyer method is usually employed; in most cases a relatively accurate determination of the gas density is sufficient for chemical purposes.

As is evident from the description of this method, it is not necessary to know the temperature of the bath, the only requirement being that it be sufficiently high to effect the complete vaporization of the substance under investigation. If the tube *ec* is constructed of suitable material, this method can be used for very high temperatures.

§ 14. **Abnormal Gas Densities.** Most gases and vapors are so constituted that the volume occupied by a given weight of the substance can be measured at certain temperatures and pressures, and, after being reduced to 0° and 760 mm, for the same substance always give the same value. Each substance has a corresponding gas density, independent of the temperature or pressure at which the measurements are conducted. This rule holds good for all substances which within certain limits of temperature and pressure obey the law of Boyle-Gay Lussac.

There are, however, certain substances, as nitrogen dioxide and acetic acid, which behave differently; their gas densities are dependent upon the temperatures and pressures employed. For such substances there exists at low temperatures a maximum value for the gas density, and at high temperatures a minimum value, which does not alter on further increase of temperature. These latter constant values are accepted as the correct values for acetic acid and similar substances. Of certain other gases the density is constant for a considerable range of temperature, but decreases at still higher temperatures. Chlorine is a gas of this nature. Especially noteworthy is the behavior of sulphur, the gas density of which at 464° is about four times greater than at 1100°, and which suffers no change between 1100° and 1700°.

The anomalies just mentioned are called *abnormal gas densities*. An explanation of this behavior will be given in the following. (See § 17, Rem. 5. Comp. also § 21, Rem. 3.)

§ 15. **On the Nature of Gaseous Bodies. Molecules. Atoms.** In physics and also in chemistry the following conception is employed: a gas consists of a great number of very small particles moving in straight lines through space. Each of these particles, called *molecules*, has the same chemical composition as the entire mass of the substance. If the gas is a compound, then the molecule consists of heterogeneous parts, each of which is composed of a single element. These parts are called *atoms;* according to our present knowledge of chemical phenomena the atoms in a chemical or physical respect are not further divisible. The molecules of gaseous elements are also composed of atoms which in this case are similar to one another. The volume of the molecules themselves is small in comparison to the space in which they move.

Remark 1. The theory of the constitution of liquids has not been so far developed as that of gases. Still less work has been done on the molecular theory of solid substances.

Remark 2. The existence of atoms was assumed by Demokritos as early as the fourth century B.C. Modern chemistry is indebted chiefly to Laurents, whose work dates from the middle of the present century, for the distinction between the conceptions, atom, molecule, and equivalent.

§ 16. **Avogadro's Hypothesis.** In equal volumes of different gases at the same pressure and the same temperature there is an equal number of molecules.

Remark 1. This hypothesis was enunciated by Avogadro in 1811 and by Ampère in 1814, but was not recognized by many chemists as the foundation of a system until the latter half of the present century.

§ 17. Deductions from Avogadro's Hypothesis.

a. Molecular Weight. The relation by weight between two equal volumes of different gases, under similar conditions of temperature and pressure, is the relation by weight between one molecule of the one substance and one molecule of the other. If the weight of one molecule of *hydrogen* is assumed to be 2, then the weight of one molecule of other gases is equal to their *molecular weight.*

The molecular weight is therefore a *ratio*, which expresses the relation between the weight of one molecule of a substance in a gaseous condition and the weight of one half-molecule of hydrogen. The molecular weight may *also* be defined as twice the quotient of the weight of one liter of the substance, in a gaseous condition at 0° and 760 mm, divided by 0.0896 gram.

Briefly stated: The molecular weight of a substance is equal to twice its gas density. (Comp. § 12.)

REMARK 1. The indefinite number 2 taken as the molecular weight of hydrogen is not an experimentally determined value, but is a conventionally *assumed* one; therefore all molecular weights which are used in chemistry are only *relative numbers*. The determination of the absolute molecular magnitudes belongs to physics; chemistry for the investigation of its problems requires only relative numbers.

REMARK 2. The molecular weight of only those substances which vaporize without decomposing can be determined directly. Comp. § 21, Rem. 3.

REMARK 3. The weight of one liter of a substance in the gaseous state can be determined directly from the molecular weight; it is equal to one-half of the molecular weight multiplied by 0.0896 gram.

REMARK 4. The *molecular quantity* of a substance is the number of grams of the substance, which contains the same number of units as the molecular weight.

Often this quantity is also called a *gram-molecule* of the substance.

REMARK 5. *Explanation of the Existence of Abnormal Gas Densities.* Substances the gas densities of which vary with the temperature vary also in molecular weight. This may be explained by assuming that the structure of the molecules is more complicated at a low temperature than at a higher temperature, and that on an increase in temperature the structure becomes simpler. This explanation of the phenomenon is supported by the fact that the specific heats of substances with abnormal gas densities are very great and are variable; only a portion of the heat added goes to increase the temperature; the rest is used for breaking down the complicated molcular structure into a more simple one.

§ 18.

b. Atomic Weight. Theoretical and Experimental Definition. The atomic weight of an element is the weight of one atom of the element with respect to a half-molecule or one atom of hydrogen.

REMARK 1. An atomic weight also is only a ratio, i.e., a *relative quantity.*

REMARK 2. In the table given in the back of this book the unit taken for the atomic weights is, for certain reasons, not the atom of hydrogen, but is one sixteenth of the atom of oxygen. The value there given for the atomic weight of hydrogen is accordingly 1.007. If all the atomic weights in the table are divided through by 1.007, their values with relation to one atom of hydrogen are obtained.

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

Example:

I. Compounds of oxygen.

Name.	Molec. Quant.	Quant. of Oxygen.
Oxygen	32	32
Water	18	16
Carbonic oxide	28	16
Carbon dioxide	44	32
Sulphur dioxide	64	32
Sulphur trioxide	80	48
Nitric acid	63	48
Arsenic trioxide	396	96

Greatest common divisor = 16 = atomic weight of oxygen.

II. Compounds of chlorine.

Chlorine......	71	71
Hydrogen chloride....	36.5	35.5
Methyl chloride	50.5	35.5
Ethylene dichloride....	99	71
Chloroform	119.5	106.5
Carbon tetrachloride...	164	142

Greatest common divisor = 35.5 = atomic weight of chlorine.

Remark 3. The existence of a greatest common divisor is in conformity with the law of multiple proportion, but is not deduced from it. If molecular quantities of different compounds of the elements A and B all contain equal quantities of **A**, then the law of multiple proportion requires that there shall be a greatest common divisor for the corresponding quantities of B. But the other condition is not contained in the law. The existence of these greatest common divisors, which are the virtual foundations of the atomic weights, is not a circumstance which can be assumed from any of the earlier mentioned laws, but is a fact derived from experience.

It is evident that the atomic weight of an element must be changed if a new compound of it is discovered, the analysis of which leads to the finding of another greatest common divisor.

Remark 4. Other methods for the determination of the atomic weight will be considered later. In these, however, the truth of Avogadro's hypothesis is accepted, so that the results obtained by them in no way diminish the value of the atomic weights obtained by the methods just described. If the number of volatile compounds of an element is small, much importance cannot be attached to the greatest common divisor, and other methods are required for determining and comparing the atomic weights.

REMARK 5. To determine the composition of molecular quantities of a substance it is not necessary to analyze these quantities. The numbers are calculated from the percentage composition of the substance and from the gas density.

REMARK 6. The greatest common divisor here mentioned is a number the accuracy of which is dependent upon that of the molecular weight and also upon that of the gas density. The latter is indeed not very great; but the *degree* of the number sought is determined by the greatest common divisor, and with the knowledge of this degree the number can be accurately determined, since choice can then be made from a great number of possible values, all of which may be determined with great accuracy. If the analysis of pure hydrogen chloride shows that the substance contains 35.46 grams of chlorine to 1 gram of hydrogen, and the molecular weight is found to be 36.5, then the atomic weight of the chlorine can only be either 35.46 or a rational fraction of this number. The greatest common divisor is, however, of the degree 35.5, and it therefore directly follows that the accurate atomic weight is 35.46.

REMARK 7. The molecular weight determined from the gas density is only approximately accurate. Since this is the case, it also is corrected with the help of analytical data, as will be described later (comp. § 21).

§ 19.

c. Number of Atoms in the Molecule. When the qualitative and quantitative composition, the molecular quantity, and atomic weights of the elements of a compound are known, the number of atoms in the molecule can be easily determined. This is done by dividing the quantities of the elements which are present in the molecular quantity of the compound by the atomic weights of the corresponding elements.

Example. The molecular quantity of ethyl alcohol is 46 grams; these 46 grams contain 24 grams carbon, 6 grams hydrogen, and 16 grams oxygen. The atomic weights of carbon, hydrogen, and oxygen are, respectively, 12, 1, and 16. The ethyl-alcohol molecule therefore contains 2 atoms of carbon, 6 atoms of hydrogen, and 1 atom of oxygen.

The molecular quantity of oxygen is 32. There are accordingly 2 atoms in the molecule.

The molecular quantity of phosphorus is 124, the atomic weight is 31; the number of atoms in the molecule is therefore 4.

REMARK. Certain reactions lead to the determination of the number of atoms in the molecule, without involving the investigation of the molecular quantity or the atomic weights.

One liter of chlorine and one liter of hydrogen combine to form two liters of hydrogen chloride. If chlorine and hydrogen were both monatomic gases, the total number of molecules after the reaction had taken place would be only half the number in the initial condition; and accordingly—from Avogadro's hypothesis—the volume of the hydrogen chloride would be only half the entire volume of the reacting gases. If, however, it be assumed that chlorine and hydrogen, as well as hydrogen chloride, are composed of diatomic molecules, then the number of molecules and also the volumes of the gases will undergo no alteration. It is a fact that in the reaction mentioned no contraction in volume takes place.

This may also be stated as follows: one liter of hydrogen occupies after the reaction a volume of two liters; each molecule has therefore split up into two halves.

Similarly to this may be viewed the formation of 2 liters of water-vapor from 2 liters of hydrogen and 1 liter of oxygen, and also the decomposition of 2 liters of ammonia-gas into 1 liter of nitrogen and 3 liters of hydrogen.

From these facts it can be assumed that hydrogen, chlorine, oxygen, and nitrogen are not monatomic, but are at least diatomic. Nevertheless such speculation does not lead to positive conclusions; since theory and fact would also agree if the number of atoms in the molecule was greater than two. It is therefore better to solve the problem with the help of the molecular quantities and the atomic weights.

§ 20.

d. Number of Atoms in the Molecules of the Elements. Many substances in the gaseous state are diatomic, i.e., nitrogen, hydrogen, oxygen, chlorine: N_2, H_2, O_2, Cl_2.

Phosphorus-vapor at 1040° is P_4, at still higher temperatures it breaks up partially into P_2. Sulphur-vapor at the boiling-point of sulphur is S_8, at higher temperatures the molecules split up into molecules S_2, which are stable at the highest temperatures. Monatomic are: potassium, sodium, zinc, cadmium, and mercury: K, Na, Zn, Cd, Hg.* The gas densities of the first four monatomic elements mentioned are determined at very high temperatures, and their atomic weights are not deduced from the molecular quantities of the compounds, but are found in another way.

The vapor density of mercury is 100, while the molecular quantity is 200. The volatile compounds of this element which have been investigated all contain 200 grams of this element in molecular quantities of the compounds. The number of these compounds is not large, and from this it might perhaps be doubted that mercury was in fact monatomic. But the specific heat of solid mercury also leads to the atomic weight 200 (comp. § 24), and the researches of Kundt on the velocity of sound in mercury-vapor have shown that the so-called factor of Laplace for this gas is 1.67: according to the kinetic theory of gases, this value for this factor belongs to a monatomic gas.

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*It is possible that the recently discovered argon is to be counted among the monatomic elements.

§ 21.

e. Deduction of the Molecular Formula of a Substance. The molecular formula of a substance expresses by certain symbols its qualitative and quantitative composition, as well as the number of atoms which, when the substance is in the gaseous state, are present in the molecule.

These symbols have already been used in this book. The elements are represented by letters, and each symbol denotes not only an element, but also its atomic weight. Furthermore, the formula gives the gas density, since this is equal to one-half the sum of the weights of the atoms.

The substance H_2SO_4 for example contains to 2 grams of hydrogen 32 grams of sulphur and 64 grams of oxygen; its gas or vapor density is 49.

The deduction of the molecular formula from experimental data will be illustrated by an example.

The analysis of acetic acid has shown that 100 parts of this substance contain 39.9 parts of carbon, 6.7 parts of hydrogen, and 53.4 parts of oxygen. The atomic weights are: $C = 12$, $H = 1$, $O = 16$. The value 30.5 has been found for the vapor density.

From the latter fact it is assumed that the molecular weight is equal to about 61.

With the help of the atomic weights the relative composition is determined in the following manner:

The formula must have the form $C_pH_qO_r$ and the substance therefore contains $12p$ parts carbon, q parts hydrogen and $16r$ parts oxygen. The quantities stand in the proportion 39.9 : 6.7 : 53.4, and the formula $C_{\frac{39.9}{12}}H_{6.7}O_{\frac{53.4}{16}}$ represents the results of the analysis. From this the formulas $C_{3.325}H_{6.7}O_{3.337}$ and $CH_{2.015}O_{1.004}$ are derived. The latter may be rounded off to CH_2O.

The results of the analysis are accurately expressed by the formula CH_2O; but by this alone its correctness is not established, since the formula $C_xH_{2x}O_x$ would also be in agreement with the results obtained. All that may be correctly assumed, therefore, is that the substance has a formula of the form $C_xH_{2x}O_x$.

A substance having this formula would give the gas density $15x$. By experiment the gas density was found to be 30.5; therefore $x = 2$ and the formula of acetic acid is $C_2H_4O_2$.

This example illustrates what has been stated in § 18, Rem. 6, namely, that it is necessary to determine the gas density with only relative accuracy. A value is required which will decide by what factor the simplest formula, in this case CH_2O, is to be multiplied.

Therefore in order to obtain the molecular formula from the experimental data, the following operations are necessary: the percentage composition of each element is divided by the corresponding atomic weight;

the quotients thus obtained are made into round numbers; the imaginary gas density of the *simplest formula* thus obtained is divided into the gas density determined by experiment; the quotient expressed in round numbers is multiplied into the simplest formula.

Problems. An attempt should be made to solve the following problems:

1. An organic compound has the following composition:

C = 51.9%
H = 13.1
O = 35

The gas density is found to have the value 22.7. What is the molecular formula of the substance?

2. A hydrocarbon contains

92% of carbon
and 7.7% of hydrogen.

The gas density is 38.8. Determine the molecular formula.

3. A substance contains in 100 parts

73.8 parts carbon,
8.7 parts hydrogen,
17.1 parts nitrogen.

The gas density is 80.2. Determine the molecular formula.

REMARK 1. If the molecular quantity can be determined by another way than by the gas density, it is likewise possible to arrive at the molecular formula.

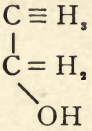
The molecular formula gives the gas density and the results of analysis, and in addition the number of atoms of each element in the molecule, but not the grouping of the atoms. This arrangement of the atoms must be shown, however, when two substances are different and yet have the same molecular formula. This condition occurs frequently in organic chemistry and is called *isomerism*. The representation of the arrangement of the atoms in the molecule makes it possible to express the behavior of the substance in many reactions.

A formula in which the grouping of the atoms is shown is generally called a *constitutional formula;* it may also be called a *structural* formula; and while too great importance must not be attached to such a formula,—since not all reactions lead to the same conclusions with regard to the grouping, and the question often arises as to which reaction shall determine *the* constitution,—in practical chemistry the need of such formulas is very great, since they at all events express many relations of the substances to one another.

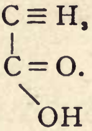
Example. Ethyl alcohol and methyl ether are isomers, the molecular formula for both being C_2H_6O. The first of these substances is attacked by sodium with the evolution of hydrogen and the formation of a substance, sodium ethylate, whose composition is represented by the formula C_2H_5ONa. Sodium has no action on methyl ether. If to the alcohol the structural formula $(C_2H_5)OH$ be given, to the ether the formula $(CH_3)_2O$, then the chemical difference mentioned as existing between the two bodies is expressed, and according to these formulæ an analogy exists between alcohol, $(C_2H_5)OH$, and water, H_2O, which explains the action of sodium. No such analogy is found in the structural formula $(CH_3)_2O$.

Acetic acid and methyl formate are isomers having the molecular formula $C_2H_4O_2$. By the action of sodium on acetic acid one hydrogen atom may be substituted by sodium; methyl formate, however, allows no such substitution; on heating with sodium it is decomposed and is transformed into methyl alcohol and sodium formate. This difference in behavior towards sodium is found expressed in the formulas $C_2H_3O.OH$ for acetic acid and $HCO.O.CH_3$ for methyl formate.

The separation of the atoms into groups is carried still further, and ethyl alcohol, for example, is represented by



and acetic acid by



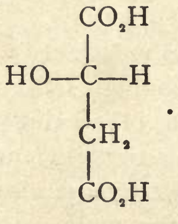
The meaning of the dashes in these formulæ will be explained later (see § 22).

In the substances mentioned above it is sufficient to show only the grouping of the atoms; but in many cases this method of writing the formulæ is not adequate to express the difference of the isomers, and it is necessary to determine also the spacial relations of the groups in the molecule, and to represent the molecule as a figure of three dimensions, and not as a flat figure, whose parts lie in one plane, for example a piece of paper.

With this point in view Van't Hoff and Le Bel have proposed (1877) a theory which makes it possible to explain many important cases of isomerism and to denote them by formulæ. One of the most important propositions of this theory will here be stated and explained.

There are cases where two substances have exactly the same chemical properties and are both represented by the same constitutional formula, but which differ from one another in that in solution one of them rotates the plane of polarization of polarized light to the right, the other to the left, and both with an equal intensity. These phenomena are in accord with the following rule: if in the constitutional formula for the molecule of an organic compound a carbon atom—combined with *four dissimilar atoms or groups*—appears, then the compound is optically active, and exists in two modifications, one of which rotates the plane of polarization just as far to the right as the other to the left.

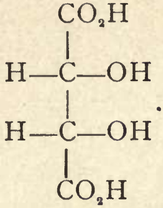
Example. The following is the constitutional formula of malic acid:



$$\begin{array}{c} CO_2H \\ | \\ HO-C-H \\ | \\ CH_2 \\ | \\ CO_2H \end{array}.$$

The carbon atom of the alcohol group $HO-\overset{|}{\underset{|}{C}}-H$ is a so-called *asymmetric* carbon atom; it is attached to four dissimilar groups: (CO_2H), H, (OH), and (CH_2CO_2H); malic acid is therefore optically active.

Tartaric acid has the constitutional formula



$$\begin{array}{rcl} & \mathrm{CO_2H} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{OH} \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{OH} \\ & | & \\ & \mathrm{CO_2H} & \end{array}.$$

In this substance there are therefore *two* asymmetric carbon atoms; it is optically active.

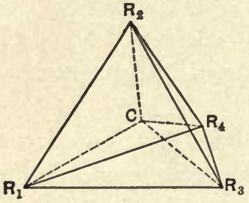
As already stated, the presence of an asymmetric carbon atom requires the existence of two active modifications; there appears, however, in addition to the first two, still another—an inactive modification—which is formed by the combination of the two active modifications. An important example of this double molecule—which is ordinarily formed when the substance is artificially prepared—is racemic acid, which is inactive, and results from the combination of dextro- and lævo-tartaric acids. An inactive substance of this nature can always be decomposed into its active constituents.

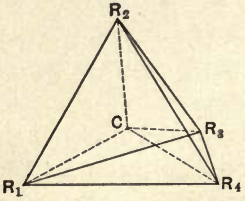
There exists still a fourth modification of tartaric acid, in addition to the two active compounds and racemic acid, which, like racemic acid, is inactive, but which can *not* be decomposed. Still this fact is not in contradiction to the theory; since tartaric acid contains *two* asymmetric carbon atoms, both having exactly equal functions, the molecule being thus divided into two exactly equal halves. Each half causes an exactly equal rotation of the plane of polarization, and therefore the two, according to their geometric relations, may both rotate the plane to the right, or both to the left, or each in an opposite direction.

In the latter case a compensation of rotation occurs, and a molecule is obtained which cannot be decomposed although it is inactive.

The following is the explanation of the behavior of active substances:

Van't Hoff represents an active compound by a figure of three dimensions. The asymmetric carbon atom is located at the centre of a tetrahedron, from which point four forces are exerted towards the apexes of the solid angles, and connect the asymmetric carbon atom with the four groups situated at these apexes. If the central carbon atom is actually asymmetric, then the groups at the apexes of the figure are dissimilar, and the substance has the formula $C R_1 R_2 R_3 R_4$, which may be represented by the two following diagrams:





These two figures are not the same; since it is not possible so to superpose them that similar groups only will come together. Further, neither one of them possesses a single symmetry plane; they are absolutely asymmetrical. If, however, two of the four groups are similar, a symmetry plane results, and the two figures are then superposable.

