WORKS OF PROF. J. L. R. MORGAN

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TRANSLATION.

The Principles of Mathematical Chemistry.

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PHYSICAL CHEMISTRY

FOR

ELECTRICAL ENGINEERS

BY

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J. LIVINGSTON R. MORGAN, PH.D.
Professor of Physical Chemistry in Columbia University

SECOND EDITION, REVISED

FIRST THOUSAND

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PREFACE TO THE SECOND EDITION.

ALTHOUGH, since the appearance of the first edition of this work, the investigations of The Svedberg (Zeit. f. phys. Chem., 65, 624–633, and 66, 752–758, 1908), and also of others, make it seem probable that the actual existence or non-existence of atoms and molecules may sometime be proven experimentally, the point of view from which the original text was written has not been altered. This is not in any way an attempt to ignore the results of such investigations, or to cast doubt upon the results of others which will undoubtedly follow, but is rather an expression of the experience actually obtained in the classroom, which shows conclusively that definitions based upon, and expressed in terms of, actual experiment, are far better and more real than those which involve less tangible things, such as the atom and molecule, at best must always be. Perhaps this can best be illustrated by a comparison of the definition of atomic weight as given on page 11 with the one in such common use, viz., *the atomic weight is the weight of an atom.*

Besides bringing the subject matter up to date, various alterations, tending to simplify the treatment, have been made, making, it is hoped, a more intelligible and useful text.

J. L. R. M.

COLUMBIA UNIVERSITY, August, 1909.

PREFACE TO THE FIRST EDITION.

THIS book is intended not only for the professional electrical engineer, but also for the use of all those who have the same object in view, viz., the attainment of a knowledge of physical chemistry sufficient in its scope for the understanding of current work in electrochemistry.

Although electrochemistry lies in that border-land between chemistry and electricity, it has been so consistently neglected by the majority of the workers in both fields that its development has rested almost entirely in the hands of a comparatively small number of specialists. The time has now arrived, however, when the results obtained by these men are generally recognized as of exceeding importance, no less from the practical than the theoretical standpoint, and consequently a working knowledge of the subject has become a very essential part of the equipment of the student who is to devote himself to either branch of science.

But even a glance on the part of such a student at one of the electrochemical contributions which at present fill so many pages of our journals is sufficient to make clear the fact that the entire work is based upon an utterly new and unfamiliar set of laws and concepts; in short, upon a knowledge of certain portions of physical chemistry, and that without this knowledge any attempt to understand the attaining of the result, or even its meaning when attained, is futile.

The purpose of this book is to aid those who find themselves in such a position, and to present, in as popular a form as is consistent with quantitative results, those laws and generalizations of physical chemistry which form the basis of the subject embracing the chemical application of electricity and the electrical application of chemistry. It is in nowise to be regarded as a text-book of electrochemistry, however, for although that subject is discussed in considerable detail, only those portions of it are considered which best illustrate the application, and methods of application, of the physical chemical principles already presented, and no complete account is attempted. But notwithstanding this the reader should gain a very clear and just idea of the elements of electrochemistry, and one which he can readily elaborate by further work.

While a cursory glance might easily lead one to infer that some portions which are treated at length are utterly unnecessary for the electrochemist, such is not the case, for everything presented, if not vitally important in electrochemistry itself, is absolutely requisite for the understanding of something else, which *is* absolutely indispensable to it. The reader is cautioned, therefore, not to omit anything, thinking it unessential or trivial, for everything is given with a definite object in view.

Since the subject of solution is also the most important portion of physical chemistry for those specializing in other branches of chemistry, the book is also adapted to the use of chemists who have but a limited time to devote to the subject, or whose need is restricted to a knowledge of the behavior of substances in solution. And it may also serve as an introduction to a more complete course in physical chemistry, for the numerous references, both to originals and to a more elaborate work,* will enable the student to readily investigate further any point upon which his interest may happen to be aroused.