The representation of the molecule as a tetrahedron makes it possible to denote the optical isomerism in the formula. The correspondence of the structure with the optical activity mentioned above is in so far in accord with the observed facts, in that all active substances have been found to contain one or more asymmetric carbon atoms. The theory is further supported by the fact that solid bodies, which possess the power of rotating the plane of polarization, appear in the form of asymmetric crystals.

Remark 2. A molecular weight exists, strictly speaking, only for such substances as may be volatilized without decomposition. The molecular weight is deduced from the gas density, or else is determined by some other method—i.e., from the osmotic pressure of solutions (§ 57, Rem. 4), or from considerations on the constitution. If the molecular weight is unknown, the simplest formula which is obtained by analysis is made use of, and this formula is then nothing more than an expression for the qualitative and quantitative composition.

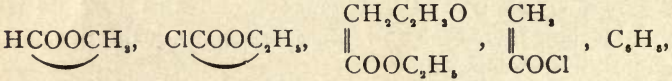
Remark 3. In the case of a number of substances whose molecular weights are not determined from the gas density, but are deduced from other data, the experimentally found gas densities do not correspond with those calculated from the molecular formulas. The molecular formula of ammonium chloride, for example, is NH_4Cl. From this the gas density should be 26.75. In practice a number equal to about one-half of this value is actually obtained. This is due to the fact that ammonium chloride cannot be converted into a gas without decomposition, but on volatilizing splits up into NH_3 and HCl. One molecule of ammonium chloride on vaporizing therefore forms two molecules, which—according to Avogadro's hypothesis—occupy a double volume. In general this phenomenon will appear in the case of substances which on volatilizing split up into simpler molecules.

If it is desired to include also these cases under *abnormal gas densities*, then it may be said that the gas density of a substance is abnormal when it does not correspond to the molecular formula. (Comp. 14, Rem. 5.)

REMARK 4. Quite recently it has been possible to gain an idea of the size of the molecules of liquids from a theoretical inquiry into the phenomena of capillarity. It has been found that in the case of the molecules of liquids chiefly *association* occurs—that is, the molecules of a liquid are generally complexes of molecules of the same substance in gaseous form.

Associated are the liquid molecules of water, all alcohols, glycols and organic acids, most ketones, propio-nitrile, nitro-ethane, phenol, nitric acid, and sulphuric acid.

Non-associated, for example, are the liquid molecules of 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}, CCl_4, C_2H_5I, C_2H_5SH, $(C_2H_5)_2O$, CCl_3CHO,



$$H\underbrace{COOCH_3}, \quad Cl\underbrace{COOC_2H_5}, \quad \begin{array}{l} CH_2C_2H_3O \\ \| \\ COOC_2H_5 \end{array}, \quad \begin{array}{l} CH_3 \\ \| \\ COCl \end{array}, \quad C_6H_6,$$

C_6H_5Cl, $C_6H_5NO_2$, pyridine, quinoline.

It has been found also that the *degree* of association is dependent on the temperature. In general on an increase of temperature the size of the liquid molecule approaches that of the gas molecule, and at relatively low temperatures there exists in the solution an equilibrium between the associated and the non-associated molecules. In the following table the relation between temperature and association is given for several substances:

	−89°.8 C.	+20°C.	100°C.	140°C.	200°C.	280°C.
Methyl alcohol..	2.65	2.32	2.08	1.97	1.81	....
Ethyl alcohol..	2.02	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 medium temperatures has the liquid molecule $(H_2SO_4)_{32}$; above 130° C. this breaks up into simpler complexes.

§ 22.

f. The Valence of the Elements. The so-called *theory of valence* has a direct bearing on Avogadro's hypothesis. If an investigation be made to determine how many atoms of any one element will combine with one atom of a certain other element to form a *saturated* compound, it will be discovered that the power of different elements varies in this respect; this power is called the *valence* of the element; it is measured by the number of hydrogen atoms with which one atom of the element in question can combine to form a molecule.

Of equal valence or *equivalent* are those elements the atoms of which can combine with a similar number of hydrogen atoms; equivalent are evidently also such elements as combine with one another to form a compound, one molecule of which contains a single atom of both elements.

Univalent are, for example, chlorine, bromine, iodine, since they form the compounds HCl, HBr, HI. Bi- or di-valent are oxygen and sulphur: H_2O, H_2S. Trivalent are nitrogen and phosphorus: NH_3, PH_3. Tetra- or quadri-valent are carbon and silicon: CH_4, SiH_4. Equivalent are chlorine, bromine, and iodine; oxygen and sulphur; nitrogen and phosphorus; carbon and silicon.

Under certain conditions the valence may also be determined from the number of atoms of other *univalent* elements with which one atom of the particular element can combine. Elements having a valence *greater than one* cannot in general be used for the determination of the valence, since in the case of such elements a *mutual* compensation of the valences may take place. Further, such elements often have a *variable valence*, i.e., the element appears in different compounds with different valences.

In ferrous chloride ($FeCl_2$) iron is *bivalent*, in ferric chloride ($FeCl_3$) it is *trivalent*. From the formulas of nitrogen dioxide (NO_2) and sulphur trioxide (SO_3) the valence of the elements nitrogen and sulphur cannot be determined with certainty.

If the theory of valence was a logically deduced and sharply defined conception, it would be possible to obtain *a priori* a knowledge of the valence of an element from the formulas of its compounds. In practice, however, the application of the theory is very much affected by the existence of variable valences and unsaturated compounds. Also, it is not in general the rule that the highest valence of the element appears in its most stable compound. $MnCl_4$ is less stable than $MnCl_2$, while ferrous compounds, on the contrary, are readily oxidized to ferric compounds. Only in the cases of the saturated compounds of C, O, and H can it be in general assumed that these elements are tetra-, di-, and uni-valent respectively, and this fact alone makes it possible to determine the constitution of a saturated organic compound from its molecular formula.

The molecular formula C_2H_6O, for example, can belong to only *two* isomeric substances. The carbon and the oxygen possess together ten valences, and of these ten valences *six* only are required to satisfy the six univalent H atoms. If six of the valences of carbon are saturated by hydrogen, there remain only *two* more, which may be used by the oxygen, and this gives the formula $H_3C.O.CH_3$, which is the formula of methyl oxide.

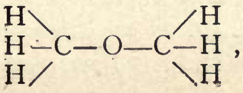
But if *one* of the valences of oxygen is satisfied by hydrogen (and in this case the oxygen cannot be combined with *two* hydrogens), then the other valence must serve to connect the oxygen to the carbon. This latter element then uses *five* of its eight valences for hydrogen, *one* for oxygen, and the remaining *two* compensate one another, resulting in the formula $HO.H_2C.CH_3$, the formula of ethyl alcohol.

Problems. 1. Determine the constitutional formulas of the *saturated* compounds the molecular formulas for which are C_3H_8O.

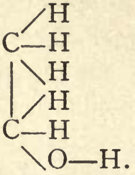
2. Determine the constitutional formulas of the substances having the molecular formula $C_2H_4O_2$, noting that in each of these compounds *one* oxygen atom is attached directly to carbon.

3. Determine the constitutional formulas of the substances with the molecular formula $C_3H_6O_3$, it being understood that all of these contain the carboxyl group OC.OH.

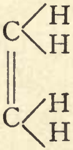
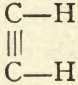
The valences, also called *affinity units*, are usually represented by dashes which extend from the symbols representing the atoms. Methyl oxide may be represented thus;



and ethyl alcohol thus:



In the case of unsaturated carbon derivatives (by this expression it is meant that the valences of the carbon atoms are not saturated), their state is denoted by connecting the carbon atoms by two or by three dashes.

For example, ethylene  ; acetylene 

$$\begin{array}{l}C-H\\ |||\\ C-H\end{array}$$

.

These relations, however, must not be confounded with *forces;* they denote nothing more than certain *unsaturated* states, such as appear in the cases of ethylene and acetylene. Also the expressions *double* and *triple* bonds never imply the actual existence of forces, but signify merely a certain state of saturation.

The tetravalence of carbon is the basis of the stereochemical theory of Van't Hoff and Le Bel. The manner in which the unsaturated compounds are represented in this theory cannot here be further considered.

§ 23.

g. Theoretical Demonstration of the Law of Gay-Lussac on the Reactions of Gaseous Bodies. In § 5, Rem. 4, it was shown how the coefficients of a chemical equation may be determined. It was evident that entirely rational values can always be obtained for the coefficients, and that every chemical equation has the form

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

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

Now if gaseous substances are represented in the equation, it follows—since according to Avogadro's hypothesis each molecule occupies one volume—that the volumes of these substances are to one another as their respective formula coefficients; and, since the latter are rational numbers, the volumes stand to one another in ratios which may be expressed by whole numbers.

Problems. 1. One liter of methane, CH_4, with the required volume of oxygen, is burned completely to carbon dioxide and water. What is the volume of the oxygen and of each of the products of the combustion?

2. Ten grams of ethyl alcohol are burned in air. What is the volume of the air required and what is the volume of each of the products of combustion? (Note. Air contains one-fifth of oxygen by volume.)

CHAPTER IV.

THERMOCHEMISTRY.

§ 24. **Law of Dulong and Petit.** The product of the atomic weight and the specific heat is the same for all elements in a solid state; it is equal to about 6.4.

REMARK 1. This law was discovered in 1818. It may also be expressed as follows: The *atomic heat* of all solid elements is a nearly constant quantity.

REMARK 2. The deviation from the value 6.4 is so great for certain elements, namely, for C, Si, B, and Be, that these cannot be included under the law of Dulong and Petit. However, the atomic heats of these elements approach the normal value if these be measured at high temperatures.

At ordinary temperatures:

Element.	At. Wt.	Spec. Heat.	Atomic Heat.
Beryllium................	9.1	0.408	3.7
Boron....................	11	0.238	2.6
Diamond......	12	0.12	1.44
Silicon..................	28.1	0.170	4.77

At higher temperatures:

Element.	At. Wt.	Spec. Heat.	Atomic Heat.
Beryllium at 257° C.......	9.1	0.58	5.28
Boron above 600° C.......	11	0.5	5.5
Diamond at 1000° C.......	12	0.459	5.5
Silicon at 232° C..........	28.1	0.203	5.7

TABLE OF THE ELEMENTS

WHICH CORRESPOND WITH THE LAW OF DULONG AND PETIT.

Element.	Atomic Weight (in round numbers).	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 (rhomb.)	32	0.1776	5.70
Potassium	39	0.1655	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	0.1067	6.35
Nickel	59	0.1092	6.44
Copper	63.6	0.093–0.095	5.9–6
Zinc	65.4	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
Tungsten	184	0.0334	6.15
Iridium	193	0.0326	6.30
Platinum	195	0.0324	6.31
Gold	197	0.0324	6.39
Osmium	191	0.0311	5.9
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

It is to be noted also that the specific heats of the allotropic modifications of a solid element are different.

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

REMARK 1. This law was enunciated in 1844. It may also be stated in the following manner: The *molecular heat* of a compound is equal to the sum of the atomic heats of the elements of which it is composed. Elements which are exceptions to the law of Dulong and Petit show similar deviations in the cases of their compounds. The law of Joule makes it possible to determine, with reasonable accuracy, the atomic heats of such elements as cannot be examined in the free state. By subtracting the atomic heat of silver from the molecular heat of silver chloride the atomic heat of solid chlorine is found to be from 6 to 6.4.

In addition, the following values have been determined from the molecular heats of compounds:

Element.	Atomic Weight.	Atomic Heat.
Hydrogen..........................	1	2.3
Hydrogen (from palladium-hydrogen)	1	5.9
Oxygen..........................	16	4
Nitrogen..........................	14	6.4?
Fluorine..........................	19	5
Chlorine..........................	35.5	6.4

The law of Joule is also employed with good results in the case of elements which cannot be prepared so pure or in such quantities that their atomic heats can be directly determined. Example: From the atomic heat of lead and the molecular heat of $PbCO_3$ the heat of the group CO_3 is obtained; if this quantity be subtracted from the directly determined molecular heats of $BaCO_3$, $SrCO_3$, and $CaCO_3$, the results obtained are the atomic heats of Ba, Sr, and Ca.

In this way the atomic heats of the following elements have been determined :

Element.	Atomic Weight.	Atomic Heat.
Rubidium..........................	85.4	6.4
Strontium	87.5	6.4
Barium..........................	137	6.4

REMARK 2. The following rule was mentioned by Neumann as early as 1831 : Equivalent quantities of chemically similar substances have the same capacity for heat. Thus, for example, the product of the specific heat and the molecular weight is very nearly constant in the case of calcite, dolomite, magnesite, siderite, and calamine.

REMARK 3. As a proof of the constancy of the molecular heat of analogous compounds the following table is given :

Substance.	Specific Heat.	Molecular Heat.
Ag_2S.	0.0746	18.5
CoAsS.....	0.1070	17.8
Cu_2S.	0.12	19.1
FeAsS	0.1012	16.5
AsS.........	0.1111	11.9
CoS	0.125	11.4
FeS	0.1357	11.9
HgS........	0.0512	11.9
NiS....	0.1281	11.6
PbS	0.0509	12.2
SnS	0.0837	12.6
ZnS	0.1230	12.0
AgCl.	0.0911	13.1
CuCl	0.1383	13.7
HgCl	0.0521	12.3
KCl	0.1730	12.9
LiCl........	0.2[illegible]1	12.0
NaCl	0.[illegible]	12.5
RbCl	0.[illegible]	13.5
NH_4Cl......	0.373	20.0
$BaCl_2$	0.0896	18.6
$CaCl_2$.......	0.1642	18.2

Substance.	Specific Heat.	Molecular Heat.
$HgCl_2$.........	0.0689	18.7
$MgCl_2$...	0.1946	18.5
$MnCl_2$...	0.1425	18.0
$PbCl_2$..........	0.0664	18.5
$SnCl_2$.........	0.1016	19.2
$SrCl_2$	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*	11.0
MnO..........	0.1570	11.1

* According to other statements 0.2439.

Substance.	Specific Heat.	Molecular Heat.
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
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

Substance.	Specific Heat.	Molecular Heat.
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 the Determination of Atomic Weight.**—When an element forms no, or only a small number of, volatile compounds, the atomic weight cannot be determined from the gas density. The knowledge of the specific heat, however, leads to the desired value, as is illustrated by the following example:

The atomic weight of platinum is required. The correct formula for the chloride is not known; it is therefore represented by the formula Pt_pCl_q. The quantitative composition may then be expressed by the formula $Pt_{\frac{p}{q}}Cl$; from the analysis it is known that 35.5 grams of chlorine occur with 48.6 grams of platinum. The specific heat of platinum has been determined, and has been found to be 0.0324; therefore the atomic weight is of the order $\frac{6.4}{0.0324} = 197.5$.

The fraction $\frac{p}{q}$ shall be a proportion between rational numbers, and cannot in fact be far from $\frac{48.6}{197.5}$. It is evident that this fraction is equal to about $\frac{1}{4}$, and therefore $\frac{p}{q}$ is taken equal to $\frac{1}{4}$. The formula of platinum chloride would then be $PtCl_4$ and the atomic weight of platinum $4 \times 48.6 = 194.4$. The accuracy of this conclusion is not affected by the possibility that the formula of platinum chloride may be a multiple of $PtCl_4$.

The law of Joule may be applied in the following manner in order, for example, to determine the atomic weight of barium: 1 kilogram of lead combines with 0.0582 kilogram of carbon and 0.233 kilogram of oxygen to form lead carbonate, the specific heat of which is 0.080. The heat capacity of 1.2912 kilograms of lead carbonate is 0.1033 calorie.* The capacity of 1 kilogram of lead is 0.031 Cal., so that 0.0582 kilogram of carbon and 0.233 kilogram of oxygen together have a capacity of 0.0723 Cal. The same quantities of carbon and oxygen, however, combine with 0.665 kilogram of barium to form 0.956 kilogram of barium carbonate. The heat capacity of this quantity of barium carbonate is 0.108 Cal. × 0.956 = 0.1032 Cal. Therefore the capacity of 0.665 kilogram of barium is 0.0309 Cal. and of 1 kilogram of barium 0.0465 Cal. From this the order of the atomic weight is $\frac{6.4}{0.0465} = 138$ (approx.). In barium chloride 35.5 parts of chlorine are combined with 68.5 parts of barium. If the substance is given the formula $BaCl_2$, then the atomic weight of barium is 137, in sufficiently close agreement with the value 138.

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* 1 Cal. denotes a *large* calorie, i.e., the quantity of heat which is required to heat 1 kilogram of water from 0° to 1°. A *small* calorie is equal to one one-thousandth of this value and is denoted by *c*. The quantity of heat equal to 100 small calories is denoted by *K*. In this book all values will be given in large calories.

§ 27. **Heat of Formation and Heat of Decomposition of a Compound. Heat of Reaction. Endothermic and Exothermic Reactions.** The *heat of formation* is the number of calories which are set free (or absorbed) when the molecular quantity of a compound is formed from the elements. For example, when 78 grams of sodium sulphide are formed from 46 grams of solid sodium and 32 grams of solid sulphur, and the products of the reaction are brought back to the initial temperature of the experiment, then the number of calories set free in the calorimeter by this change is equal to 87 calories, and this quantity is the heat of formation of sodium sulphide. This fact is denoted by the equation

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

The meaning of the term *heat of decomposition* should be evident from the above.

The *heat of reaction* is the quantity of heat which is withdrawn from molecular quantities of reacting substances if after the reaction the system is again brought back to the initial temperature. Thus 87 Cal. is the heat of reaction of the change

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

The heat of reaction is represented in the following manner:

$2Na$ (solid) + S (solid) = Na_2S (solid) . . . + 87 Cal.

NaOH (dissolved) + HCl (dissolved)
= NaCl (dissolved) + H_2O . . . + 13.7 Cal.

Na (solid) + H_2O (liquid)
= NaOH (dissolved) + H (gaseous) . . . + 43.4 Cal.

REMARK 1. The state of aggregation of the reacting substances must in most cases be stated, since the heat of reaction is dependent on it. Thus

NaOH (dissolved) + HCl (dissolved)
= NaCl (dissolved) + H_2O (liquid) . . . + 13.7 Cal.,

while

NaOH (dissolved) + HCl (gaseous)
= NaCl (dissolved) + H_2O (liquid) . . . + 31 Cal.;

C (diamond) + O_2 (gaseous)
= CO_2 (gaseous) . . . + 94.3 Cal.,

C (charcoal) + O_2 (gaseous)
= CO_2 (gaseous) . . . + 97.6 Cal.

The physical state of the substance is generally denoted by printing the formulæ in certain styles of type. In this book, however, it has been considered preferable to mention the physical condition, as has been done in the above equations.

An *exothermic* reaction is one in which heat is set free; an *endothermic* reaction is one in which, on the contrary, heat is absorbed.

The reaction

$2H_2$ (gas) + O_2 (gas) = H_2O (liquid) . . . + 136.8 Cal.

is exothermic, but

N_2 (gas) + $3Cl_2$ (gas) = $2NCl_3$ (liquid) . . . − 77 Cal.

is endothermic.

REMARK 2. If a reaction is to be considered only from a calorimetric standpoint, it is not necessary to adhere strictly to the molecular relations. Thus, for example, it is allowable to write :

$2H$ (gas) + O (gas) = H_2O (liquid) . . . + 68.4 Cal.

REMARK 3. In the case of certain important reactions the quantity of heat evolved is denoted by a special name. Thus, for example, it is customary to speak of the *heat of neutralization.*

§ 28. **Calorimetric Methods.** To be suitable for examination in a calorimeter reactions must possess one important characteristic, namely: they must pass from the initial to the final state in a relatively short period of time. Suitable reactions can be divided into two classes: first, those involving the formation and the reciprocal action of salts, and the phenomena of solution and dilution; and second, combustion reactions.

The *mixing-calorimeter* is a vessel, sometimes of glass, but usually of platinum, into which the solution of one of the reacting substances is introduced. The calorimeter is protected from the variations in temperature of its surroundings by an insulating jacket, and is brought to the temperature of the room. A sensitive thermometer is inserted in the liquid and is moved continually. A second insulated receptacle, placed near the first, contains a small glass flask, likewise provided with a thermometer, and in this flask is contained the second of the reacting liquids. It is only in exceptional cases that the mercury columns of the thermometers are motionless; but as soon as the movement of the menisci is regular, the contents of the flask are poured into the calorimeter, the whole is stirred briskly, the extreme position of the thermometer-column is noted, and the variation in temperature from the extreme position is observed for the first few minutes.

In order to carry out the calculation we must know: the heat capacity, in water units, of the liquids, the calorimeter and the thermometer; the position of both thermometers at the moment of mixing; the extreme position of the thermometer inserted in the calorimeter; and the quantities of the reacting substances. In addition to this, a correction must be made for the variations in temperature before and after mixing.

REMARK. In calorimetric investigations of the formation and interreaction of salts, the work is conducted with very dilute solutions, which have no appreciable heats of dilution. With such solutions it is allowable to consider their heat capacity as equal to that of the water contained in them. For determining heats of dilution, the solution is placed in the calorimeter and the glass flask is filled with water.

The heat of solution of a substance is determined by introducing the substance into the calorimeter, which in this case is filled with pure water.

The *combustion-calorimeter* consists of a vessel of water containing another vessel in which the combustion is conducted. Into this second vessel the gases required for the combustion are introduced, and the arrangement of the apparatus is such that the gases formed by the combustion, on escaping, transmit all of their heat to the water of the calorimeter.

In the *explosion method* the second vessel has the form of a bomb. This is filled with compressed oxygen and an explosion of the contents is produced with the aid of an electric spark. This method may be used for both liquid and gaseous substances.

§ 29. **Law of Lavoisier and Laplace.** Every compound has a fixed heat of formation, which is equal to its heat of decomposition.

It is only from the truth of the first part of this law that we are placed in a position to speak of definite heats of formation. The truth of the second part is a deduction from the law of the conservation of energy.

§ 30. **Law of Hess.** The quantity of heat which is evolved on the transformation of one chemical system into another is independent of the intermediate states through which the system passes.

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

Second formulation. The evolution of heat which accompanies a certain chemical process is always the same, whether the process takes place in a single step or consists of a series of phases.

Example·

$$\begin{aligned}&\mathrm{K}\ (\text{solid}) + \mathrm{HCl}\ (\text{dissolved})\\&\qquad = \mathrm{KCl}\ (\text{dissolved}) + \mathrm{H}\ .\ .\ . + 61.8\ \text{Cal.}\end{aligned}$$

This process may take place in two reactions:

$$\mathrm{K\,(solid)} + n\mathrm{H_2O}^{*} = \mathrm{KOH\,(dissolved)} + \mathrm{H} + (n-1)\mathrm{H_2O} \ldots + 48.1\ \mathrm{Cal.}$$

and

$$\left.\mathrm{KOH\,(dissolved)} + \mathrm{HCl\,(dissolved)}\right\} = \mathrm{KCl\,(dissolved)} + \mathrm{H_2O} \ldots + 13.7\ \mathrm{Cal.}$$

The sum of the heats evolved in the last two reactions is equal to the heat evolved in the first.

Remark. This law was enunciated by Hess in 1840. It is also called the law of constant heat summation. It is a special case of the law of the conservation of energy, and can, when so considered, be formulated as follows: The energy of a system of substances is a function of its state, and not of the manner in which this state is attained; or also, the alteration in energy on the change of a system from one state to another is dependent only on the initial and final states, not on the intermediate states through which it passes.

§ 31. Applications of the Law of Hess.

a. The heat evolved in a reaction is equal to the difference between the heat of formation of the products and the heat of formation of the substances in the initial condition.

That this highly important law is to be considered as a deduction from the law of Hess is evident from the following:

The given reaction is

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

in which AB, etc., are compounds of the elements A, B, C, and D. The left, as well as the right, member

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[*] $n\mathrm{H_2O}$ denotes a large quantity of water.

of the equation represents a form of the system $(A + B + C + D)$.

The first form may be represented by the reaction

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

the second by

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

According to the method of notation employed in § 27,

$$r = A, B + C, D, \text{ and } s = A, C + B, D.$$

If we now pass to the form $(AC + BD)$, *first* passing from the elements to the form $(AB + CD)$, and *then* carrying out a double decomposition with the latter, then, according to the law of Hess,

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

and finally

$$q = (A, C + B, D) - (A, B + C, D).$$

Remark. If the reaction under consideration involves the formation of a compound from its elements, then the heat of reaction is the same as the heat of formation of the compound, and this reaction is a special case of the law mentioned. Thus in the reaction

$$K \text{ (solid)} + Cl \text{ (gas)} = KCl \text{ (solid)} \ldots + 105.6 \text{ Cal.}$$

the heat of reaction 105.6 Cal. = the heat of formation of KCl.

b. Determination of the Heat of Formation with the Help of the Above Law. This law is of great importance, since by it the heats of formation may be determined for those substances which are either not formed at all, or only with great difficulty, by the direct combination of their elements. If such a substance enters into a reaction which takes place quickly and can be examined in a calorimeter, and if the heat of formation of the other substances which enter into the reaction is known, then the heat of formation of the substance in question can be deduced from the heat of the reaction and the heat of formation of the other substances.

Example:

Heat of Formation of KOH. The following reaction is known:

$$\text{K (solid)} + H_2O\text{ (liquid)} + \text{Aq}^* \\ = \text{KOH (dissolved)} + \text{H (gas)} + \text{Aq} + 48.1\text{ Cal.}$$

From the above law

$$48.1\text{ Cal.} = \text{K, O, H, Aq} - H_2\text{, O (liquid)}.$$

But

$$2\text{H (gas)} + \text{O (gas)} = H_2O\text{ (liquid)} \ldots + 68.4\text{ Cal.};$$

that is: H_2, O (liquid) = 68.4 Cal.

and K, O, H, Aq = 116.5 Cal.

On the solution of KOH in water we find

$$\text{KOH} + \text{Aq} = \text{KOHAq} \ldots + 13.3\text{ Cal.},$$

which gives

$$\text{K, O, H} = \text{K, O, H, Aq} - \text{KOH, Aq} = 103.2\text{ Cal.}$$

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[*] Aq here denotes *much water.*

Heat of Formation of KCl. The direct formation of potassium chloride from its elements cannot be examined in the calorimeter; the heat of formation can, however, be deduced from the following reaction, which may be readily carried out in the calorimeter:

$$\begin{aligned}&\text{KOH (dissolved)} + \text{HCl (dissolved)}\\ &\qquad = \text{KCl (dissolved)} + H_2O \;\ldots + 13.7\ \text{Cal.}\end{aligned}$$

According to the rule,

$$\begin{aligned}+ 13.7\ \text{Cal.} = \text{K,Cl, Aq} + H_2O\ \text{(liquid)} - \text{Cl, H, Aq}\\ - \text{K, O, H,Aq.}\end{aligned}$$

Of the quantities appearing in the equation only K, Cl, Aq is unknown. If the known values are substituted in the equation, we obtain

$$\begin{aligned}13.7\ \text{Cal.} = \text{K, Cl, Aq} + 68.4\ \text{Cal.} - 39.3\ \text{Cal.}\\ - 116.5\ \text{Cal.};\end{aligned}$$

therefore $\text{K, Cl, Aq} = + 101.1\ \text{Cal.}$

But $\text{KCl, Aq} = - 4.4\ \text{Cal.};$

therefore $\text{K, Cl} = + 105.5\ \text{Cal.}$

From the heats of formation of KCl, KOH, and H_2O that of KClO may be easily calculated with the aid of the reaction, readily examined in the calorimeter:

$$\begin{aligned}&2\text{KOH (dissolved)} + 2\text{Cl (gas)}\\ &= \text{KCl (dissolved)} + \text{KOCl (dissolved)} \;\ldots + 25.4\ \text{Cal.}\end{aligned}$$

Heat of Formation of Ammonia-gas. The combustion of ammonia-gas in oxygen may be readily observed in the calorimeter:

$$2NH_3 \text{ (gas)} + 3O \text{ (gas)}$$
$$= 2N \text{ (gas)} + 3H_2O \text{ (liquid)} \ldots + 181.2 \text{ Cal.};$$

$$3H_2, O \text{ (liquid)} = +(3 \times 68.4 \text{ Cal.}) = + 205.2 \text{ Cal.};$$

therefore

$$N, H_3 = \tfrac{1}{2}(205.2 \text{ Cal.} - 181.2 \text{ Cal.}) = + 12 \text{ Cal.}$$

Heat of Formation of Carbon Monoxide. This is deduced from the combustion of diamond to carbon dioxide and the combustion of carbon monoxide to carbon dioxide:

$$C \text{ (diamond)} + 2O \text{ (gas)} = CO_2 \text{ (gas)} \ldots + 94.3 \text{ Cal.};$$
$$CO \text{ (gas)} + O \text{ (gas)} = CO_2 \text{ (gas)} \ldots + 68 \text{ Cal.};$$

therefore $C, O = C, O_2 - CO, O = + 26.3 \text{ Cal.}$

Heat of Formation of Hydrocarbons. Of all hydrocarbons only acetylene can be prepared directly from its elements, but this reaction is not suitable for calorimetric determination. Most hydrocarbons, however, burn readily in oxygen; usually also it is possible to produce an explosion of the two gases, and in both these cases the heats of combustion may be measured. The products of the combustion are always carbon dioxide and water, the heat of formation of both of these substances has been determined, and therefore, in the calorimetric equation for the combustion, the only unknown quantity is the heat of formation of the hydrocarbon in question.

The following, however, is an objection to this indirect method: The heats of combustion of hydrocarbons are large; their heats of formation, on the contrary, are relatively small. As a result of this an error (not avoidable even in the most careful determinations of the heat of formation and relatively large in comparison to this quantity) is introduced into the value of the heat of formation, and this therefore differs considerably from the correct value.

This drawback often explains the variations in the results of the best investigators. Thus J. Thomsen found the *heat of combustion* of ethane to be 370 Cal.; Berthelot, on the other hand, obtained the value 390 Cal.—a variation of 5–6 per cent. If the heat of formation of ethane is calculated from these two values, that of Thomsen gives 23 Cal. and that of Berthelot 4 Cal., two numbers which show great divergence.

The measurements of the heat of combustion of *acetylene* show a fairly close agreement:

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

$2C, O_2 = + 188.6$ Cal.; H_2, O (liquid) $= + 68.4$ Cal.;

therefore $C_2H_2 = - 58$ Cal.

Heat of Formation of Compounds which are composed of Carbon, Hydrogen, and Oxygen. The heats of formation of these compounds are deduced from their heats of combustion, the latter being determined by burning or exploding the compounds with oxygen. The same difficulties mentioned above also occur here.

For the heat of combustion of methyl alcohol in the form of vapor Thomsen found:

$$CH_4O \text{ (vapor)} + 3O \text{ (gas)}$$
$$= CO_2 \text{ (gas)} + 2H_2O \text{ (liquid)} \ldots + 182.2 \text{ Cal.};$$

therefore

$$C, H_4, O \text{ (vapor)}$$
$$= - 182.2 \text{ Cal.} + (94.3 + 136.8) \text{ Cal.} = + 48.9 \text{ Cal.}$$

c. Application of the Law for Predicting the Heat of Reaction. In the above cases the heats of reaction were used for determining the heats of formation; on the other hand, the former can be calculated if the heats of formation of the substances taking part in the reaction are known. And although it is not always known whether the reaction is actually practicable, still it can be stated in advance how great the heat of reaction *would be* if the reaction did take place according to a certain equation.

If it is known that

$$H_2, S, O_4, Aq = + 210.9 \text{ Cal.}$$

and

$$Zn, S, O_4, Aq = + 248.5 \text{ Cal.},$$

then in the reaction

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

a quantity of heat equal to + 37.6 Cal. will be set free.

If it is found that

$$K, Cl \text{ (solid)} = + 105.6 \text{ Cal.}$$

and

$$K, I \text{ (solid)} = + 80.1 \text{ Cal.},$$

then in a reaction which takes place according to the equation

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

a quantity of heat equal to 25.5 Cal. will be *absorbed.*

REMARK. In the determination of the heats of formation of gaseous substances the following conditions must be observed: If the total volume of the products of the reaction is not the same as that of the substances in the initial condition, as is the case, for example, in the reactions

$$2NH_3\ (2\ \text{liters}) = N_2\ (1\ \text{liter}) + 3H_2\ (3\ \text{liters}),$$

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

$$2H_2\ (2\ \text{liters}) + O_2\ (1\ \text{liter}) = 2H_2O\ (2\ \text{liters}),$$

then the experimentally determined calorimetric quantity is a result, not only of the chemical action, but of the work done in the displacement of the air on increase in volume. If the initial and final conditions are compared, it will be found that both internal and external work are performed in this process. As a result the value of the heat of formation is often given at *constant pressure*, containing, in this case, the equivalent of the external work, and also at *constant volume*, where a correction for the external work has been introduced. Generally, however, this correction is of slight importance in comparison with the actual heat of formation, and has therefore been neglected in the above calculations.

§ 32. **Some General Results of Investigations on Heat of Formation**. *Stable and Unstable Compounds.* In general those compounds are stable with respect to heat and shock whose heats of formation are positive, and the stability increases the greater the heat of formation. A negative heat of formation is, on the contrary, in most cases an evidence of instability. Water vapor and hydrogen chloride, the heats of formation of which are + 58 Cal. and + 22 Cal. respectively, are decomposed at high temperatures only to a very slight extent, and are entirely unaffected by pressure or shock. Nitrogen chloride, on the other hand, with a heat of formation of — 38 Cal., is extremely unstable and on the slightest jar decomposes into chlorine and nitrogen. Many substances having negative heats of formation behave, nevertheless, under many conditions like stable compounds. Thus, for example, acetylene, although its heat of formation is — 58 Cal., may be subjected to many operations without undergoing decomposition. Nevertheless this substance has been shown to be unstable under the combined action of a suddenly applied high pressure and a high temperature.

Substances having a positive heat of formation and undergoing partial decomposition at high temperatures have the property of regenerating themselves from their decomposition products on cooling; they exhibit the phenomenon of *dissociation;* the alteration which they undergo as a result of the increase in temperature is *reversible*—i.e., one which increases with an increase in temperature, but which decreases when the temperature is again lowered. The result of this action is that when the original temperature is again reached the state of the system is the same as it was in the beginning. In the case of substances having negative heats of formation the decomposition, when it has once appeared, is, on the contray, *complete* and is *not reversible;* the term dissociation is not used to express the decomposition of this class of bodies.

REMARK. The heat of formation of a substance which undergoes dissociation must be considered as a *latent* heat, comparable to the internal latent heat of vaporization of water. As a matter of fact it is really determined as an actual quantity of heat, but nevertheless it appears in the theory as a latent heat, i.e., as the quantity of heat which must be added to the system in order that an alteration of condition can take place *isothermically.*

In the study of the phenomenon of dissociation, when reactions which take place at high temperatures are under consideration, it is necessary to employ the heat of formation, which is determined at a lower temperature and is equal to the heat of dissociation. This is necessary since the dissociation can be observed and studied only at very high temperatures. It is, however, very evident that the value of the heat of formation is influenced by the temperature at which formation and decomposition occur.

Values of the Heats of Reaction. Compounds of a halogen with different metals follow the rule that the heat of formation is large for the compounds of the so-called strongly positive metals, and is in fact larger the more positive the metal. In general the chlorides have a greater heat of formation than the bromides, the bromides greater than the iodides. Oxygen stands intermediate between chlorine and bromine; sulphur, however, is exceeded by oxygen and iodine.

Strong acids in dilute solution all give with strong bases exactly the same value for the heat of neutralization, namely, + 13.7 Cal.

The mixing of dilute solutions of neutral salts which give no precipitates usually causes no evolution of heat (*law of thermo-neutrality*).

The heats of combustion of the hydrocarbons differ for two neighboring members of the series by about + 158 Cal. The same phenomenon is observed in the case of many homologous unsaturated hydrocarbons and homologous alcohols; and, further, in the case of homologous fatty acids a constant increase in the value of the heat of combustion can be observed.

A series of tables follow in which special results of thermochemical research are summed up.

Concerning the heat of combustion of organic substances it is again mentioned that Thomsen's results generally differ considerably from those of Berthelot.

It must be further noted that the elements are taken in those states of aggregation in which they normally occur. Thus in H, Br = + 8.4 Cal. H is gaseous, Br is liquid, and HBr is gaseous. In H_2S the octahedral sulphur is taken. In the case of the hydrocarbon compounds the carbon is always considered in the form of diamond. Thus C, H_3, Br = + 11.6 Cal. is to be understood

$$\text{C (diamond)} + \text{Br (liquid)} + 3\text{H (gas)} = \text{CH}_3\text{Br (gas)} \ldots + 11.6 \text{ Cal.}$$

HEATS OF FORMATION OF CERTAIN COMPOUNDS OF THE METALLOIDS AT NORMAL TEMPERATURE.

Substance.	Formation.	Heat Evolved.			
		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, 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
"	$\frac{1}{2}$(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
H_2SeO_4	Se, O_4, H_2	.....	.....	.....	+ 145.2
TeO_2	Te, O_2	.....	.....	.....	+ 77.3
H_2TeO_4	Te, O_3, H_2 O	.....	.....	.....	+ 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

HEATS OF FORMATION OF CERTAIN COMPOUNDS OF THE METALLOIDS.—(*Continued.*)

Substance.	Formation.	Heat Evolved.			
		Gaseous.	Liquid.	Solid.	Dissolved.
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	.....	.....
Cl I	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_3, Cl_2	.....	.....	+ 29.7	.....
PCl_3O	P, Cl_3, O	.....	+ 146	.....	.....
$AsCl_3$	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	.....
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 determined from the difference between the heats of formation of the same for the dry and for the dissolved condition.

HEATS OF FORMATION OF CERTAIN COMPOUNDS OF THE METALS.

A. Oxides and Halides.

Substance.	Heat of Formation.		Substance.	Heat of Formation.	
	Solid.	Dissolved.		Solid.	Dissolved.
K, H, O	+ 103.2	+ 116.5	Ca, O	+ 131	+ 149.5
K_2, O	....	+ 164.6	Sr, O	+ 128.4	+ 157.7
Na, H, O	+ 101.9	+ 111.8	Ba, O	+ 124.2	+ 158.7
Na_2, O	+ 100.2	+ 155.2	Ca, O_2, H_2	+ 214.9	+ 217.9
Li, H, O	....	+ 117.4	Sr, O_2, H_2	+ 214.5	+ 226.1
N, H_3, Aq	....	+ 20.3	Ba, O_2, H_2	+ 214.9	+ 227.1
Mg, O	+ 144	....	Mg, O_2, H_2	+ 217.3	...
Al_2, O_6, H_6	+ 594	....	Ca, Br_2	+ 140.9	+ 165.4
Mn, O, H_2O	+ 94.8	....	Ca, I_2	+ 107.3	+ 135
Zn, O	+ 85.3	....	Ba, Cl_2	+ 194.7	+ 196.8
Zn, O, H_2O	+ 82.7	....	Ba, Br_2	+ 170	+ 175
Cd, O, H_2O	+ 65.7	....	Sr, Cl_2	+ 184.6	+ 195.7
Fe, O, H_2O	+ 68.3	....	Sr, Br_2	+ 157.7	+ 173.8
Fe_2, O_6, H_6	+ 396.4	....	Mg, Cl_2	+ 151	+ 186.9
Ni, O, H_2O	+ 60.8	....	Zn, Cl_2	+ 97.2	+ 112.8
Co, O, H_2O	+ 63.4	....	Zn, Br_2	+ 76	+ 91
Pb, O	+ 50.3	....	Zn, I_2	+ 49.2	+ 60.5
Cu, O	+ 37.2	....	Mn, Cl_2	+ 112	+ 128
Cu_2, O	+ 40.8	....	Fe, Cl_2	+ 82.1	+ 100
Ag_2, O	+ 5.9	....	Fe, Br_2	....	+ 78.2
Hg_2, O	+ 22	....	Fe, I_2	....	+ 46.4
Hg, O	+ 20.1	....	Fe, Cl_3	+ 96.1	+ 126.1
Sn, O, H_2O	+ 68.1	....	Al, Cl_3	+ 161	+ 237.8
$Au_2,O_3,(H_2O)_3$	— 13.2	....	Al, Br_3	+ 119.7	+ 205
Pt, O, H_2O	+ 17.9	...	Al, I_3	+ 70.4	+ 159.4
			Co, Cl_2	+ 76.5	+ 94.8
K, Cl	+ 105.6	+ 101.2	Ni, Cl_2	+ 74.5	+ 93.7
K, Br	+ 95.3	+ 90.2	Hg, Cl	+ 31.4	....
K, I	+ 80.1	+ 75	Hg, Br	+ 24.1	....
K, F	+ 109.5	+ 113.1	Hg, I	+ 14.1	..
Na, Cl	+ 97.6	+ 96.4	Hg, Cl_2	+ 53.3	+ 50
Na, Br	+ 85.8	+ 83.9	Hg, Br_2	+ 40.5	....
Na, I	+ 69.1	+ 70.3	Hg, I_2	+ 24.2	....
Na, F	+ 109	+ 108.4	Cu, Cl	+ 32.9	....
N, H_4, Cl	+ 75.8	+ 71.9	Cu, Br	+ 25	....
N, H_4, Br	+ 65.4	+ 61	Cu, I	+ 16.3	....
N, H_4, I	+ 49.3	+ 45.8	Cu, Cl_2	+ 51.6	+ 62.7
Li, Cl	+ 93.8	+ 102.2	Cu, Br_2	+ 32.6	+ 40.8
Ca, Cl_2	+ 169.8	+ 187.2	Cd, Cl_2	+ 93.2	+ 96.2
Cd, Br_2	+ 75.2	+ 75.6	Au, Br	— 0.1	....
Cd, I_2	+ 48.8	+ 47.9	Au, I	— 5.5	....