In order that the reader may gain a *working* idea of the subject, a collection of problems, together with their answers, is given in the final chapter. The solution of these will not only make the principles of the subject more real and clear, but will serve to impress more deeply upon the reader's mind the essential and generally useful portions of the various laws.

But one other point need be mentioned here. Throughout the presentation *I have avoided the use of any hypothesis*, feeling that, by placing the subject upon an absolutely experimental basis, giving a *practical experimental definition* of each concept as it is used, and drawing no inference not justified *in all its parts* by actual results, the reader's idea will be the more clear and scientific.

J. L. R. M.

COLUMBIA UNIVERSITY, September, 1905.

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* Morgan, The Elements of Physical Chemistry.

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CHAPTER I.

SOME FUNDAMENTAL PRINCIPLES.

Atomic and molecular weights.—From the very definition of physical chemistry—*that portion of science which has for its object the study and investigation of the laws governing chemical phenomena*—it is apparent that we have to do with the most general and inclusive of all the branches of chemistry. Certain of its fundamental concepts, therefore, are those which are also fundamental to all these branches, and it is essential that we at least recall them to mind before proceeding to the consideration of the things based upon them.

Two of the concepts common to all branches of chemistry, the atomic weight and the molecular weight, play an especially important rôle in physical chemistry, as they do, indeed, in all the other branches of chemistry. It is unfortunate, however, that the student's usual idea of these is such an utter confusion of fact and hypothesis that no very clear conception of their meaning is possible. This is particularly evident at the present time, when it is by no means an uncommon thing to find those who actually fear for the security of the quantitative, experimental results of chemistry, because of the possibility of the so-called atom proving divisible; in other words, making the definition of the hypothetical atom, and hence apparently *also that of atomic weight*, a meaningless collection of words.

Without in any way condemning these hypotheses more than the others in common use, it must be admitted as far better to recognize that our science is based upon no such insecure and uncertain foundation, but upon facts which will continue to exist under any hypothesis, or lack of hypothesis, and which at any time can be confirmed by experiment. That such is the foundation of chemistry is undeniably true, but, unfortunately, the lay mind, and, still more unfortunately, the average professional mind, refuses utterly to recognize and acknowledge it.

As in our present work we are to depend solely upon fact, avoiding all hypothesis, it is quite essential that we secure from the very beginning a hypothesis-free idea of atomic and molecular weight. The first step toward this end, however, is to define exactly what we mean by the word hypothesis, for common usage indicates that its significance is not uniform. *A hypothesis*, in the sense we are to use it, *is a theory into which is incorporated something that is foreign to the facts observed;* the word *theory*, as we shall continue to employ it, *signifying a generalization of observed facts, containing nothing beyond what is expressed by these facts. A theory*, then, *is a law of nature holding between certain well-defined, if narrow, limits, which becomes a general law when the limits have been sufficiently extended.* A mathematical formula, thus, provided each term is determinable by experiment, is no hypothesis, but a theory or a general law, according as its limits are restricted or wide. A hypothesis, on the other hand, when in the form of an equation, contains a term or terms which cannot be determined by direct experiment; and in any other form contains assumptions foreign to the facts observed, assumptions which sooner or later may be found to be in disagreement with fact.*

In our work, therefore, we must test each concept as it arises in order to see that it is free from hypothesis, and to be assured that we have to do solely with facts. Later, naturally, these facts, when supplemented by others, may be included in more general laws, but facts they will always remain, notwithstanding, and independent of any hypothesis which at that time may happen to be in vogue. Our progress will thus be continuous, and it will never become necessary to halt for the purpose of inquiring what is fact and what hypothesis.

At worst, in this way (retaining hypotheses), one may be certain that the greater emphasis is laid upon the facts themselves, and that the hypotheses can lead to no serious confusion. At best, on the other hand (relinquishing all hypotheses, as we shall do), we can devote all our energy to the facts and their generalization, and thus avoid wasting the time and effort requisite for the making of unwarranted assumptions, which the subsequent experimental progress of science may only prove to be utterly untenable.