HEATS OF FORMATION OF CERTAIN COMPOUNDS OF THE METALS.—(*Continued*).

A. OXIDES AND HALIDES.—(*Continued*).

Substance.	Heat of Formation.		Substance.	Heat of Formation.	
	Solid.	Dissolved.		Solid.	Dissolved.
Pb, Cl_2	+ 82.8	+ 76	Au, Cl_3	+ 22.8	+ 27.3
Pb, Br_2	+ 64.5	+ 54.5	Au, Br_3	....	+ 5.1
Pb, I_2	+ 39.8	....	Sn, Cl_2	+ 80.8	+ 81.1
Ag, Cl	+ 29.4	....	Sn, Cl_4	+ 127.3	+ 157.2
Ag, Br	+ 22.7	....	Pt, Cl_4	+ 59.8	+ 79.4
Ag, I	+ 13.8	....	Pt, Br_4	+ 42.4	+ 52.3
Au, Cl	+ 5.8	....			

B. SULPHIDES.

Substance.	Solid.	Dissolved.	Substance.	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 *	....
Ca, S	+ 89.6	....	Cu_2, S	+ 18.3	....
Mg, S	+ 77.6	....	Hg, S	+ 4.8 *	....
Al_2, S_3	+ 122.4	....	Ag_2, S	+ 3.3 *	....
Mn, S, nH_2O	+ 44.4	....	Pb, S	+ 18.4	....

C. OXY-SALTS.

Substance.	Solid.	Dissolved.	Substance.	Solid.	Dissolved.
Carbonates (*$C =$ diamond*).			Mn, C, O_3	+ 210.8	....
K_2, C, O_3	+ 278.4	+ 284.9	Cd, C, O_3	+ 179.2	....
Na_2, C, O_3	+ 269.9	+ 275.4	Ag_2, C, O_3	+ 120.2	....
Ba, C, O_3	+ 280.5	....	Pb, C, O_3	+ 166.9	....
Sr, C, O_3	+ 277.5	....	K, H, C, O_3	+ 232.9	+ 227.6
Ca, C, O_3	+ 267.7	....	Na, H, C, O_3	+ 227	+ 223.7

* Not certain.

HEATS OF FORMATION OF CERTAIN COMPOUNDS OF THE METALS.—(*Continued.*)

C. OXY-SALTS.—(*Continued.*)

Substance.	Heat of Formation.	
	Solid.	Dissolved.
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, 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
$Ca, N_2, O_6, 4H_2O$	+ 213.8	+ 206.6
$Zn, N_2, O_6, 6H_2O$	+ 138.1	+ 132.3
$Cu, N_2, O_6, 6H_2O$	+ 93	+ 82.3
$Cd, N_2, O_6, 4H_2O$	+ 121.1	+ 116.1
Pb, N_2, O_6	+ 105.5	+ 97.9
Ag, N, O_3	+ 28.7	+ 23.3
Other salts.		
K, O, Cl		+ 88.8
K, Cl, O_3	+ 95	+ 85
K, Cl, O_4	+ 113.1	+ 101
K, Br, O_3	+ 84.1	+ 74.3
K, I, O_3	+ 124.5	+ 117.4
Na, O, Cl	....	+ 83.4
Na, Cl, O_3	+ 86.8	+ 81.2
$Na_2 S, O_3$	+ 260.5	+ 262.9
Na_2, S_2, O_6	+ 398.9	+ 393.5
Na_2, H, P, O_4	+ 413.9	+ 419.5
N, H_4, N, O_2	+ 64.9	+ 60.2
K, Mn, O_4	+ 195	+ 184.8
Bi, Cl_3	+ 90.6	....
Bi, O, Cl	+ 88.2	....
$Na_2, Pt, Cl_6 6H_2O$	+ 288.3	+ 277.7
K, C, N	+ 29.8	+ 26.8
Na, C, N	+ 25.5	+ 25
Hg, C_2, N_2	— 52	— 55
Ag, C, N	— 31.2	....
AgCN, KCN Aq	....	+ 6.5
K, O, C, N	+ 34.3	+ 29.1

HEATS OF COMBUSTION AND HEATS OF FORMATION OF SOME ORGANIC COMPOUNDS.

C = diamond.

Substance.	Formula.	Heat of Comb.	Heat of Formation. Vol. const.	Observer.
SATURATED HYDROCARBONS.				
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 "	C_7H_{16} (normal)	+ 1137.5	....	Louguinine
UNSATURATED HYDROCARBONS.				
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 "	C_3H_5Cl	+ 321.9	+ 24.2	"
Propyl "	C_3H_7Cl	+ 480.2	+ 27.8	"
Butyl "	C_4H_9Cl	+ 637.9	+ 32.2	"
Vinyl "	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 "	C_2H_5Br	+ 341.8	+ 16.6	"
Propyl "	C_3H_7Br	+ 499.3	+ 21.1	"
Amyl "	$C_5H_{11}Br$		+ 27.1	Berthelot
Allyl "	C_3H_5Br	+ 462.1	− 9.6	Thomsen
Ethylene bromide (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	"

HEATS OF COMBUSTION AND HEATS OF FORMATION OF SOME ORGANIC COMPOUNDS.—(*Continued.*)

Substance.	Formula.	Heat of Comb.	Heat of Formation. Vol. const.	Observer.
ALCOHOLS (Gaseous).				
Methyl alcohol	CH_3OH	+ 182.2	+ 47.9	Thomsen
Ethyl "	C_2H_5OH	+ 340.5	+ 51.5	"
Propyl "	C_3H_7OH	+ 498.6	+ 56	"
Isobutyl "	C_4H_9OH	+ 658 5	+ 57.5	"
Isoamyl "	$C_5H_{11}OH$	+ 820.1	+ 58	"
Allyl "	C_3H_5OH	+ 464.8	+ 21.6	"
Propargyl "	C_3H_3OH	+ 431.1	− 12.7	"
ACIDS.				
Gaseous. Formic acid	CH_2O_2	+ 69.4	+ 92.8	Thomsen
Gaseous. Acetic "	$C_2H_4O_2$	+ 225.4	+ 98.6	"
Gaseous. Propionic "	$C_3H_6O_2$	+ 386.5	+ 99.1	"
Capric acid	$C_{10}H_{20}O_2$	+ 1455.6	....	Stohmann
Lauric "	$C_{12}H_{24}O_2$	+ 1747.6	....	"
Myristic "	$C_{14}H_{28}O_2$	+ 2052 9	....	"
Palmitic "	$C_{16}H_{32}O_2$	+ 2361.9	....	"
Stearic "	$C_{18}H_{36}O_2$	+ 2677.8	....	"
Oxalic "	$C_2H_2O_4$	+ 60.2	+ 196.7	"
Malonic "	$C_3H_4O_4$	+ 207.3	....	"
Succinic "	$C_4H_6O_4$	+ 356.8	....	"
Tartaric "	$C_4H_6O_6$	+ 261.8	....	"
OTHER SUBSTANCES.				
Dimethyl ether (gaseous)	$(CH_3)_2O$	+ 349.4	+ 42.7	Thomsen
Diethyl " "	$(C_2H_5)_2O$	+ 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 "	CNH	+ 158.6	− 30.2	"
Cyanogen "	$(CN)_2$	+ 259.6	− 71	"
Acetonitrile "	CH_3CN	+ 312.1	− 21.6	"
Methylamine "	CH_3NH_2	+ 258.3	+ 5.7	"
Dimethylamine "	$(CH_3)_2NH$	+ 420.5	+ 5.6	"
Urea	$CO(NH_2)_2$	+ 152.2	+ 77.5	Stohmann
Mercaptan (gaseous)	CH_3SH	+ 298.8	+ 5.4	Thomsen
Benzol	C_6H_6	+ 787.8	− 17.1 (gas.) − 9.1 (liq.)	Stohmann
Phenol (solid)	C_6H_5OH	+ 731.9	....	"
Benzoic acid	$C_7H_6O_2$	+ 770.5	....	"
Phthalic "	$C_8H_6O_4$	+ 771.9	....	"
Salicylic "	$C_7H_6O_3$	+ 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 VAPORIZATION OF SOME ORGANIC COMPOUNDS.

Carbon bisulphide.....	6.4 Cal.	Methyl iodide........	6.5 Cal.
Ethyl alcohol..........	9.8 "	Chloroform..........	7.3 "
Amyl "	10.7 "	Carbon tetrachloride..	7.2 "
Aldehyde......	6.0 "	Ethyl chloride........	6.45 "
Acetone...............	7.5 "	" bromide........	7.5 "
Chloral...............	8.0 "	" iodide..........	0.8 "
Chloral hydrate........	21.9 "	Ethylen bromide.....	8.2 "
Formic acid...........	5.6 "	Methyl alcohol.......	8.45 "
Acetic "	7.25 "	Butyric acid..........	10.1 "
Hydrocianic acid......	5.7 "	Valeric acid....	10.6 "
Benzole.	7.2 "	Ether................	6.7 "

HEAT OF NEUTRALIZATION OF BASES.

The solutions contain two equivalents of base or acid dissolved in 400 mols. of water. Many bases, however, are not soluble.

Bases.	H_2SO_4, Aq.	2ClH, Aq.	$2NO_3H$, Aq.	$C_2H_4O_2$, 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	....
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 parenthesis denote the formation of insoluble salts. In these cases

Heat evolved = Heat of neutralization + Heat of precipitation.

NEUTRALIZATION OF ACIDS BY SODIUM HYDROXIDE.

One molecule of the acid and *a* equivalents of sodium hydroxide, both in dilute solution, are mixed together.

Acids.	$a = \frac{1}{2}$	$a = 1$	$a = 2$	$a = 3$	$a = 4$	$a = 6$
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	....	....
$(COOH)_2$	6.9	13.8	28.3	....	28.5	....
$C_2H_4(COOH)_2$	....	12.4	24.0	24.1	....	....
Malic acid	....	13.0	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

HEATS OF SOLUTION.

When one gram molecule of the substance dissolves in the given quantity of water at 18°, then the number of calories stated are set free.

Substance Dissolved.	Quant. Water in mol.	Heat Evolved in Cal.	Substance Dissolved.	Quant. Water in mol.	Heat Evolved in Cal.
$NaCl$	200	− 1.18	$NaBr + 2H_2O$	200	− 4.7
KCl	"	− 4.4	$NaBr$	"	− 0.19
NH_4Cl	"	− 3.9	KI	"	− 5.1
$BaCl_2 + 2H_2O$	400	− 4.8	$NaI + 2H_2O$	"	− 4.0
$BaCl_2$	"	+ 2.1	NaI	"	+ 1.2
$CaCl_2 + 6H_2O$	"	− 4.34	$NaNO_3$	"	− 5.0
$CaCl_2$	"	+ 17.4	KNO_3	"	− 8.5
$CaBr_2$	"	+ 24.5	NH_4NO_3	"	− 6.3
CaI_2	"	+ 27.7	$Ba(NO_3)_2$	400	− 9.4
$MgCl_2 + 6H_2O$	"	+ 2.9	$Sr(NO_3)_2 + 4H_2O$	"	− 12.5
$MgCl_2$	"	+ 35.9	$Sr(NO_3)_2$	"	− 4.6
$MnCl_2 + 4H_2O$	"	+ 1.5	$Ca(NO_3)_2 + 4H_2O$	"	− 7.2
$MnCl_2$	"	+ 16.0	$Ca(NO_3)_2$	"	+ 4.0
$FeCl_2 + 4H_2O$	"	+ 2.7	$Mg(NO_3)_2 + 6H_2O$	"	− 4.2
$FeCl_2$	"	+ 17.9	$Mn(NO_3)_2 + 6H_2O$	"	− 6.2
$FeCl_3 + 12H_2O$	"	+ 11.3	$Zn(NO_3)_2 + 6H_2O$	"	− 5.8
$FeCl_3$	"	+ 63.3	$Cd(NO_3)_2 + 4H_2O$	"	− 5.0
$CoCl_2 + 6H_2O$	"	− 2.9	$Cu(NO_3)_2 + 6H_2O$	"	− 10.7
$CoCl_2$	"	+ 18.3	$AgNO_3$	200	− 5.4
$NiCl_2 + 6H_2O$	"	− 1.1	$Pb(NO_3)_2$	400	− 7.6
$NiCl_2$	"	+ 19.2			
$ZnCl_2$	"	+ 15.6	$Na_2SO_4 + 10H_2O$	400	− 18.76
$ZnBr_2$	"	+ 15	Na_2SO_4	"	+ 0.46
ZnI_2	"	+ 11.3	K_2SO_4	"	− 6.4
$CuCl_2 + 2H_2O$	"	+ 4.2	$(NH_4)_2SO_4$	"	− 2.4
$CuCl_2$	"	+ 11.1	$CaSO_4 + 2H_2O$	"	0.0*
$HgCl_2$	"	− 3.3	$CaSO_4$	"	+ 4.7
$PbCl_2$	"	− 6.8	$MgSO_4 + 7H_3O$	"	− 3.8
$SnCl_2 + 2H_2O$	"	− 5.4	$MgSO_4$	"	+ 20.3
$SnCl_2$	"	+ 0.3	$MnSO_4 + 5H_2O$	"	+ 0.04
$SnCl_4$	300	+ 29.9	$MnSO_4$	"	+ 13.8
$AuCl_3 + 2H_2O$	"	− 1.7	$FeSO_4 + 7H_2O$	"	− 4.5
$AuCl_3$	"	+ 4.5	$CoSO_4 + 7H_2O$	"	− 3.6
$PtCl_4 + 4H_2O$	"	− 1.7	$NiSO_4 + 7H_2O$	"	− 4.3
$PtCl_4$	"	+ 19.6	$ZnSO_4 + 7H_2O$	"	− 4.24
KBr	200	− 5.08	$ZnSO_4$	"	+ 18.5
			$CdSO_4 + \frac{8}{3} H_2O$	"	+ 6.0

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* Apparently weakly positive

HEATS OF SOLUTION. (*Continued.*)

Substance Dissolved.	Quantity of Water in Molecules.	Heat Evolved in Calories.
$CdSO_4$	400	$+10.7$
$CuSO_4+5H_2O$	"	-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

Substance Dissolved.	Quantity of Water in Molecules.	Heat Evolved in Calories.
Heat of solution in completely 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

Problems. 1. How great is the quantity of heat which is set free on the combination of 100 grams of Na_2CO_3 with sufficient water to form the hydrate $Na_2CO_3.10H_2O$?

2. Calculate the heat of the reaction represented by the equation

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

3. What is the heat of reaction of

$$AgNO_3Aq + HClAq = AgCl + HNO_3Aq?$$

4. What is the quantity of heat evolved on the combination of C_2H_4 with gaseous bromine, the volume being kept constant?

5. Calculate the quantity of heat set free when 10 grams of zinc is dissolved in dilute sulphuric acid.

6. What is the heat of formation of dipropargyl

(C_6H_6) at constant pressure if the heat of combustion is equal to + 882.9 Cal.?

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

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

and found that the quantity of heat set free was equal to + 131.2 Cal. What is the heat of formation of C_2Cl_6?

8. 20 cc of a 10-per-cent solution of cupric chloride are treated with an excess of iron-filings until the copper is completely precipitated. Calculate approximately the increase in temperature of the water, considering the specific gravity, as well as the specific heat of the liquid, to be equal to 1, and neglecting the value of the heat of the iron and the copper.

9. A calorimeter contains 350 cc of a tenth-normal solution of HCl. With this is mixed 250 cc of a solution of NaOH containing sufficient NaOH to exactly neutralize the HCl in the first solution. Before mixing the temperature of the two solutions is the same. What will be the increase in temperature ?

10. 350 cc of a tenth-normal H_2SO_4 solution are mixed with 250 cc of a fifth-normal NaOH solution at the same temperature. What is the increase in temperature ?

§ 33. **Principle of Greatest Work.** Substances which enter into chemical reaction with one another when brought together under normal conditions tend to produce those systems which are formed with the maximum evolution of heat.

Differently formulated. Of the possible reactions in which a system of substances can take part, that one results in which the greatest quantity of heat is set free.

Examples. In a system composed of potassium, chlorine and iodine, KCl and not KI, is formed, since

$$K + I = KI \quad . \; . \; . \quad 80.1 \text{ Cal.},$$

while $$K + Cl = KCl \quad . \; . \; . \quad 105.6 \text{ Cal.}$$

The system (KI + Cl) would change to the system (KCl + I), since

$$KI + Cl = KCl + I \quad . \; . \; . \quad 25.5 \text{ Cal.}$$

Acids and bases act on one another because the formation of salts is attended by the evolution of heat; for example,

$$KOHAq + HClAq = KClAq + H_2O \quad . \; . \; . \quad +13.7 \text{ Cal.}$$

Gaseous chlorine does *not* decompose water-vapor, since at 100° the reaction *would be*

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

This equation is evident from the following:

$$H_2, O \text{ (gas) at } 100° = +58 \text{ Cal.}$$

and $$H, Cl \text{ (gas)} = +22 \text{ Cal.}$$

At ordinary temperatures, however, *liquid* water is decomposed, though very slowly, by chlorine, for

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

since

$$\text{H, Cl (gas)} = +22 \text{ Cal.}, \qquad \text{HCl, Aq} = +17.2 \text{ Cal.},$$

and $$\text{H}_2\text{, O (liquid)} = +68.4 \text{ Cal.}$$

Copper does not replace iron in a solution of ferrous chloride, the reverse substitution taking place, however, since

$$\text{Fe (solid)} + \text{CuCl}_2\text{Aq}$$
$$= \text{FeCl}_2\text{Aq} + \text{Cu (solid)} \;.\;.\;.\; +37.3 \text{ Cal.}$$

REMARK. This principle was first enunciated by J. Thomsen, but soon after renounced. It was later taken up by Berthelot, who defended it for thirty years. Its application is extremely wide-reaching and important, notwithstanding the appreciable errors which it often involves. The fundamental idea of this principle is that chemical action takes place only when the change through which the system passes is accompanied by the evolution of heat. This principle of course holds only for reactions which take place at low temperatures; and Van't Hoff has in fact shown that its validity is greater the nearer the absolute zero is approached.

The enunciation of this principle involves a difficulty since it is conditionally assumed that the substances, of their own *free* reciprocal action, shall react without the influence of an external influence, an external energy. Under ordinary conditions, however, external influences do exist, namely, the temperature and the pressure of the surroundings. It should be stated here that the universal application of this principle was very recently renounced by Berthelot himself.

§ 34. Application of the Principle of Greatest Work.

a. Law of Simultaneously Occurring Reactions. A reaction takes place the more readily if its products can immediately enter into another reaction.

REMARK. This law covers the action of elements in the so-called *nascent state*, as well as the phenomena which were originally attributed to *predisposed affinities*. The law may be deduced from the principle of greatest work, since the second reaction involves a certain evolution of heat, which is added to that of the first. As a result the heat of reaction is raised; from a negative heat it may increase to a positive one, from one of low positive value to one of higher value, so that finally the total heat of reaction may be equal to a large number of calories.

First Example. As already stated, chlorine has no action on water-vapor, but does react with liquid water. In the latter case the HCl formed can dissolve immediately in water, which process considerably increases the quantity of heat evolved.

This action takes place slowly. If, however, the conditions are such that the HCl or the oxygen may immediately on their formation enter into a chemical reaction, the decomposition of the water is much more rapid.

Thus the reaction

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

proceeds slowly, while the reaction

$$\begin{aligned} &H_2O\ (\text{liquid}) + SO_2Aq + 2Cl\ (\text{gas}) \\ &\qquad = H_2SO_4Aq + 2HClAq\ \ldots\ +73.7\ \text{Cal.} \end{aligned}$$

quickly takes place.

The latter reaction is an example of the action of oxygen in the nascent state, and may perhaps be explained by the assumption that this element is set free in the form of atoms, and these act immediately, before combining to form molecules. This explanation may be the correct one, but it is nevertheless certain that the small heat of reaction of the change

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

is considerably increased by the heat of the reaction

$$SO_2Aq + O = H_2SO_4Aq \;.\;.\;. + 63.7 \text{ Cal.}$$

In the above case the second reaction is produced by the oxygen; under proper conditions, however, the hydrochloric acid may take part in this second action. Thus, when KOH is dissolved in the solution, the following reaction takes place:

$$KOHAq + HClAq = KClAq + H_2O \;.\;.\;. + 13.7 \text{ Cal.}$$

The two reactions combined would then give

$$2KOHAq + Cl_2 = 2KClAq + H_2O + O \;.\;.\;. + 37.4 \text{ Cal.}$$

This equation is, however, not yet complete, since the oxygen combines with KCl, with the formation of KClO:

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

making the total reaction

$$\begin{aligned} &2KOHAq + Cl_2 \text{ (gas)} \\ &\quad = KClAq + KClOAq + H_2O \;.\;.\;. + 25.4 \text{ Cal.} \end{aligned}$$

The formation of KClO causes a *decrease* in the heat of reaction. In fact this decrease is considerably greater than the heat resulting from the action of chlorine on water; nevertheless the fact that a secondary reaction like the formation of KClO can take place must be considered as a defect in logic existing in the principle itself, since with these exceptions reactions of this nature may be included under one general rule.