That any one who has read of the determination of

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* For a masterly discussion of these things see Ostwald, Vorlesungen über Naturphilosophie, pp. 202–227, 1902, a book to which I am indebted for this point of view.

an atomic weight can retain the idea that it depends in any way other than name upon hypothesis, seems impossible, and yet the proof of the non-existence of the hypothetical atom would seriously disturb the ideas of many such, notwithstanding. That an event of the sort could affect the actual results of the science, and certainly the actual results constitute the science, is not to be imagined for an instant, however. In the words of Ostwald—the stoichiometrical laws will continue to be a part of chemistry, even after the time when the atom is only to be found in the dust of the libraries.

The atomic weight of an element, as we determine it, is simply the weight which will combine with 16 units of weight of oxygen, or some small multiple or submultiple of 16; or which will combine with the atomic weight so determined, or some small multiple or submultiple of it, of any other element. In each case, therefore, the atomic weight is an experimentally determined combining weight. Which combining ratio is to be selected in case two are discovered (CO and CO_2, for example), and which weight of oxygen is to be employed as the standard for any one element, are matters that are dependent only upon other facts, i.e., those relating to compound substances.

An atomic weight, therefore, has no vital connection with the atomic hypothesis, but is based solely upon the experimental law—*that elements combine with one another only in definite proportions by weight* (*their combining weights*), *or small multiples of these.* Naturally, *if* atoms exist (in accordance with the usual definition) they must be individually related in weight as the experimentally determined combining weights, called atomic weights; but, whether atoms exist or not, these combining weights must continue to be true, for they are facts, independent of time, and can always be tested by experiment. A moment's thought, indeed, will show that the connection between the hypothesis and the actual results is always as slight as this. Whenever we make use of the word atom, in practical work (for no other use is warranted), it is the atomic weight, the gram-atom, the experimentally determined combining weight that is intended, and never the hypothetical atom. It is only the name atomic weight, then, which leads to the inference that the atomic hypothesis is fundamental to chemistry. To avoid all possibility of such a misconception here, we shall employ throughout the book the word *combining weight, meaning by it that combining weight which is usually designated as the atomic weight.*

Much that has been said concerning the atomic weight is also true of the molecular weight. For *the molecular weight,* as we determine it *in the gaseous state* (we shall consider the other states of aggregation later), *is the actually observed weight of gas which occupies the same volume as 32 units of weight of oxygen under like conditions of temperature and pressure.* And again here, *if we assume* the gas to be composed of ultimate particles (molecules) of uniform size, the weight of the molecule of one substance will be related to that of another as are the molecular weights. But, whether molecules exist or not, the so-called molecular weights are experimentally observed facts, and as such are independent of hypothesis.

According to hypothesis the molecular weight of a substance is equal to the sum of the atomic weights of the constituents, each multiplied by the proper factor. Speaking solely from the experimental standpoint, the molecular weight is that weight, found by a summation of the respective combining weights (p. 5), each multiplied by the proper factor, which will occupy the same volume as 32 units of weight of oxygen. As the various symbols of the elements represent the combining weights of these elements, and the number of combining weights (atoms) is always given by the subnumerals, the molecular weight thus being indicated by the formula, we shall designate throughout, in our later work, the so-called molecular weight as *the formula weight of the substance.* Any method, then, for the determination of the formula (excluding the analytical methods, for they enable us only to ascertain the *ratios* of the weights of the elements combining) will offer a means of finding the molecular, i.e., *the formula weight.* And in place of the expression, *the molecular (formula) weight in grams, we shall employ the abbreviation suggested by Ostwald, and call it the mole.**

A glance at the methods of using these concepts of atomic and molecular weight is amply sufficient to show that it is upon the practical results that everything is based, and not the hypothesis. According to hypothesis, the equation

$$H_2 + Cl_2 = 2HCl$$

means that 1 molecule (2 atoms) of hydrogen and 1 molecule (2 atoms) of chlorine unite to form 2 molecules of hydrochloric acid gas. This, of course, may be true,