Second Example. Manganese dioxide and dilute sulphuric acid do not react with one another according to the scheme

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

If, however, oxalic acid be added, the reaction takes place immediately, the oxalic acid being oxidized to carbon dioxide and water. The first reaction is presumably attended by a *negative* heat of reaction; the second increases this by the high heat of combustion of oxalic acid.

In a similar manner the action of sulphuric acid on potassium permanganate is made possible by the presence of oxalic acid.

Third Example. In the reaction

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

a quantity of heat equal to 42 calories is *absorbed.* As a result of this water is *not* decomposed by iodine according to the above equation. The decomposition, however, takes place immediately if the conditions are such that the oxygen can oxidize SO_2 with the formation of H_2SO_4, $Na_2S_2O_3$ with the formation of $Na_2S_4O_6$ and NaI, or arsenious acid with the formation of As_2O_5.

b. The Prediction of Reactions. The following rules are often confirmed:

1. A and B will combine if $A, B = + q$ Cal. For if

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

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

and the system (A + B) will tend to change to the form AB, and the form (A + B) will be unstable.

Example. KCl is formed directly from K and Cl; and K, Cl = + 105.6 Cal.

2. A and B will not combine without the action of some external energy if A, B = − q Cal., for in this case

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

and the system (A + B) will remain in this form.

Example. Chlorine and nitrogen do not combine directly; NCl_3 = − 38.5 Cal.

3. A will displace B from its compounds with C if (A, C − B, C) = + q Cal., since in this case

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

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

Example.

$$\begin{aligned}&\text{KI (solid)} + \text{Cl (gas)}\\ &\qquad = \text{KCl (solid)} + \text{I (solid)} \;.\;.\;.\; + 25.5 \text{ Cal.};\end{aligned}$$

$$\text{K, Cl} = + 105 \text{ Cal.,} \quad \text{K, I} = + 80.1 \text{ Cal.}$$

The reverse reaction takes place only under special conditions.

4. AB and CD enter into a double decomposition:

$$AB + CD = AC + BD,$$

if
$$(A,\ C + B,\ D) > (A,\ B + C,\ D);$$

that is, if

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

since in this case the form (AC + BD) is the more stable form of the system (A + B + C + D).

c. Experimental Proof of the Above Rules. If only those reactions are considered which take place at ordinary temperatures or at temperatures approaching these, the above rules will be fairly well confirmed in practice. The heat of formation of chlorides is greater than that of the corresponding bromides and iodides, and bromine and iodine are in fact generally displaced from their compounds by chlorine. The heats of formation of compounds of the metals with halogens follow the rule that these are greatest in the cases of the strongly positive metals, and decrease with the positive properties of the metals; practical experience agrees with the rule, the weakly positive metals being displaced from their compounds by those which are more strongly positive. The formation of salts from acids and bases is a double decomposition, in which the sums of the heats of formation of the products are greater than those of the substances in the initial states, and as a matter of fact the formation of salts of this nature takes place without difficulty.

d. Formation of Compounds with Negative Heats of Formation. The formation of such compounds is rendered possible by their appearance as secondary products in a reaction in which the other products have high heats of formation. In such cases, to be sure, the heat of reaction need not be relatively great; still it can be positive and would be greater if the secondary products were not formed.

Examples.

Formation of Potassium Hypochlorite (see p. 85).

Formation of Nitrogen Trichloride.

$$N, Cl_3 = - 38 \text{ Cal.}$$

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

$$NH_4ClAq + 6Cl = 4HClAq + NCl_3;$$

$$N, H_4, Cl, Aq = + 71.9 \text{ Cal.};$$

$$4Cl, H, Aq = + 156.8 \text{ Cal.}$$

The heat of reaction is therefore + 46.9 Cal.

e. Explosive Substances and Mixtures. Systems whose heat of reaction is great will generally undergo alteration. Generally, also, if in such a system the reaction is started at *any one* point, sufficient heat will be there developed to raise the material in the immediate neighborhood to the temperature at which the reaction takes place; as a result of this the reaction is propagated throughout the entire mass. When this propagation takes place with great velocity and is accompanied by a great increase in pressure, the result is known as an explosion. It is often possible to start the reaction at one point by a strong pressure or shock.

Explosive substances (*compounds*) are substances the formation of which is accompanied by the absorption of much heat, and which produce gaseous products on their explosion. This is the case with nitrogen trichloride, nitroglycerine, and acetylene.

These substances decompose when subjected to pressure at any one point, since the pressure starts the reaction at this point and it is then communicated to the entire mass. The pressure which induces the explosion is not the same for all substances. Nitrogen chloride and nitroglycerine decompose when subjected to a very slight shock; acetylene, on the contrary, requires a very strong one.

Explosive *mixtures* contain components the reaction between which develops much heat, gaseous products being at the same time formed. Examples of such mixtures are gunpowder and oxyhydrogen-gas.

The force of an explosion depends upon the velocity of propagation of the reaction, upon the heat evolved, and upon the nature of the products formed. The explosion is, moreover, the more violent when the exploding substance is a liquid or a solid and the products are gaseous, since in this case the increase in pressure is due not only to the increase in temperature, but also, and in fact chiefly, to the change from the solid or liquid to the gaseous state: a given weight of the substance occupying a given space, before the reaction as a liquid or solid and immediately after as a gas. This alteration in condition alone causes a pressure the magnitude of which is not far from a thousand atmospheres, and this value is further increased by the high temperature. These statements are true for nitrogen trichloride, nitroglycerine, and gunpowder.

The values of the pressure and temperature of an explosion when calculated from the theory give larger numbers than are found by actual experiment. The reasons for this are that the reactions are not complete, and that the values for the heats of reaction and specific heats of the products used in the calculation are determined at temperatures and pressures entirely different from those at which the explosion takes place.

§ 35. **Causes for the Starting of Reactions.** Substances which enter into reaction with one another can often remain mixed together for a long period without any reaction taking place, the starting of the reaction requiring certain special conditions. This is especially true in the case of substances having negative heats of formation; without special provocation they do not undergo any alteration.

Examples. Oxyhydrogen-gas at ordinary temperatures, gunpowder, acetylene, a mixture of metallic iron and sulphur.

The causes which induce the reaction are not always the same: sometimes it is a shock, as in the case of fulminate of mercury, NCl_3, and nitroglycerine; sometimes the application of fire, as with gunpowder and oxyhydrogen-gas; and again the action of light is sufficient, as in the case of a mixture of hydrogen and chlorine.

Occasionally the entire mass of the substance or mixture must be heated, and then the reaction, having once started, continues without the application of further heat. A case of this sort is the formation of chloroform from chloride of lime, calcium hydroxide, alcohol, and water.

§ 36. **Criticism of the Principle of Greatest Work.** This principle may be very extensively applied to reactions which take place under normal conditions of temperature and pressure, and especially to the cases of the reactions of such substances as show great stability on increase of temperature.

One difficulty, however, has already been mentioned: the appearance of *endothermic* reactions as results of complicated actions which, taken as a whole, are *exothermic* (comp. § 34, *a* and *d*).

The general applicability of this principle is very much impaired by numerous other important considerations, which will now be mentioned.

§ 37. **Endothermic Reactions which take place at Normal Temperatures.** The following chemical reaction is endothermic:

$$\mathrm{NaFAq+HClAq=NaClAq+HFAq} \quad . \ . \ . \quad -2.3 \text{ Cal.}$$

Also in many other cases heat is absorbed if the solution of an acid be mixed with the solution of a salt. It is not necessary, however, to consider only the strictly chemical change, since the distinction between chemical and physical processes is not always clear, and, what is of still more importance, the theory upon which the principle of greatest work is based holds equally good for alterations in the physical condition. The existence of many *endothermic* physical processes which take place spontaneously may be readily demonstrated.

Freezing-mixtures. Snow and sodium chloride mixed together at 0° give a liquid, a salt solution, the temperature of which lies a number of degrees below 0°. Crystallized sodium sulphate (Glauber's salt) and concentrated hydrochloric acid when mixed absorb an appreciable quantity of heat.

In both these cases the action is *spontaneous* and *strongly endothermic.*

The Solution of Salts in Water. Most salts dissolve in water with the absorption of heat. However, this action is self-inducing, i.e., takes place of its own accord.

REMARK. Salts which form crystalline compounds with water usually dissolve in water with the absorption of heat only when they are introduced in the form of the compounds containing the same number of molecules of water with which they crystallize at ordinary temperatures.

The Evaporation of Liquids. Many liquids evaporate at normal temperatures, absorbing at the same time an appreciable quantity of heat, known as the *heat of vaporization.* Water, alcohol, and ether are such liquids. This process is endothermic and takes place spontaneously.

§ 38. **Mass Action.** Very often an element C can cause the decomposition of a compound AB—although A, B > A, C—if the quantity of C is very great in proportion to the quantity of AB. This is true in the case of double decompositions.

Examples. 1. A small quantity of potassium chloride is decomposed by a large quantity of bromine, with the formation of potassium bromide, notwithstanding the fact that

$$\text{K, Cl} = 105.5 \text{ Cal.,} \quad \text{while} \quad \text{K, Br} = +95 \text{ Cal.}$$

2. Ethyl alcohol and acetic acid mixed in molecular proportion form ethyl acetate, but only two-thirds of the alcohol and acid enter into this reaction, the other third remaining in the form of the unaltered materials. If, however, more alcohol or acid be added, the quantity of the ethyl acetate is increased. The heat of reaction in this case is nearly equal to zero.

3. Dilute hydrochloric acid mixed with a dilute solution of sodium sulphate partially decomposes the salt, an endothermic reaction taking place, and this reaction proceeds further if more acid is added.

§ 39. **Dissociation.** Compounds which are formed at ordinary temperatures by an exothermic reaction are generally decomposed at very much higher temperatures (comp. § 32). This decomposition, however, is an endothermic reaction.

REMARK. Investigations of the phenomena of dissociation were first carried out by Georges Aimé (1837) and later by Henri Sainte Claire Déville (1857).

Examples. Water, hydrogen chloride, and carbon dioxide are partially decomposed at high temperatures. Ammonium chloride and many other ammonium salts decompose into acid and ammonia-gas. Calcium carbonate gives off carbon dioxide on heating. The so-called *efflorescence*, the spontaneous loss of water from hydrated salts, may be considered as a dissociation phenomenon.

§ 40. **The Principle of Variable Equilibrium.** This principle includes many of the exceptions to the principle of greatest work which have been mentioned.

If a chemical system of a certain form changes to another form by a reversible process, then at every temperature each of the two forms will be present in a fixed concentration.*

If the transformation of the form A into the form B takes place with the evolution of heat, then an increase of temperature will cause an increase in the quantity of matter in the form A.

If A changes to B with the absorption of heat, then an increase of temperature will cause an increase in the quantity of matter in the form B.

If the transformation of A into B takes place without any caloric effect, then an increase in temperature will in no way alter the distribution of the system between the two forms as they exist at normal temperatures.

REMARK. This principle was introduced into chemistry in 1884 by Van't Hoff.

Examples. *Dissociation Phenomena.* The phenomena of dissociation mentioned above are examples of exothermic reactions, into which, however, at higher temperatures endothermic considerations also enter. Water is formed from hydrogen and oxygen with the evolution of a large quantity of heat; at high temperatures, however, a part of the water dissociates according to the equation

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

The reaction

$$CaO + CO_2 = CaCO_3$$

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* Another rule applies to *condensed* equilibrium (see § 45, *c*).

is exothermic, but at higher temperatures the reaction

$$CaCO_3 = CaO + CO_2$$

takes place, and this is endothermic: $-$ 30.8 Cal.

Salt Solutions. Good examples are also found in the phenomena accompanying the dissolving of salts.

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

On heating, the concentration of the solution changes: it either increases or decreases, only in special cases does it remain constant.

In most cases the concentration increases with the temperature—for example, in the case of KNO_3, $Na_2SO_4 10H_2O$, $CuSO_4 5H_2O$. The salts dissolve with the absorption of heat, an endothermic reaction takes place, and as a result of this reaction that form of the system results in which on an increase of temperature an increased quantity of the reacting substance appears (comp. § 53, Rem. 1).

The concentration decreases in the case of ethyl acetate and calcium sulphate. These substances, whose solution in water is an exothermic process, separate from the solvent on an increase in temperature; that form of the system which results from an exothermic action decreases in quantity when the temperature is raised.

The concentration of a saturated solution of sodium chloride is but very slightly affected by the temperature; the heat of solution of this salt is in fact very nearly equal to zero.

Formation of Esters. The formation of ethyl acetate and water from ethyl alcohol and acetic acid is a strictly chemical example of a reaction which proceeds without caloric effect. At normal temperature only two-thirds of the molecular quantities of the mixed substances are converted into the second form; at high temperatures this reaction takes place very rapidly, but the quantities of the original substances which take part in it are neither greater nor less than at the normal temperature.

Remark. The principle of greatest work, if viewed from the standpoint of the principle of variable equilibrium, may, according to Van't Hoff, be briefly summed up as follows: the principle of greatest work is the more correct the nearer the temperature of the reaction approaches the absolute zero; at the absolute zero it is of universal validity. The frequent confirmation of the principle at normal temperature is due to the fact that this temperature, in comparison with the highest attainable temperature, is not far removed from the absolute zero.

It may also be said that at the absolute zero no dissociation takes place.

§ 41. **Chemical Equilibrium.** The principle of greatest work prescribes the complete transformation of reacting substances, and requires the existence of a single form for every chemical system—namely, that form which is produced with the greatest evolution of heat.

As already mentioned, this condition is contradicted by a number of circumstances, including the endothermic reactions which take place at normal temperatures, the action of the chemical mass, the phenomenon of dissociation, and the phenomenon of variable equilibrium.

All of these different facts may be summed up in one general theory, called the *theory of chemical equilibrium.* The elements of this theory may be stated as follows:

Reacting substances do not enter completely into a transformation, the quantity of unaltered material depending upon the relative quantities of the reacting substances, upon the pressure, and upon the temperature.

The elements of this theory may, however, be differently stated. A chemical system can exist in more than a single form; generally the different forms exist side by side, and the system is distributed between them in quantities which depend upon the mass of the substances, the pressure, and the temperature.

The expression *equilibrium of the forms* is derived from the fact that the final state of the system is to be considered, not as a state of rest, but as a state of motion; a continual transformation and re-formation of the different forms taking place, but the actual quantity of each of the forms existing at any one moment being always the same. When this condition arises, then the quantities of the forms stand to one another in a fixed relation.

§ 42. **Graphic Representation.** If AB and CD enter into a double decomposition, then in the final state of the system, besides a fixed quantity of AC and BD, a certain quantity of AB and CD will also be present. The final state of the system can be represented by the equation

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

In this manner both the qualitative and quantitative relations may be shown. If also the formation and re-formation is to be expressed, then the equation is written

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

It is evident that both simple decompositions and substitutions can be represented in this manner:

$$AB \leftrightarrows A + B; \quad AB + C \rightleftarrows AC + B.$$

Examples. 1. The elements hydrogen and oxygen combine to form water, but may also exist in the form (hydrogen + oxygen). At high temperatures both forms can exist side by side, and the state of the system may be thus represented:

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

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

2. Action of nitric acid on sodium sulphate:

$$Na_2SO_4Aq + 2HNO_3Aq \rightleftarrows 2NaNO_3Aq + H_2SO_4Aq$$

and

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

3. The colorless nitrogen tetroxide decomposes on increase in temperature and decrease in pressure, forming the colored modification:

$$N_2O_4 \rightleftarrows 2NO_2.$$

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

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

§ 43. **Proof of the Existence of Equilibrium between Simultaneous Reactions.** That a final state of equilibrium must exist between the two reactions.

$$\text{Form A} = \text{Form B} \quad \text{and} \quad \text{Form B} = \text{Form A}$$

follows from the fact—which is indeed the characteristic of equilibrium reactions—that the final state of the system is independent of the form in the initial condition.

When ethyl alcohol is mixed with acetic acid in molecular quantities, the final state attained is the following:

$$\tfrac{1}{3}(C_2H_6O + C_2H_4O_2) + \tfrac{2}{3}(C_2H_5OC_2H_3O + H_2O).$$

The same result is obtained, however, when ethyl acetate and water are mixed in molecular quantities.

From this it is evident that not only the molecules C_2H_6O and $C_2H_4O_2$ but also the molecules of the ester and the water act on one another. And there is no reason for believing that this action ceases when the permanent, final state is reached.

With relation to these facts equilibrium reactions are also often called *reciprocal* reactions in contradistinction to reactions which proceed only in one direction. Although it is possible that all reactions are under certain conditions reciprocal, nevertheless these conditions have not been observed in all cases. It is also a fact that in many cases the existence of a reciprocal reaction at *all* temperatures is assumed from the observation of the existence of such a reaction at certain definite temperatures. A very evident dissociation of water-vapor can be observed at high temperatures; at lower temperatures, however, a dissociation cannot be detected. It is nevertheless assumed that it exists, although the quantity of the dissociation-products is infinitely small.

§ 44. The Three Kinds of Chemical Equilibrium.

a. Homogeneous Equilibrium. This term is applied to equilibrium between substances which form physically homogeneous mixtures, viz., water-vapor and oxyhydrogen-gas; N_2O_4 and $2NO_2$; $Na_2SO_4Aq + HNO_3Aq + HNaSO_4Aq + NaNO_3Aq$, etc.

b. Heterogeneous Equilibrium. This expression is used in the case of equilibrium between substances which are not in the same states of aggregation; for example,

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

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

$$Na_2SO_4 10H_2O\text{(sol.)} \rightleftarrows Na_2SO_4 9H_2O\text{(sol.)} + H_2O\text{(vapor)}.$$

c. Condensed Equilibrium. This denotes: equilibrium between substances which are all solid or all liquid, but are not mixed; or part solid and part liquid, but not mixed.

Examples. Monoclinic sulphur $\rightleftarrows$ Orthorhombic sulphur.

$$Na_2SO_4 10H_2O \text{ (solid)} \rightleftarrows Na_2SO_4 \text{ (sol.)} + 10H_2O \text{ (liq.)}.$$

§ 45. Effect of Temperature on Equilibrium.

a. On Homogeneous Equilibrium. The state of a system of two substances which are in equilibrium with one another, at a certain temperature and at a certain pressure, is determined by the relative quantities of both forms present.

The relation of the two substances to one another is further dependent upon the temperature of the system and stands in a direct relation to the heat-toning * which accompanies the transformation of the one form into the other.

The laws which govern the relation between the quantities of the substances entering into the transformation and the temperature and heat of transformation are the same as the rules given under the *principle of variable equilibrium* in § 40.

REMARK. In the case of homogeneous equilibrium the relative quantities of both forms can generally be determined from the specific gravity of the system. If the weight of one liter of nitrogen tetroxide at a certain temperature and pressure be determined,—it being known what this value *would be* if the space were filled with N_2O_4, and also if it were filled with NO_2,—then the composition of a mixture which would correspond to the observed weight can be calculated.

In the case of reactions between solutions of acids and salts the quantities which enter into the transformations, and also the equilibrium relations, can be calculated from the results of *calorimetric*, *volumetric*, and *optical* investigations. J. Thomsen determined the heat evolved on mixing solutions of salts and acids, and, by comparing this heat-toning with that which *would* appear if the decompositions were complete, was able to calculate the quantities of substances which had actually undergone decomposition. W. Ostwald determined the specific gravities and indices of refraction of mixed solutions, as well as the corresponding values for the separate solutions of the salts, acids, and products of the reactions, and used these values for calculating the extent of the decomposition.

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* Heat-toning is the thermal effect measured in calorimetric units.

There are also other special methods.

b. Effect of Temperature on Heterogeneous Equilibrium. When a condensed form is in contact with a dilute form,—a solid or liquid body in contact with a gas, vapor, or solution,—the equilibrium of the system is not determined by a certain *distribution* of the system between two forms, but by a fixed *concentration* of the dilute form. If the latter is a gas or a vapor, then this fixed concentration is manifested through a certain pressure, known as the *dissociation-pressure*, which is independent of the quantity of the substance existing in the condensed form.

The concentration increases with the temperature if the heat-toning of the transformation of the condensed into the dilute form is negative; if the latter is positive, then the condensation decreases in accordance with the principle of variable equilibrium (§ 40).