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* Since the normal solution of analytical chemistry contains *one equivalent* mole per liter, we shall use the word *molar* when speaking of the number of *moles* per liter. In certain cases, then, hydrochloric acid for example, the two expressions will be identical, while in others, sulphuric acid, for instance, the molar solution will contain twice as much as the normal one, etc.

and it may not, for we can neither prove it nor yet disprove it, but, whether it be true or false, the fact still remains that 2 units of weight (i.e. 2 combining weights, or 1 formula weight) of hydrogen and 71 units of weight (i.e. 2 combining weights, or 1 formula weight) of chlorine unite to form 73 units of weight (i.e. 2 formula or combining weights, HCl) of hydrochloric acid gas. And this was true before the hypothesis was formulated, and can always be proven to be true at any time in the future, independent of the hypothesis. In the latter case we have simply expressed facts which have been observed, and can be observed at any time; in the former, we have added to the observed facts the assumption of an atomic structure of matter, which is foreign to the facts themselves, and which cannot, like them, be proven by experiment to be true.

That is all very simple and true, the reader may say, now that we have formed the conceptions of atomic weight and molecular weight, but how could such results have been attained without the aid of hypothesis? The answer to this question is that everything which has been attained is only the result of experiment, and that such conceptions, similar in all but name, can be obtained without difficulty directly from the actually observed relations. Starting, for example, with the law of combining weights—*that elements combine with one another only in the proportions of their combining* * *weights or of small multiples of them*—and the law of combining volumes—*that gaseous elements combine in simple relations as to volume, or in small multiples of them*, the volume of the gaseous product formed standing in simple relation to the volume occupied by the constitu-

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* Used here in its general sense, not as on pp. 5 and 6.

ents originally—it is quite evident that *the weights of equal volumes of gases are related as their combining weights, or as small multiples of them.* We might infer from this, then, that the combining (atomic) weights could be so selected that the density of the various gases would be proportional to their combining weights.*

Experiment, however, shows this assumption to be incorrect. For example, it has been found that 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of gaseous water; that 1 volume of chlorine with 1 volume of hydrogen forms 2 volumes of hydrochloric acid gas, and that 1 volume of gaseous phosphorus with 6 volumes of hydrogen produces 4 volumes of phosphine. And the assumption that the unit of volume is that volume which is occupied by the combining (atomic) weight of an element leads to the result that the weight of unit volume of the water vapor formed is but *one-half* the sum of the combining (atomic) weights of its constituents, which is also true for the gaseous hydrochloric acid, while the density of phosphine is but *one-fourth* the sum of the combining (atomic) weights of the constituents.

If we retain the combining weights as they have been determined, however, and assume the unit of volume to be that occupied by a small number of combining (atomic) weights, where the number is dependent upon the element, it is at once evident that a general result is obtained. And this assumption is perfectly justifiable and unconnected with hypothesis, for, although

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* The combining weight of a compound being identical, naturally, with its formula weight, i.e., equal to the sum of the combining (atomic) weights of its constituents, each multiplied by the proper factor, Thus for water the value is 18, i.e., $O + 2 \times H$.

the combining ratios (both for volumes and weights) are experimental facts, the choice of the units for their expression is perfectly arbitrary, as is the choice of any other unit, and purely a matter of convenience.

In the case of hydrochloric acid gas, then, for example, assuming the unit of volume to be that occupied by 2 units of weight of hydrogen, we obtain the following result: 1 volume of hydrogen (2 units of weight) will combine with 1 volume of chlorine (2×35.5 units of weight) to form 2 volumes (73 units of weight) of hydrochloric acid gas, and the weight of *unit* volume of this formed will be equal to the sum of the combining (atomic) weights of the constituents (i.e., $35.5 + 1 = 36.5$ units of weight). And this will also be true for water vapor and phosphine when we use the factor 2 for oxygen and 4 for phosphorus.