An example is furnished by the decomposition of calcium carbonate, which, if heated in an inclosed space, dissociates into calcium oxide and carbon dioxide until the gas reaches a certain pressure. Other examples are furnished by hydrated salts, which have a certain vapor-tension, depending on the temperature; and also by saturated solutions of salts (§ 40).

c. Effect of Temperature on Condensed Equilibrium. At a fixed pressure this type of equilibrium occurs at only a single temperature, and the quantities of the substances appearing in the coexistent forms are indefinite; at 96° rhombohedral and monoclinic sulphur exist side by side in arbitrary quantities. On an increase in temperature the equilibrium vanishes, and the change of one form into the other takes place in accordance with the rule given in § 40; that form appearing which is produced from the other with the absorption of heat.

In the case of condensed systems the conditions are such that the two forms can only coexist at a single temperature, above which one form, and below which the other form, is stable. The temperature at which both forms appear is called the *temperature of transformation* or the *transformation-point.*

§ 46. Effect of Pressure on Equilibrium.

a. Effect on Homogeneous Equilibrium. When a gaseous homogeneous mixture of reacting substances has attained a state of equilibrium and the temperature remains constant, an increase in the pressure causes a change of the transformed quantities, and *that* form results which is produced from the other by a *decrease in the number of molecules.*

Briefly stated, the system, on an increase in pressure, tends to pass over into the more condensed form.

Example.

$$N_2O_4 \leftrightarrows 2NO_2.$$

The compression of this system causes an increase in the quantity of the N_2O_4.

A special case is illustrated by the equimolecular reaction

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

In such a reaction the condition of equilibrium is not affected by the pressure, if this is not too great.

b. Effect of Pressure on Heterogeneous Equilibrium. When the dilute form is a gas, an increase in the pressure at constant temperature does not have a permanent effect on the equilibrium:

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

At constant temperature an increase in the pressure of the carbon dioxide—corresponding to an increase in the concentration of the carbon dioxide—causes the formation of $CaCO_3$, which continues until the pressure has attained its original value.

The same behavior has been observed in the case of hydrated salts: compression of the vapor causes the recombination of the vapor with the dehydrated salt.

For salts which are in contact with their saturated solutions the rule applies that an increase in pressure increases the quantity of dissolved material, if the total volume of the salt and the water required for its solution is greater than the volume of the solution, or, what amounts to the same thing, if the process of solution is accompanied by a contraction in volume.

In such cases the rule also applies, that on increase in pressure the system tends to pass into the more condensed form.

c. Effect of Pressure on Condensed Equilibrium. In cases of equilibrium of this nature the relation between the quantities of the two forms is not directly dependent on the pressure, if the temperature is constant, since at the temperature of transformation the two forms exist side by side in arbitrary quantities. The temperature of transformation, however, is altered by an increase in pressure, and is in most cases lowered.

§ 47. **Effect of Chemical Mass on Equilibrium.** The influence of this factor is evident only in the case of homogeneous equilibrium. An increase in the quantity of one of the reacting substances increases the products of that reaction which is promoted by the presence of the substance added.

In the reaction

$$\text{Alcohol} + \text{acid} \rightleftarrows \text{Ester} + \text{water}$$

the formation of the ester is promoted by an increase in the quantity of the acid and also by an increase in the quantity of the alcohol. The addition of water, on the contrary, retards the formation of the ester.

Remark 1. If the action of one of the substances is impeded, this is equivalent to a decrease in its mass. For example: In the formation of esters the reaction is promoted by leading a current of hydrogen chloride through the mixture of acid and alcohol. The hydrogen chloride combines with the water, and the action of the latter on the ester is thus checked.

Remark 2. The idea of mass action was brought forward by Berthollet in the beginning of the present century.

In later chemistry the first important application of this idea was made by Guldberg and Waage (1867).

§ 48. **Analogy between Changes in Physical and Chemical State.** An insight into the laws of chemical equilibrium is obtained by a consideration of the conditions under which a substance changes its physical state.

Water can be solid, liquid and vaporous, and the transformation of one of these forms into the others is accompanied by certain thermal effects. These transformations are influenced by temperature and pressure, and they are reversible; a change in condition, caused by an alteration in pressure or temperature, is reproduced when the temperature and pressure are again re-established.

A state of equilibrium exists in the case of the physical forms: at 0° ice is in equilibrium with water, below 0° ice is in equilibrium with vapor, above 0° water is in equilibrium with vapor.

Increase in temperature leads to the appearance of that physical form the production of which is accompanied by the absorption of heat (principle of variable equilibrium, § 40). Ice on heating is converted into water. In this transformation a considerable quantity of heat, called the *latent heat of fusion*, is absorbed.

Water on heating forms vapor of increasing density and pressure; this vapor is formed with the absorption of heat, the *latent heat of vaporization.*

The system

$$\text{Water} + \text{Vapor}$$

is in equilibrium according to the equation

$$\text{Water} \rightleftarrows \text{Vapor},$$

and furnishes a case analogous to that of heterogeneous equilibrium. The state of equilibrium is such that at a certain temperature the density and pressure of the vapor have a fixed and definite value. Compression does not permanently affect these values, since when this occurs the vapor changes to liquid water, and the original pressure is again established.

A condensed equilibrium exists at 0° in the case of

$$\text{Ice} \rightleftarrows \text{Water}.$$

By an increase in pressure the temperature of transformation (corresponding in this case to the *freezing point*) is lowered.

§ 49. **Berthollet's Law.**

Principle. 1. When two substances A and B, each of which can enter into a reaction with a third substance, C, are present in a homogeneous mixture together with C, then there will exist in the final state neither AC only nor BC only, but AC and BC will occur in a state of *equilibrium*, their relative quantities depending on the mutual affinities, as well as on the chemical masses, of A and B.

2. If the substances AC and BC are either insoluble or only very slightly soluble in the liquid, then they will separate out, and the substances which remain dissolved in the liquid will tend to establish a new state of equilibrium, thereby causing the formation of fresh quantities of AC or BC.

Berthollet's First Law. When dissolved substances by their mutual action bring about the formation of an *insoluble* substance, then the reaction will proceed until the reacting substances are entirely decomposed.

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

Berthollet's Second Law. When the reacting substances form a volatile compound, then the reaction proceeds, until the original substances have undergone complete transformation, the volatile substance being continuously eliminated.

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

REMARK. These laws were published in "*Essai de statique chimique*" (1804).

Explanation. Berthollet's laws correspond with modern theory, since they state the existence of an equilibrium between two forms, and since they introduce the idea of *mass action* into the consideration. The influence of temperature and pressure, however, are not taken into account, and in addition to this the thermal effect of the alteration in form is entirely neglected.

Nevertheless these laws are of great practical value, since they include many reactions which take place under normal conditions and since they in most cases apply to the reactions, which are met with in the ordinary course of laboratory work. They are lacking, however, in logical rigor, since the conditions of insolubility and volatility with respect to the liquid are not sharply defined. From the first law it cannot be predicted that AgCN will dissolve in KCN, nor that

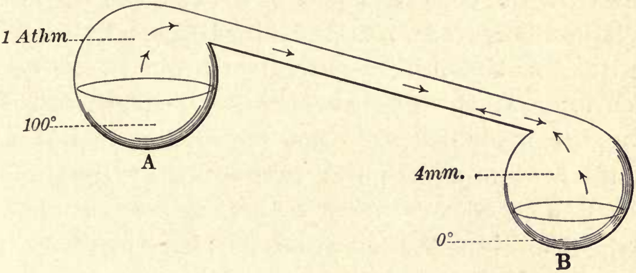
AgCl will be decomposed by KCN. The second law does not explain why sulphide of iron, but not sulphide of copper, is decomposed by hydrochloric acid; the first law furnishes no explanation as to why, in a mixture of ferrous chloride and cupric chloride dissolved in acidified water, sulphide of copper and not sulphide of iron is precipitated by hydrogen sulphide. Problems of this sort, however, can often be solved with the help of the principle of greatest work.

§ 50. **Watt's Principle.** When a space, in which at two points different but constant temperatures are maintained, contains a liquid at these points, then the vapor of the liquid moves to the point of lower temperature; at this point it condenses, and in the end the liquid will be found only at this point of lower temperature, the space then being filled with vapor, the pressure of which is equal to the maximum vapor pressure of the liquid at the lower temperature.

Example. If water be heated to boiling, in a still which is connected with a receiver cooled to 0°, the vapor passes over into the receiver; there it will be transformed almost completely into liquid, and finally all the water will have passed into the receiver, and the space within the still will be filled with vapor at a pressure of 4 mm.

Explanation. Water at 100° is in equilibrium with water vapor having a pressure equal to 1 atmosphere; water at 0° is in equilibrium with vapor the density of which corresponds to a pressure of 4 mm.

In A the vapor pressure has a constant value equal to 1 atmosphere, in B, however, this value cannot exceed 4 mm. Since the tendency of the vapor from both vessels is to fill the space offered to it, the cool vapor is forced back by the hot vapor, since the pressure of the latter is much greater than that of the former. The hot vapor therefore passes into B, where it is mostly converted into liquid, since in B only vapor having a pressure of 4 mm can exist. It is evident that this transfer will cease only when all liquid has disappeared from A, and when a pressure of 4 mm exists at all points in the enclosed space.



Application.

Distillation. A liquid is separated from a non-volatile substance with which it is mixed, by heating the mixture in a vessel, and connecting this vessel with a cooled receiver. The vapor of the volatile liquid passes over into the receiver and there condenses, while the non-volatile substance remains in the distilling vessel.

In this manner water can be separated from dissolved salts.—Thus also nitric acid is separated from the mixture which results on adding sulphuric acid to sodium nitrate, this operation causing the complete decomposition of the mixed materials; since the equilibrium existing in the mixture first formed is destroyed by the removal of nitric acid, and the *tendency towards the formation of a new state of equilibrium results in the formation of fresh quantities of nitric acid.*

Fractional Distillation. A mixture of liquids, when heated in a distillation apparatus, produces vapor, which at first consists chiefly of the vapor of the most volatile liquid. As a result this substance is present in the distillate in a purer state than in the original mixture. If the vapor which has condensed to a liquid be again distilled, then the first portion of this distillate will be a purer product than the liquid obtained in the previous operation. By fractional distillation, however, an absolutely pure product cannot be obtained; first, because by each distillation the quantity of admixed substance becomes indeed smaller, but does not entirely disappear; secondly, since in many cases a mixture is finally formed, which without alteration in composition may be converted into vapor and again condensed. This takes place because the boiling-point of this mixture is both *lower* than the boiling-point of its components and also lower than that of a mixture of different composition. The result is that on distillation first the mixture having the lowest boiling-point and later the other mixtures pass over into the distillate. The same behavior is observed in cases where a certain mixture has a boiling-point which is *higher* than that of its components and than that of a mixture of different composition. In such cases the more volatile mixtures first pass over, and the least volatile remain behind in the distilling vessel.

The occurrence of such mixtures of constant composition as are mentioned above is the explanation of why ethyl alcohol cannot be separated from water by fractional distillation, a mixture containing 94 per cent of alcohol and 6 per cent of water distilling over. It is also impossible to concentrate aqueous hydrochloric acid beyond a certain point, the concentration of the vapor continually approaching that of the liquid remaining in the retort, until finally the vapor and liquid have the same composition, this composition remaining unaltered on further distillation.

The composition of the unaltered mixture passing over is dependent on the pressure, and therefore such a mixture can not be considered a chemical compound.

A very important instance of fractional distillation is found in the purification of mineral oils by distillation.

Liquefaction of Gases under their own Pressure. If one arm of a closed tube bent at an angle in the middle contains crystals of chlorine hydrate ($Cl_2 10H_2O$), and the other arm be placed in a cooling mixture, then, if the arm containing the chlorine hydrate be cautiously heated, chlorine will be evolved and will pass over into the cooler end. If an excess of the gas is present, a point will be reached where the pressure of the gaseous chlorine slightly exceeds its maximum pressure at the temperature of the cooling mixture, and the chlorine will therefore liquefy in that end of the tube. From this point distillation will continue, in accordance with Watt's principle.

Ammonia-gas can also be liquefied by a similar process, the solid compound, ammonium silver chloride, being heated in a closed tube, one end of which dips into a freezing-mixture.

The temperature of the freezing-mixture must, of course, be lower than the critical temperature of the gas.

Applications of the Theory of Points of Transformation. As has been already stated, a substance which is in contact with its vapor in an inclosed space in which more than one temperature exists, tends to pass to that form of the system in which the vapor has the lowest pressure. Further, when more than one form can exist at the lowest temperature, the system tends to assume that form the vapor pressure of which is the lowest. Liquid water can, under certain conditions, exist below 0°, in contact with vapor having a definite temperature and pressure. But ice also is in equilibrium with vapor below 0°. For every temperature below 0°, however, the vapor pressure of water is greater than that of ice. Therefore, when ice and liquid water coexist at any temperature below 0°, the vapor will distill from the water to the ice, and will be transformed into ice. Also above 0° ice and water cannot form a stable system (comp. § 48).

At 0°, however, the vapor of both water and ice has the same density and the same pressure; therefore at this temperature the coexistence of both forms is possible, while at higher temperatures only one form is stable.

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

$$\text{Ice } (+ \text{ vapor}) \rightleftarrows \text{ Water } (+ \text{ vapor}).$$

By a similar course of reasoning the conclusion may be reached that at a certain temperature rhombohedral and monoclinic sulphur can exist side by side, since above this temperature the one only, below this temperature the other only, of the two forms is stable.

§ 51. **Watt's Principle applied to Matter at Normal Temperature.** The soundness of Watt's law is established by two facts. *First:* A condensed substance constitutes with its vapor a stable system, since a certain pressure and density correspond to every definite temperature. *Secondly:* No equilibrium exists if two systems of different density and different pressure are present in the same inclosed space; the vapor, under such conditions, passing from the region of higher pressure to the region of lower pressure.

In the previous paragraph those cases were considered where the differences in density and pressure were caused by differences in temperature. It is evident, however, that the transfer of matter in the form of vapor can also occur when the differences of vapor pressure are due to other causes. The principle of Watt may be still further expanded, and may be stated as follows:

When in any given space there are two centres, characterized by a difference in pressure of the vapor of one and the same substance in contact with a condensed form of this substance, the vapor of the substance will pass from the centre of higher to the centre of lower pressure.

A tendency to establish an equality of pressure exists in the system comprising the two centres.

Example. If pure water and a salt solution are contained in an inclosed space, water vapor will pass from the pure water to the solution.

Application.

Hygroscopic Salts and Acids. By hygroscopic salts and acids are meant such substances as are strongly soluble in water; their saturated solution is in equilibrium with vapor the pressure of which is much lower than that of pure water at the same temperature. When water is contained in an inclosed space in which a substance of this nature is also present, vapor passes from the water to the substance, since a small quantity of water brought into contact with this substance forms on its surface a very concentrated solution; this solution has a very low vapor pressure and constitutes a *centre of low pressure*, to which the vapor of the pure water continually passes, i.e., *distills over* at normal temperature.

Since the vapor pressure of all salt solutions is lower than that of pure water, such solutions will therefore attract to them the vapor of pure water. The vapor pressures of solutions of difficultly soluble substances are only very slightly lower than that of water; the distillation will therefore take place very slowly.

The atmosphere always contains water vapor, the density and pressure of which vary greatly with different localities and at different times. If a salt solution be exposed to the air it absorbs water vapor if its own vapor pressure be lower than that of the water vapor in the atmosphere; in such cases the solution is said to exert a *hygroscopic* action. The hygroscopic action of very soluble salts is considerable. On the surface of such substances the moist air forms a film, consisting of a very concentrated, saturated solution, which produces a centre of low vapor pressure. As soon as this centre is created, the water vapor of the atmosphere, the pressure of which ordinarily exceeds that of the salt solution, passes to this centre. Fresh quantities of the solution are formed, and this remains saturated and has a very low vapor pressure, so long as an excess of the undissolved salt remains. When the salt has completely dissolved, then the solution continues to absorb water vapor until the dilution reaches the point where the vapor pressure of the solution is equal to that of the atmosphere.

REMARK. These considerations do not apply in the case of hygroscopic action of a purely *chemical* nature, as for example that of P_2O_5. P_2O_5 is not in equilibrium with water vapor at any pressure, since it forms with it a compound H_3PO_4. It may be said, however, that P_2O_5 represents a centre the vapor pressure of which is equal to *zero*. The same is true for anhydrous calcium chloride; the first hygroscopic action of this salt being confined to the formation of the hydrated salt, $CaCl_2.6H_2O$, the salt in the meantime constituting a centre with the vapor pressure zero; later a saturated solution is formed.

The saturated solutions of slightly soluble substances do not exert any hygroscopic action, their vapor pressures being greater than the pressure of the water vapor of the atmosphere. Such solutions lose water vapor until no more water remains.

The Deliquescence of Solid Substances in the Air. It is now not difficult to determine what substances *deliquesce* in the air. They are those substances the saturated solutions of which at normal temperatures have a vapor pressure *less* than the pressure of the atmospheric water vapor; if their vapor pressure is *greater* than the vapor pressure of the atmospheric water, then the substances do not deliquesce, but, on the contrary, when they are moist they dry in the air.

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

Potassium carbonate deliquesces, because a trace of water forms with it a small quantity of a saturated and *very concentrated* solution having a very low vapor pressure, more water vapor being continually absorbed by this solution. Potassium sulphate, on the contrary, does not deliquesce, since, although it may perhaps be already moist, it can form only a very dilute solution the vapor pressure of which is greater than the tension of the atmospheric water vapor, and therefore the sulphate will lose water vapor in the air.

Pure sodium chloride is but slightly soluble and does not deliquesce. Commercial sodium chloride, however, generally contains small quantities of very soluble magnesium chloride, and since this latter substance deliquesces, the sodium chloride itself appears to be hygroscopic.

Sodium nitrate (Chili saltpeter) is, at normal temperatures, *very readily* soluble in water, potassium nitrate (potassium saltpeter) but *very slightly.* The Chili saltpeter is so hygroscopic that it cannot be used in the manufacture of gunpowder, while potassium saltpeter is very well suited to this purpose. The difference in solubility of the two salts is the basis of the method for preparing potassium nitrate from sodium nitrate according to the reaction:

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

Hot solutions of $NaNO_3$ and KCl are mixed and boiled, the potassium nitrate remaining dissolved in the hot water. On cooling it crystallizes out, since it is only slightly soluble in cold water. The solubility of sodium chloride in hot and cold water is, however, about the same; the sodium chloride therefore remains in solution. The same conditions that make potassium saltpeter suitable for the manufacture of gunpowder also make it possible to prepare this saltpeter from sodium nitrate and potassium chloride.

The Efflorescence of Hydrated Salts. As already stated, a hydrated salt is at a given temperature in equilibrium with water vapor of a definite density and pressure. For every salt, as for pure water, there is a certain characteristic *table of vapor pressures.* A hydrated salt at a certain temperature therefore represents a centre of definite vapor tension.

When at normal temperature the vapor tension of the salt exceeds that of the atmospheric water vapor, then the crystals will lose water in the air and will effloresce. If, however, the vapor tension of the crystals is exceeded by that of the atmospheric vapor, then the crystals will lose no water, or, as it may be more correctly stated, the water lost will be immediately replaced by the atmospheric vapor, and the crystals will *not* effloresce.

Example. Sodium sulphate (Glauber's salt) effloresces, calcium sulphate (gypsum) does not effloresce. If fresh crystals of both salts are exposed to the air, their identity can, after a short time, be readily determined, since the first will, but the second will not, have effloresced.

REMARK 2. In the above considerations it is assumed that the relative amount of water in the air is nearly constant. It is clear, however, that when the amount of water is small many substances will not deliquesce, but will effloresce, while when the amount of water is large the same substances will deliquesce and not effloresce.

CHAPTER V.

SOLUTIONS.

§ 52. **Definitions.** Many substances can form with water a homogeneous liquid mixture; a mixture of this sort is called a *solution*.

REMARK. Water is not the only liquid which can dissolve substances; in this book, however, chiefly *aqueous solutions* will be considered.

A solution is *saturated* at a certain temperature if, when brought in contact with the substance a quantity of which it already contains, no further quantities of the substance pass into the solution. If the solution contains more of the substance than is required to form a saturated solution, then the solution is *supersaturated*. Supersaturation can only occur when the solution is not in contact with solid particles of the dissolved substance; since this would immediately cause the separation of a part of the substance contained in the solution, and the strength of the solution would be reduced.

A saturated solution of a substance in contact with the same substance in the undissolved state represents, at a constant temperature, a system of stable equilibrium. With most substances the quantity of material which can be dissolved is greater the higher the temperature. There are other substances, however, the solubilities of which decrease with an increase in temperature.