Representing, then the combining weight of an element by its symbol, and designating by a sub-numeral the number of these combining weights which will occupy, under standard conditions, the unit of volume, we shall obtain the formula of the element, and the weight thus represented by this formula will occupy the same volume, under like conditions, as the formula weight of any other element or compound. Applying this to the three cases just considered, we obtain

$$H_2 + Cl_2 = 2HCl,$$

$$2H_2 + O_2 = 2H_2O,$$

$$P_4 + 6H_2 = 4PH_3,$$

where although the weights represented by the terms H_2, Cl_2, O_2, P_4, HCl, H_2O, and PH_3, i.e. the formula weights, are all different, the volumes occupied by them are identical, provided the conditions of pressure and temperature are the same.

But these are the formula weights, i.e. are what, according to hypothesis, have been and are designated as molecular weights, although here they have been arrived at wholly *without the aid of hypothesis.*

Since our customary unit of weight is the gram, and the combining weight is usually based upon oxygen (=16), *we can define a formula (molecular) weight in the gaseous state as that weight which will occupy the volume of* 2×16 *grams of oxygen under like conditions.* From this definition, however, it is at once obvious *that equal volumes of gas under like conditions must contain the same number of formula weights.* But this, in its *practical* meaning, is identical with what has long been known, from its hypothetical origin, as Avogadro's *hypothesis*, which now, having been derived from experimental results, without the aid of any hypothesis, becomes Avogadro's *law.*

As has been mentioned, the factor necessary to transform the combining (atomic) weight of an element into the formula weight according to this definition (i.e. the number of combining weights which will occupy the normal volume under standard conditions) varies for the different elements. These factors, however, are usually small, ranging from 1, for most of the gaseous metallic elements, to 8 for gaseous sulphur under certain conditions.*

Starting with the above fundamental and experimental definition of molecular weight, we can now obtain a

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* For a list of these factors, and a similar derivation of these concepts, see Ostwald, Grundriss der allgemeinen Chemie, 1899, pp. 65-73.

more satisfactory experimental definition of atomic weight than that given on page 4; for it must be confessed that to the lay mind this means little, involving, as it does, the necessity of the further knowledge as to what multiple of 1 gram of hydrogen, or what multiple or submultiple of 16 grams of oxygen, is to be taken as the unit in any one case. It almost seems, indeed, at first glance, as if hypothesis were necessary here in order to establish in each case the unit weight of hydrogen or oxygen which is to be employed. A purely experimental definition of atomic weight, which is free from the superficial disadvantages of the above (for it must be remembered that that is in other respects a perfect definition) is as follows: *The atomic weight of an element is the smallest weight that is found in the molecular weight of a compound, i.e., in that weight which occupies under like conditions the same volume as 32 grams of oxygen.*

We have arrived thus at a purely experimental, hypothesis-free, conception of the atomic and molecular weight of a substance in the gaseous state. It is not to be assumed, though, that the formula (molecular) weight necessarily remains the same in the other states of aggregation, although this is true for the combining weight, so far as we know. Experiment shows, indeed, that the formula weight depends, even in the gaseous state, according to this definition, upon the temperature (sulphur for example); while in the state of solution (according to an experimental definition derived later) it often depends upon the nature of the solvent (acetic acid in benzene and in water); and in the liquid state upon the presence of another liquid (alcohol alone and with water.)

Experimental determination of the molecular weight.—Although the definition of molecular weight already given—*the weight that occupies the same volume as 32 grams of oxygen under like conditions*—is perfectly satisfactory, the actual determination according to it would present some experimental difficulty, owing to the large volumes of gas which would have to be weighed. To avoid such difficulties it is customary to find either the actual weight of 1 cc. of the gas to be determined, or its relative weight in terms of some standard gas. Since the molecular weight always occupies the same volume, under like conditions, independent of the nature of the substance, it is evident that the weight of 1 cc. of any gas (its density, d) must be proportional to its molecular weight. We have thus $M_1:d_1::M_2:d_2::M_3:d_3$, etc., or $M_1d_2=M_2d_1$ and $M_1d_3=M_3d_1$, or

$$M_1=\frac{d_1}{d_2}M_2=\frac{d_1}{d_3}M_3, \text{ etc.},$$

so that if the subnumerals 2 and 3 represent standard gases, we have the law: *The molecular weight of any gas* (M_1) *is equal to its density in terms of the standard gas* $\left(\frac{d_1}{d_2} \text{ or } \frac{d_1}{d_3}\right)$ *multiplied by the molecular weight of the standard gas* (M_2 or M_3).