Examples. Potassium nitrate, sodium nitrate, sodium sulphate, and many other salts are more soluble in warm water than in cold. Calcium sulphate and ethyl acetate, on the contrary, are least soluble in hot solutions. Sodium chloride is about equally soluble in cold and warm water.

§ 53. **General Laws of Solubility.** The coefficient of solubility of a substance is the number of grams of the substance which at a given temperature will dissolve in 100 grams of water.

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

REMARK 1. It should be noted that the expression 'heat of solution' mentioned in paragraph 40 denotes the quantity of heat which is evolved when a substance dissolves to form an almost saturated solution, corresponding therefore to the *heat of solution in nearly saturated solution.*

The solubility of solids and liquids is only very slightly affected even by very great pressures. Compare § 46.

REMARK 2. The relations between solubility and pressure, and between solubility and temperature, only hold when the water and the dissolved substance do not mix in all proportions. Alcohol, for example, has no coefficient of solubility, since it mixes with water in all proportions.

Gases, which are but slightly soluble in water, follow the *law of Henry;* their solubility at a fixed temperature is proportional to the pressure.

§ 54. **Solubility of Hydrates.** Salts containing water of crystallization conform to the rule that each hydrate has its particular solubility. It is therefore possible for a solution to be saturated with respect to several different substances, namely, to different hydrates. A concentrated solution of sodium sulphate, prepared at 40°, and afterwards cooled to the temperature of the room, is not only saturated with respect to (i.e., deposits crystals not only on contact with) $Na_2SO_4 10H_2O$, but also with respect to $Na_2SO_4 7H_2O$.

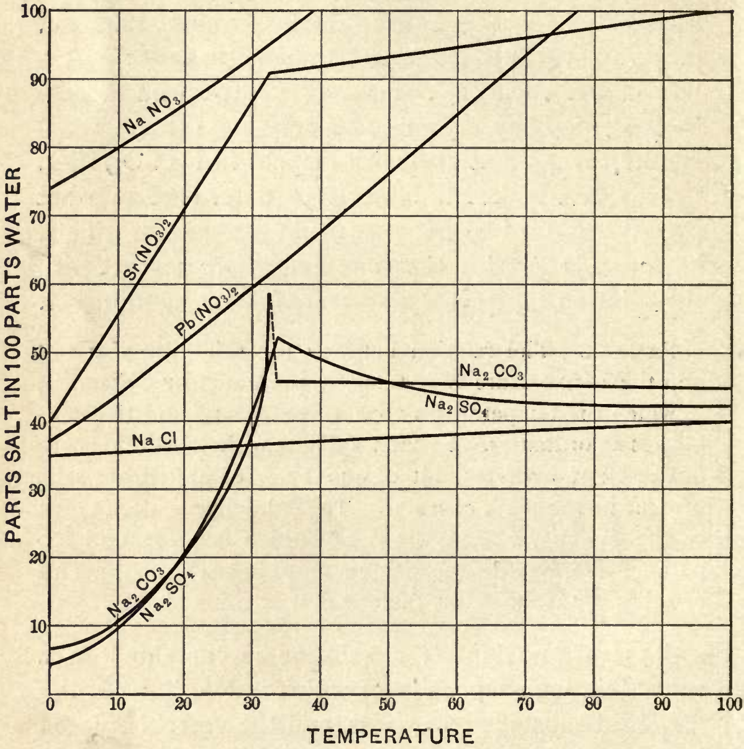
This fact makes it difficult to determine in what state a dissolved salt is present in a solution. This, however, is certain: that one hydrate in contact with the solution represents a system of stable equilibrium.

REMARK. The relation between the solubility of a salt and the temperature is generally represented by a diagram, in which the temperatures appear as abscissas and the solubilities as ordinates. In such a diagram the solubilities are not those of hydrates, but of quantities of anhydrous salts present in 100 parts of water. The solubility is often taken as the quantity of anhydrous salt which is present in 100 parts of *solution*. In the diagram on page 124 the coefficient of solubility is, however, the one first mentioned.

§ 55. **Osmosis.** If a solution is contained in a vessel, through the walls of which water, but not the dissolved substance, can pass, and the vessel is placed in water, then water will pass from the outside through the walls of the vessel into the solution (osmosis).

The property of partial permeability is possessed by many vegetable and animal membranes; but osmosis has been most accurately studied by the use of artificially prepared *semipermeable* membranes.

The passage of water through the walls of the vessel can be prevented by applying a pressure to the solution. Such a pressure, *in equilibrium with the force exerted by the water in passing into the solution,* is equal to the *osmotic pressure.*



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

§ 56. **Osmotic Phenomena in Dilute Solutions.** If a solution is contained in a cylinder into one end of which a piston is fitted, the other end being closed by a semipermeable membrane and surrounded by water, the solution may be compared to a gas which is contained in a cylinder closed at one end, and kept in equilibrium with the atmosphere by a frictionless piston at the other. If the piston be raised, then the dissolved substance expands,—that is, water passes in through the membrane from the outside,—the volume of the solution increases, and the osmotic pressure falls. If the piston be now pressed into the cylinder, then water passes out through the membrane, the volume of the solution diminishes, and the osmotic pressure becomes greater. If the system be heated, and the piston be held at one position, then the pressure on the piston must be increased, and the osmotic pressure becomes correspondingly higher.

Both concentrated and dilute solutions are in this respect analogous to gases. Dilute solutions, moreover, show a *complete quantitative agreement* with gases, as has been shown by Van't Hoff (1886). When a dilute solution is contained in a cell with a semipermeable membrane, and the cell is placed in water, then the solution follows *the laws of Boyle and Gay-Lussac and the law of Avogadro.*

Further, for solutions of one and the same substance:

1 At constant temperature the osmotic pressure is proportional to the concentration;

2 At constant volume the osmotic pressure is proportional to the absolute temperature.

For solutions of different substances:

Under conditions of equal temperature and equal concentration the osmotic pressure is inversely proportional to the molecular weight; or:

Solutions of the same molecular concentration* have at the same temperature an equal osmotic pressure. And lastly:

The osmotic pressure of a dissolved substance at a certain temperature and concentration is equal to the gas pressure which the same substance in a gaseous state would exert at the same temperature and concentration.

Example. The following osmotic pressures have been observed in solutions of cane-sugar at 14° C.:

Per Cent Solution.	Osmotic Pressure.
1	535 mm
2	1016 "
4	2082 "
6	3075 "

If cane-sugar *could* exist as a gas, then at a concentration of 10 grams per liter and at a temperature of 14° its pressure *would* be

$$760 \times 22.32 \times \frac{10}{342} \times \frac{287}{273} \text{ mm} = 521 \text{ mm}.$$

REMARK. It is evident that the molecular quantity of the dissolved substance can be calculated from the osmotic pressure of a solution of known concentration (compare § 21, Rem. 1).

§ 57. **Experimental Basis.** This is partly found in measurements of the osmotic pressure. Such measurements, however, involve considerable difficulty, and it is found almost impossible to prepare membranes which are absolutely impervious to the dissolved substances.

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* The molecular concentration is the number of molecular quantities of the substance in one liter of the solution.

Important data are, however, found in the phenomena which stand in close relation to the osmotic pressure, as has been pointed out by Van't Hoff. These phenomena are the *lowering of the freezing-point*, *the elevation of the boiling-point*, *and the decrease in the vapor pressure.*

a. Lowering of the Freezing-point. It has long been known that the freezing-point of water is lowered by the addition of a soluble compound. This lowering is, within certain limits, proportional to the concentration of the solution. According to the theory of osmotic pressure, this pressure is proportional to the number of molecules dissolved in a liter, and also for one and the same substance the lowering of the freezing-point is proportional to the concentration, while for the solutions of different substances, but of equal concentration, the lowering is inversely proportional to the molecular weights of the dissolved substances.

REMARK 1. If the depression of the freezing-point for a one-per-cent solution of any substance in a given solvent be determined, then the depression produced by dissolving a molecular quantity of the same substance in 100 grams of the given solvent can be calculated, it being assumed that such a solution would be possible and that it would obey the law for dilute solutions. The value of the result obtained is purely fictitious, but is of great assistance in experimental work and is known as the *molecular depression* for the given solvent. The *molecular depression* of the freezing-point depends upon the nature of the liquid, and is the same for all dissolved substances (compare § 58).

Remark 2. The constant for the molecular depression of the freezing-point has a different value for every solvent. Van't Hoff has pointed out the fact that a direct quantitative relation exists between this constant and the *latent heat of fusion* of the solvent, so that either one of the two quantities can be calculated from the other.

b. Elevation of the Boiling-point. For the same dissolved substance the elevation of the boiling-point is proportional to the concentration.

For equally concentrated solutions of different substances the elevation of the boiling-point is *inversely proportional* to the molecular weights of the substances.

c. Decrease in the Vapor Pressure. Similar rules apply to the lowering of the vapor pressure of solvents.

Remark 3. The above rules may be summed up as follows: the osmotic pressure, depression of the freezing-point, elevation of the boiling-point and decrease in vapor pressure are equally great for solutions which contain an equal number of molecules dissolved per liter in the same solvent.

Remark 4. The molecular quantity of the dissolved substance can be determined from any one of the three rules given. The depression of the freezing-point method is, however, the one most generally used.

Many substances the molecular weights of which had been previously determined have given similar values when examined by the more recent methods. Nevertheless the molecular weight is to a certain extent dependent on the nature of the solvent.

Remark 5. Important osmotic phenomena may be observed in the case of living organic cells.

If a plant-cell be brought into a salt solution osmosis takes place. The protoplasm which surrounds the liquid, the sap of the cell, under normal conditions adheres to the cell-wall, and acts as a semipermeable membrane, permitting only water, but not the substances dissolved in the sap or the water, to pass through. According as the salt solution used is more or less concentrated, the sap of the cell will absorb water or send out water through the protoplasm. A certain concentration of the salt solution must naturally exist which is in equilibrium with the sap, so that the solution does not remove water from the sap, nor does the sap remove water from the solution. At this concentration the sap and the solution have an equal osmotic pressure; they are isosmotic or *isotonic.* The solutions of different salts are isotonic and of equal osmotic pressure when they are in equilibrium with the sap of the same cell. Stronger solutions withdraw all water from the cell. The elastic protoplasm contracts and breaks loose from the rigid wall of the cell. This phenomenon, known as *plasmolysis*, is observed by the use of a microscope.

The isotonic coefficient of a substance is the osmotic pressure of its aqueous solution when this has the same molecular concentration as a potassium nitrate solution, the osmotic pressure of which is arbitrarily chosen as 3. The isotonic coefficient of cane-sugar is 1.88; therefore a solution of cane-sugar is isotonic with a sodium nitrate solution when the molecular concentration of the former stands to the concentration of the latter in the proportion 3 : 1.88 (H. de Vries).

Equal osmotic pressures are observed in the cases of equimolecular solutions of various neutral organic compounds and organic acids. The behavior of blood-corpuscles is very similar to that of plant-cells, and was first investigated by Donders and Hamburger. The latter worked out a method for the determination of molecular weights which was based upon phenomena observed in the course of the investigation.

§ 58. **Exceptions.** The methods for the determination of the molecular weight described in this chapter lead in the case of a large number of substances to results which are not in accord with the general osmotic theory. These substances comprise the strong acids, the strong bases and salts. Attention was called by Arrhenius (1887) to the rule that exceptions occur in the cases of all substances which are *electrolytes*.

CHAPTER VI.

ELECTROCHEMISTRY.

§ 59. **Definitions.** A chemical compound which in the dissolved or melted condition conducts the electric current is called an *electrolyte.*

If an electric current is passed through the aqueous solution of an electrolyte, certain chemical changes are produced. The process is called *electrolysis.*

The point at which the positive electricity enters the solution is called the *anode;* the point at which it leaves, the *cathode.* Both anode and cathode are known as the *electrodes.*

The little particles charged with electricity which collectively constitute a molecule of the electrolyte are called the *ions* of the latter.

The ions which during electrolysis move to the anode are called the *anions;* those which move toward the cathode, the *cathions.*

§ 60. **Electrolytic Dissociation.** When an electrolyte dissolves in water a part of its molecules split up into ions. This process is called *electrolytic dissociation.*

If the solution takes place in a large volume of water, i.e., if the solution is very dilute, all of the molecules are split up into ions. In such a solution the electrolyte is present only in the form of ions.

Examples. Potassium chloride in aqueous solutions is partly split up into the ions $\overset{+}{K}$ and $\overset{-}{Cl}$; potassium nitrate into $\overset{+}{K}$ and $\overset{-}{NO_3}$; sulphuric acid according to the dilution into $\overset{+}{H}$ and $\overset{-}{HSO_4}$ or into $\overset{+}{H}$, $\overset{+}{H}$ and $\overset{-}{SO_4}$; potassium acetate into $\overset{+}{K}$ and $\overset{-}{C_2H_3O_2}$.

Remark. Clausius was the first to put forward the hypothesis that electrolytes on passing into solution in water partly split up into their ions. If such a solution is electrolyzed, then the ions, which at first move in all directions through the solution, will be guided by the current, the cathions to the cathode and the anions to the anode.

The action of the current on the electrolyte is therefore not the decomposition—since the electrolyte is already decomposed into its ions in the solution—but the transportation of the ions to the electrodes.

Later (1887) Arrhenius chose this hypothesis as a starting-point and founded upon it his theory of electrolytic dissociation.

Since the ions are charged with electricity they can exist in water without action on it. A normal potassium atom would instantly decompose water; a charged potassium atom (potassium ion), however, is neutral in its action towards water until the electric charge which it bears has been removed from it, as occurs when it comes in contact with the cathode.

§ 61. **Faraday's Law.** This can be stated as follows: The movement of electricity in electrolytes takes place only with the simultaneous movement of the ions.

Chemically equivalent quantities of different ions move with equal quantities of electricity.

If equal quantities of electricity pass through solutions of different electrolytes, for example, silver nitrate and copper sulphate, then, according to Faraday, the weights of silver and copper ions which move through these solutions with this quantity of electricity will stand to each other in the ratio of the chemical equivalent weights of silver and copper; i.e., $\frac{107.93}{1} : \frac{63.6}{2}$.

During electrolysis, when the transported ions are discharged at the electrodes and the silver and copper ions pass into the neutral condition, the weights of the metals deposited will stand in the ratios of their chemical equivalent weights.

Remarks. Experiment has demonstrated that when in one second the unit quantity of electricity (one coulomb) passes through a solution of a silver salt, in this time there will be deposited 1.118 milligrams of metallic silver. This quantity is called the *electrochemical equivalent* of silver.

From these data, by applying Faraday's law, the electrochemical equivalent of every other ion can be calculated.

Thus, for example, the electrochemical equivalent of lead (x) is obtained from the equation

$$1.118 : x = \frac{107.93}{1} : \frac{206.9}{2};$$

$$x = 1.071.$$

§ 62. **Conductivity of Organic and Inorganic Compounds.** In general, organic compounds in aqueous solutions are poor conductors and similar solutions of inorganic compounds are good conductors. Solutions of strong acids in water conduct better than solutions of weak acids; organic acids in solutions conduct to a perceptible extent only when greatly diluted. Organic salts are good conductors.

The exceptions mentioned in § 58 are not observed, or at most the variations from the general law are only slight, when solvents other than water are used.

§ 63. Some Laws Governing Electrolytic Dissociation.

a. This dissociation increases with the dilution, and with increasing dilution approaches a maximum value.

Example. Potassium chloride in fairly concentrated solutions is partially dissociated into the ions K and Cl. The state of the system is therefore

$$x\text{KCl} + (1 - x)\overset{+}{\text{K}} + (1 - x)\overset{-}{\text{Cl}}.$$

The degree of dissociation, at a certain temperature and concentration, has a fixed value. With increasing dilution x decreases and $(1 - x)$ increases, until finally when infinite dilution is reached all the molecules of KCl have dissociated into ions.

b. In the case of *strong* acids and bases and their salts, in general in the cases of substances which enter into strong reactions, the dissociation is nearly complete in fairly concentrated solutions.

The reactions of analytical chemistry are chiefly reactions between ions.

Example. The formation of silver chloride from silver nitrate and sodium chloride takes place according to the equation:

$$\overset{+}{Na} \mid \overset{-}{Cl}Aq + \overset{+}{Ag} \mid \overset{-}{NO_3}Aq = AgCl\ (solid) + \overset{+}{Na} \mid \overset{-}{NO_3}Aq.$$

Remark 1. At first thought it might appear remarkable that such bodies as HCl, NaOH, and KCl exist in solution chiefly in the form of ions. It must be remembered, however, that these substances enter most readily into reactions, and the ability to enter into reaction depends upon the readiness with which the substances interchange their constituents.

Remark 2. The existence of electrolytic dissociation explains why, for example, chlorine does not always show the same reactions. According to the theory of Arrhenius the reactions are not reactions between atoms, but between ions. Therefore $\overset{+}{K} \mid \overset{-}{ClO_3}$ with $\overset{+}{Ag} \mid \overset{-}{NO_3}$ will not form AgCl, since the reaction involves the ion $\overset{-}{ClO_3}$, and not the atom Cl.

Remark 3. The part played by phenol-phthaline in volumetric-analysis titrations is explained by the theory of Arrhenius.

Phenol-phthalein is a substance of very complex constitution and contains two phenol residues, the radicals C_6H_4OH. These groups impart to the substance to a certain degree the properties of an acid, so that phenol-phthalein may be considered as an organic acid of the character RH. Like all organic acids, this substance in aqueous solutions is but very slightly dissociated, a condition which is quite different in the case of its salts. On neutralization with a base a salt RK is formed, and this salt is dissociated into the ions $\overset{-}{\mathrm{R}}$ and $\overset{+}{\mathrm{K}}$. The *red color* observed when phenol-phthalein is used as an indicator, is therefore due to the *formations of the ions* $\overset{-}{\mathrm{R}}$ from the non-dissociated substance RH.

That this explanation is correct is proved, first, by the fact that all soluble bases produce with phenol-phthalein the same red coloration, and, secondly, by the fact that *the red coloration is extremely weak in alcoholic solutions*—alcohol almost completely retarding electrolytic dissociation (§ 58),—but becomes much more intense when the alcoholic solution is diluted with water.

c. With respect to the osmotic pressure and the corresponding phenomena each ion has the value of a molecule, since each ion moves about in the liquid as an independent unit.

This rule explains the appearance of exceptions to the theory of osmotic pressure as enunciated by Van't Hoff. An example illustrating this will be given:

As previously stated, the condition of potassium chloride in an aqueous solution is the following:

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

If n molecules of KCl were originally introduced into the solution, then the above equation would become

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

The number of separate particles existing in the solution is therefore not n, but is equal to

$$n(1 - x) + 2x = n(1 + x).$$

Since the osmotic pressure is proportional to the number of dissolved molecules, and since each ion acts as a separate individual particle, the value of the osmotic pressure is a result of the action of, not n molecules, but $n(1 + x)$ particles.

The value of x increases with increasing dilution and approaches the maximum value 1. Therefore at extreme dilution the value of the osmotic pressure is *twice* as great as that prescribed by theory.

These considerations also apply to the phenomena of the depression of the freezing-point, etc.

If the depression of the freezing-point is determined for a solution of potassium chloride of certain concentration, the value thus obtained may be compared with that which *would* be obtained if no dissociation took place, and the value of x may be calculated. This follows since the relation between the observed value and the theoretical number is, according to the above explanation, $(1 + x)$.

§ 64. Proof of the Theory of Electrolytic Dissociation.

a. The exceptions to the general law of osmotic pressure appear in the case of electrolytes.

This fact has already been mentioned.

b. The variation is greater with greater dilution.

c. The degree of dissociation, calculated from the depression of the freezing-point, is equal to that determined from the conductivity of the solution.

According to the theory of Arrhenius the ions conduct the electricity in a solution, the undissociated molecules taking no part in this process. To determine the degree of dissociation, at a certain concentration, the conductivity of the solution at this concentration is compared with the conductivity of a solution of the same substance at infinite dilution; in the latter case the conductivity reaches its maximum value. From these data the number of free ions and the degree of dissociation at the given concentration can be calculated.

REMARK. The conductivity must always be reduced to a fixed concentration of the solution; since although the dissociation increases with the dilution, the concentration of the dissolved substance decreases at the same time.

The degree of dissociation, as determined from the conductivity of the solution, is the same as that calculated from the depression of the freezing-point.

d. The law of thermoneutrality (compare § 32).

The mixing of dilute salt solutions produces no thermal effect. This fact is readily explained by the theory of dissociation; since in dilute solutions the salts are almost completely dissociated, and when they are mixed *no alteration in their condition takes place.*

$$\overset{+}{\mathrm{Na}} \mid \overset{-}{\mathrm{Cl}}\mathrm{Aq} + \overset{+}{\mathrm{K}} \mid \overset{-}{\mathrm{NO_3}}\mathrm{Aq},$$

both before and after mixing, is a solution of the ions ($\overset{+}{\mathrm{Na}}$, $\overset{-}{\mathrm{Cl}}$, $\overset{+}{\mathrm{K}}$, $\overset{-}{\mathrm{NO_3}}$) in water.

e. The neutralization of a strong base by a strong acid always gives the same heat-toning.

Hydrochloric acid, nitric acid, hydrobromic acid, and hydriodic acid, when in dilute solution, give for molecular quantities nearly the same quantity of heat, + 13.7 Cal. For example,

$$\mathrm{HClAq} + \mathrm{KOHAq} = \mathrm{KClAq} + \mathrm{H_2O} \ldots + 13.7\ \mathrm{Cal.}$$

According to the theory of electrolytic dissociation, this reaction must, however, be expressed as follows:

$$\begin{aligned}\overset{+}{\mathrm{H}} \,\big|\, \overset{-}{\mathrm{Cl}}\mathrm{Aq} + \overset{+}{\mathrm{K}} \,\big|\, \overset{-}{\mathrm{O}}\mathrm{HAq} \\ = \overset{+}{\mathrm{K}} \,\big|\, \overset{-}{\mathrm{Cl}}\mathrm{Aq} + \mathrm{H_2O} \;.\;.\;.\; + 13.7 \text{ Cal.}\end{aligned}$$

Therefore the thermal effect of mixing the two solutions is due solely to *the formation of water from its ions.* The heat of formation of water from its ions is accordingly equal to + 13.7 Cal.

Since the strong bases and the strong acids are allmost entirely dissociated into their ions by water, the only action on mixing the solutions is in all cases the formation of water from its ions, and therefore the thermal effect is in all cases the same

CHAPTER VII.

PHENOMENA OF LIGHT.

§ 65. **Colored Flames.** Many salts introduced into a nonluminous gas-flame impart to the flame a coloration which is characteristic of the metal of the salt. Sodium salts color the flame yellow, potassium salts violet, barium salts green. In analytical chemistry this coloration is used to identify many metals.

Often, however, the color effect is not sufficient for the identification of an element, since the characteristic color of one element may be masked by that of another, and indeed the intense yellow color of sodium is almost never absent. It is therefore necessary to analyze the effect, and to separate the light into its components. A rough method for accomplishing this is by the use of cobalt glass or an indigo prism; these allow the potassium light, but not the sodium light, to pass through them, and it is thus possible to identify the color of potassium in a mixture of it with sodium.

§ 66. **The Spectroscope.** The analysis of the light by means of the spectroscope is, however, much more accurate. In this apparatus a ray of light from the flame passes through a narrow slit and falls on a glass prism. The action of the prism on the ray of complex light passing through it is such that this ray is broken up into a series of other rays, each of which consists of light of a single wave-length (i.e., of a single simple color), and these simple rays issue from the prism at different angles. It is therefore possible to observe the separate components of the original complex light, and in the spectroscope this is done by placing a small telescope in the path of the simple rays. The action of the prism on the ray of complex light depends upon the fact that lights of different wave-lengths have different coefficients of refraction.

Every coloration imparted to the flame by a metal in the vaporous condition consists of a definite number of different kinds of light of certain wave-lengths. The observation of these different kinds of light and the determination of their wave-lengths furnishes an accurate means for determining the presence of metals in the flame.

REMARK 1. While the light emitted by luminous vapors consists of but relatively few simple components, the *spectrum* (i.e., the collection of simple rays) of glowing solid or liquid bodies consists of a continuous series of different kinds of light.

Generally the spectrum of *only* the free metal is observed when a salt is introduced into the flame, the constituents of the flame decomposing and reducing the compounds of the metal. When salts and oxides vaporize in the flame without decomposition, then other spectra are obtained.

REMARK 2. According to an investigation made by Pringsheim, the luminosity of the metals is not dependent on the temperature, but on the chemical action of the flame on the salt or the oxide, therefore on the reduction.

For many metals the temperature of the gas-flame is not sufficiently high to convert them into luminous vapor. In such cases electrodes are prepared from these metals, and electric sparks are allowed to pass between them. By the action of the spark small quantities of the metals are removed from the poles and converted into vapor.

The spectrum of a gaseous substance is obtained by introducing the gas into a tube under diminished pressure and passing through it the current from an induction-coil; the gas is heated to glowing and the color is analyzed by the spectroscope.

Since the light of every vaporous element is composed of a series of rays of definite wave-length, certain lines in the spectrum are characteristic of certain elements, and the discovery of new lines may lead to the identification of a new element. As a matter of fact a number of elements have been discovered in this manner by the use of the spectroscope,—namely; cæsium, indium, gallium, and germanium.

REMARK 3. Characteristic phenomena appear in the spectroscopic investigation of salts of the so-called *rare earths*—earths of the didymium group, of the erbium group, and of the yttrium group. On the basis of a well-founded theory on the nature of these earths it does not necessarily follow, but it is nevertheless possible, that these substances are *mixtures of different oxides*, and do not consist of a single oxide only.

§ 67. **Absorption Phenomena.** The light which we call white is in reality very complex and consists of rays of all possible wave-lengths. White light gives a continuous spectrum, that is, a spectrum which is not broken up into lines of especial brilliancy or intensity, but which, on the contrary, shades off uniformly from infra-red to ultra-violet. When white light is allowed to pass through the luminous vapor of an element, the vapor absorbs from the white light those components *which the vapor itself is able to emit*, and as a result the spectrum of the white light is found to contain a series of dark lines which correspond to the bright lines in the spectrum of the vaporous element. Also non-luminous vapors show a similar property of absorption.

These facts play an important part in the explanation of the dark lines which appear in the solar spectrum. Many of the dark lines in the solar spectrum correspond to the bright lines of certain luminous elements. From these facts Kirchoff deduced the following hypothesis: The sun consists of a solid or liquid nucleus which is surrounded by an atmosphere of luminous vapor. The nucleus emits white light, and when this light reaches the earth it is destitute of those rays which have been absorbed by the solar atmosphere. The dark lines of the solar spectrum correspond to elements which exist in the solar atmosphere, but which must be present in the nucleus also. Since, however, many of the dark lines of the solar spectrum correspond to the bright lines in the spectrum of the light emitted by the luminous vapor of terrestrial elements, it may safely be assumed that the earth and sun are largely composed of the same elements. The fixed stars also give a spectrum containing dark lines.

§ 68. **Photochemical Action.** In the phenomena of light which have been described the substances which absorb the light undergo no chemical alteration. There are, however, a large number of cases known where the action of the light on the illuminated body produces an alteration which is of a purely chemical nature. A consideration of these cases leads to the following general laws:

a. All kinds of light from infra-red to ultra-violet are capable of exerting a *photochemical* action.

REMARK 1. The assumption that only violet light can produce chemical action is incorrect. The most evident photochemical action in nature, the decomposition of the atmospheric carbon dioxide under the influence of the green chlorophyll of plants, is due chiefly to the yellow constituents of sunlight. It is also incorrect to speak of certain kinds of light as being especially active from a chemical standpoint, since every kinds of light can produce certain, characteristic chemical action.

b. Photochemical action is exerted only by those rays which are absorbed by the illuminated substance.

REMARK 2. The reverse of this law, that absorption is necessarily associated with chemical action, is not true.

c. The nature of the illuminated substance determines the nature of the chemical action. Red light, however, exerts chiefly an oxidizing, violet light chiefly a reducing, action on compounds of the metals. The reciprocal action of metalloids is generally promoted by violet light.

d. The readiness with which a substance is affected by rays of a certain wave-length is increased by the admixture of other substances which absorb these rays.

e. A substance is usually more readily decomposed by light if it be mixed with other substances which can combine with the products of the decomposition.

REMARK 3. The explanation of this fact is that the removal of the decomposition-products prevents the re-formation of the original substance.

§ 69. **Photochemical Extinction.** Photochemical extinction is that phenomenon which is exhibited when rays which pass through a medium which is sensitive to light are weaker in their chemical action when they pass through a second layer of the same medium, this weakening not being assignable to a purely optical absorption.

Example. Light which has passed through a mixture of equal parts of chlorine and hydrogen in a layer of given thickness has a much more feeble chemical action than that which has passed through a layer of chlorine of half the thickness, although the optical absorption is in both cases the same.

When the chemical action of light reaches its greatest intensity, not immediately after absorption, but after a certain time has elapsed, the phenomenon is called *photochemical induction*.

REMARK. The combination of hydrogen with chlorine is explained by assuming that these gases do not act directly upon one another, but combine through the agency of water-vapor, with which an intermediate compound is first formed. It is possible that the reactions are the following:

$$H_2O + Cl_2 = Cl_2O + H_2;$$

$$2H_2 + Cl_2O = H_2O + 2HCl.$$

An appreciable time would be required before a quantity of Cl_2O would be formed sufficient to produce the second reaction.

This hypothesis is founded on the fact that a mixture of *moist chlorine* and *hydrogen* is much more sensitive to light than a *dry* mixture of the same gases.

§ 70. **Development and Fixing of a Photographic Image.** In all the various photographic methods the light acts for only a short time on the sensitive plate, and in this time no visible image is produced. After the exposure, when the plate is treated with a so-called *developer*, the image gradually appears. In the modern methods of photography the developer is a reducing substance which reduces the silver salt of the sensitive plate, this reduction occurring only at those points where the light has acted and has produced a latent image.

REMARK. The explanation of the process of development is purely hypothetical, and depends upon the process of daguerreotyping, which has not been practised for many years. Daguerre (1838) exposed a silver plate, weakly iodized on the surface, for several seconds to the action of light. In this period no visible picture was produced, and Daguerre then brought the surface of the plate into contact with the vapor of mercury. This vapor was precipitated most rapidly on those points of the plate where the light had caused the decomposition of the silver iodide with the formation of slight traces of silver, and as a result the surface of the plate became rougher at those points.

On the basis of these facts, it may be assumed that in the modern methods of development the developer first attacks the sensitive surface of the plate at those points where partial decomposition has already taken place. The silver bromide of the silver-bromide gelatine plates, partially decomposed by light, concentrates the action of the developer at those points where the decomposition has already begun, and at those points a more rapid reduction, and accordingly a more rapid separation of silver, takes place.

It must be clearly understood that this explanation is of a very hypothetical nature.

When the image is developed, it is made permanent or *fixed*. The plate is immersed in a solution of some substance which dissolves the undecomposed portion of the sensitive material and thus removes it.

By this process, however, only a so-called *negative* is obtained: the high lights of the object photographed have sent out many rays, have caused a strong separation of silver, and have produced a dark image; the shadows, on the contrary, have produced a lighter image. A positive is obtained by placing the negative plate on a piece of sensitive paper and exposing this to the light; the relations of light and shadow are now exactly reversed.

§ 71. **Color Photography.** Lippmann in 1891 succeeded in photographing the solar spectrum in its natural colors. The sensitive film which he exposed to the light was backed by a layer of mercury. The light-waves passed through the film and were reflected back by the surface of the mercury; the reflected waves interfered with the direct waves and formed *standing waves*. The wave-lengths of these waves is extremely small, and accordingly a large number of crests and nodes were formed in the sensitive film, the decomposition of the silver salts reaching a maximum at the crests and being equal to zero at the nodes. The films were developed and fixed in the usual manner, and layers of reduced silver were formed in the sensitive film. The distances between the layers of silver were equal to one-half the wave-length of the color which produced them. When the film was viewed by white light, the layers of silver caused interference phenomena, and therefore reflected light of a color corresponding to that by which they had been produced.

CHAPTER VIII.

THE PERIODIC SYSTEM.

§ 72. **Definition.** The periodic system is a grouping of the elements which depends upon the law that *the properties of the elements*, so far as these may be expressed by numbers, *are periodic functions of their atomic weights.*

REMARK I. The quantity A is a function of the quantity B, if they alter simultaneously, and if to every value of B there corresponds one or more values of A. Thus A is a function of B in the following equations:

$$A = 3B;$$
$$A = B^n;$$
$$A = B^n + p;$$
$$A = \sqrt{(B^n + p)};$$
$$A = \text{arc sin } B.$$

A is a *periodic* function of B if on a continuous increase in the value of B the value of A is the same at regular intervals. Thus in the equation

$$A = \sin B$$

A is a periodic function of B, since for every value of B A has a certain value; A will, however, have the same value if B is 360° or 720° or n times 360° greater, and accordingly for every interval of 360° A again receives the same value.

This interval is called a *period*, and the series of values which A receives while B is passing through an interval is *also* called a *period.*

Remark 2. The basis of the periodic system is the periodic function. Nevertheless the periodicity is not associated with mathematical exactitude with a period of definite interval. The theory may therefore be brought into closer agreement with the facts if it be stated that when the elements are arranged in the order of their increasing atomic weights they may be separated into definite groups, and the properties of any one group can be found recurring in the others at certain stated positions.

Remark 3. A relation between the properties of the elements and their atomic weights has long been sought, it having been observed that a mathematical relation exists between the atomic weights of those elements which, from their general properties, form a natural group or family. Thus the atomic weight of strontium is approximately the mean of the atomic weight of calcium and the atomic weight of barium; the atomic weight of sodium is approximately the mean of the atomic weights of lithium and potassium. Zeuner (1857) divided the elements known at that time into *triads.*

In the years 1862 and 1863 de Chancourtois and Newlands attempted to carry out a classification of the elements according to their atomic weights; the latter pointed out that similar properties appeared in the case of every eighth element in the series. This was known as *the law of octaves.*

In the year 1869 attention was first called, by Mendelejeff and Lothar Meyer, to the periodicity of the properties with respect to the atomic weights, and by them a system was established in which the idea of periodicity was rigidly applied. This system is the one at present in use.

§ 73. **Graphic Representation.** If in a plane points are so determined with respect to two axes that the abscissas are proportional to the atomic weights and the ordinates are proportional to some property of the elements which may be expressed by numbers, and the points thus determined are connected by straight lines, a broken curve is obtained which rises and falls in a series of waves. The characteristics of the particular property under consideration in one wave recur in the other waves at corresponding positions. The periodic variation of the physical properties of the elements is most strikingly shown in the graphic representation of the atomic volume.

An undulating curve of this nature is therefore a graphic representation of the periodic system.

§ 74. **Tabular Representation.** If the groups of kindred elements in a horizontal row are arranged one below the other, then the periodic system is obtained in the form of a table. Passing from left to right, the elements follow their atomic weights, and the properties which appear in one of the horizontal rows will be found to occur again in other rows in analogous positions. As a result the elements having similar properties are found in the same vertical row.*

§ 75. **Small and Large Periods.** In the case of the first two periods, each of which contains 7 elements, the agreement of the corresponding members is very great. The third period begins with potassium, which corresponds with sodium; but between potassium and rubidium, with which the fourth period begins, there are 16 elements, and after rubidium 16* elements must be passed before cæsium, an element showing great analogy to potassium and rubidium, is reached. In this case two periods of 17 elements each must be assumed, and as a matter of fact these groups of 17 may, with respect to most of their properties, be considered as independent periods. They are therefore called *large* periods, in contradistinction to the *small* periods which are formed by the groups Li—Fl and Na—Cl.

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* In the back of this book there is given a table of the elements arranged chiefly according to the scheme proposed by Lothar Meyer, from which, however, the table given by Mendelejeff does not materially differ.

The large periods fall with respect to certain properties into two groups of seven elements, in which a slight analogy to the small periods can be observed; the remaining *three* elements show no analogy and are therefore placed in a separate column. In Lothar Meyer's table the first large period is formed by the third and fourth horizontal rows; the first seven elements of the first row form the first, the seven elements of the second row form the second, group. The chief analogy with the small periods is shown when the large periods are considered entire; the secondary analogy, that of valence, appears in each of the groups.

§ 76. **Variation of Physical Properties in Periods.** Not only does there exist the mentioned regularity in the recurrence of the properties of the elements, but also the variation of the properties of the elements in one and the same period may often be included under a general rule. In general the physical properties, when these can be expressed by numbers, attain a maximum or a minimum in the middle of a period.

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* The existence of an element having an atomic weight of about 100 is here assumed.

The *specific gravity* (in the solid state) increases until the middle of the period is reached, there attains a maximum, and then decreases.

The *atomic volume* (the quotient of the atomic weight and the specific gravity in the solid state) decreases to the middle of the period, there reaches a minimum, and then increases.

If the relation between the atomic volume and the atomic weight is graphically represented by means of a curve (compare § 73), a series of waves are obtained which very clearly express the idea of periodicity of the properties. Other properties are also represented by the position of elements on this curve. The *rising* portions of the waves, including the lowest points, contain the *difficultly fusible* and *nonvolatile elements;* the *descending* portions contain those elements which are *readily fusible* and *volatile.*

The *atomic heat*, which for most elements is a nearly constant quantity (§ 24), can also be considered as one of the magnitudes included under the periodic law, in so much as its variation is nearly zero in the case of all the periods. If, as in the case of the atomic volume, the relation between the atomic heat and the atomic weight be represented graphically, a straight line is obtained.

The elements which do not correspond to the law of Dulong and Petit are found in the first and second periods, a certain regularity being observable in their variations; the atomic heat becomes lower to the middle of the period and then increases.

The *valence* increases in the first and second horizontal rows from 1 to 4, and then falls again to 1. (The valence is here determined from the hydrogen and hydrocarbon compounds and, in case such compounds are not formed by the element, is deduced from the chlorine compounds.) On the right-hand side of the system are found those elements which have more than one valence, and while the lowest falls from 4 to 1 the highest rises from 4 to 7, as is seen in the case of the oxygen compounds.

In the large periods the existence of a *double periodicity* with respect to the valence may be observed. From potassium to manganese the valence increases from 1 to 7, as may be seen in the case of the salt-forming oxides (K_2O—Mn_2O_7), and in the same period a second series is formed from copper to bromine (Cu_2O—Br_2O_7). Each two rows show a secondary analogy with the small periods, and upon this fact is based the arrangement of the large periods in Lothar Meyer's table, in which the three elements which in their valence show no analogy to the elements in the small periods are placed in a separate column.

Still other properties of the elements are more or less accurately expressed in the periodic system, but the most important cases have been mentioned.

§ 77. Application of the Periodic System.

a. Correction of the Atomic Weights. Since the general properties of an element are related to its atomic weight, these properties may, like the atomic weight, be used for determining the position of the element in the periodic system. The introduction of the natural system has therefore resulted in the case of a number of elements in an alteration of their atomic weights. Indium, for which the atomic weight 75.6 was adopted, must from its general properties occupy a position between tin and cadmium; therefore the atomic weight of this element has been doubled and increased to 113.4. Also the metals of the platinum group have been reinvestigated, and the values of their atomic weights have been found to agree with the position which had been assigned to them from a consideration of their properties.

REMARK 1. For nickel and cobalt, however, as well as for tellurium, the atomic weights most recently determined do not correspond to the positions of these elements in the natural system.

b. Predicting the Existence of Undiscovered Elements. Many vacancies may be noticed in the table; it is to be expected that these should be occupied by elements which are still undiscovered and which from their atomic weights and general properties are entitled to these positions. It is therefore possible to predict in advance the atomic weight and properties of such elements. Expectations of this sort have already been realized in the case of gallium, scandium, and germanium.

c. Determination of the Atomic Weights. As was explained in *a*, the determination of the position of an element in the system leads to the fixing of the magnitude of its atomic weight, and this quantity can then be corrected with the help of analytical data.

d. The Unit of the Elements. The fact that many properties of the elements are so closely related to a purely mathematical property, the atomic weight, has given much encouragement to the idea, which has already been the subject of considerable speculation, that the elements may be considered as formed by the condensation of a single primordial substance. Prout suggested (1817) that all the atomic weights were multiples of the atomic weight of hydrogen. The more accurate analyses of later investigators have shown that the atomic weights are in no way equal multiples of this unit, and that no simple least-common-divisor can be discovered for the atomic weights.

It is nevertheless noteworthy that the atomic weights of many elements are very near whole numbers.

REMARK 2. The methods for determining atomic weight are therefore:

1. The analysis of molecular quantities of the compounds of the element.

The molecular quantity, or the magnitude of the gram molecule, is determined:

a. From the gas density and Avogadro's hypothesis.

b. From the osmotic pressure of solutions of the compounds and the corresponding magnitudes—i.e., the depression of the freezing-point, the elevation of the boiling-point, etc.

c. From special considerations on the constitution of the compounds.

NOTE: The method *a* is the most important.

2. Application of the law of Dulong and Petit and the law of Joule.

3. Application of the periodic system.

Each of the three methods gives the value of the atomic weight with only relative accuracy; its exact value must be determined by the analysis of compounds of the particular element under consideration.

§ 78. **Closing Remarks on the Periodic System.** The elements helium, neon, argon, krypton, and xenon, discovered by Rayleigh and Ramsay, judging from the determinations thus far made, have the atomic weights 4, 20, 39.9, 81.8, and 128, respectively.

The position of these elements in the periodic system has not yet been satisfactorily determined and a discussion of their significance cannot be entered into at this point.

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