Thus since the molecular weight of hydrogen is two, the molecular weight of any gas is twice its density in terms of hydrogen. In the same way the molecular *weight of any gas is equal to 32, 28, 71,* etc., times its density referred to oxygen, nitrogen, chlorine, etc., for these are their molecular weights.

Energy.—*Energy is work or anything which can be transformed into work or produced from work.* Although energy may appear in many different forms, it is to be remembered that all these forms can be transformed, the one into the other. The principal forms under which the common manifestations of energy may be grouped are as follows: Kinetic energy, i.e. the energy of motion, distance or potential energy, i.e. the energy of position, electrical energy, magnetic energy, heat, chemical energy, surface energy, volume energy, and radiant energy. But since these forms are only phases, as we may say, of the fundamental concept of energy, and each can be transformed into the other, one form, viz. that which can be most readily defined, has been chosen as the standard of reference. In other words, all kinds of energy are measured and expressed in terms of a standard form, into which they could all be transformed. This standard form is that manifested in the ordinary mechanical relations.

The unit of work is the *erg*, which is the work done when unit force is overcome through unit distance, the unit of force being the *dyne*, i.e. that force which, acting for 1 second, will impart to 1 gram the velocity of 1 centimeter per second. Naturally, then, n dynes will impart a velocity of n centimeters per second to one gram. Since at Washington a body falling freely will acquire the velocity of 980.1 centimeters per second, the force of gravitation there is equivalent to 980.1 dynes, and the work of raising 1 gram through 1 centimeter is 980.1 ergs. Or, in general, the force of gravitation is equal to g dynes, and the work of raising 1 gram through 1 centimeter is g ergs, where g is the gravitational constant, i.e. the velocity per second acquired by 1 gram in falling freely. As this unit is exceedingly small, and results expressed in it are cumbersome to handle, a larger unit, i.e. one that is equal to ten million ergs, is often employed. This larger unit is called the *joule* and is equal to 10^7 ergs, while a still larger one, without a name and designated by J (the joule being abbreviated to j) is equal to 10^{10} ergs.

Although this method of expressing the amount of energy involved, independent of the special form in which it is at the time, is ideal, it is not in general use in all cases, for many of the forms of energy were studied long before the system was commonly accepted. For this reason we still find, for certain forms of energy, that the older, arbitrary, units are still in vogue (calorie, coulomb, etc.). One unfortunate consequence of this older nomenclature is that it does not keep clearly before the mind the fact that the forms of energy are but phases of the general concept of energy, and hence are mutually capable of transformation. To accentuate this fact we shall always give the value of these arbitrary units, i.e., those which are applicable to but one definite form of energy, in terms of the general standard.

CHAPTER II.

THE GENERAL PROPERTIES OF GASES.

The gas laws.—In spite of the intangibility which characterizes the gaseous state, and the consequent difficulty in the investigation of it, our knowledge of the laws governing the behavior of gases is far more complete than is that of the laws regulating the behavior of substances in the other, more tangible, states. It is not to be assumed from this statement, however, that we know *why* gases behave as they do, for that is just what we do *not* know. The gas laws simply state *how* substances in the gaseous state will behave under those conditions which can influence them; and have, and can have, nothing to do with the question as to the cause of this behavior.

Indeed, the difference between our hypothesis-free standpoint and one that retains hypotheses is very well illustrated by the difference in meaning of these two words, *how* and *why*. To say *how* a thing will behave we need only be familiar with the thing, and the more familiar we are with it the more accurate will be our prediction. In other words, we can say *how* a thing will behave under any condition by citing facts that have been observed, or an experimental law, i.e. a generalization of such facts. To be able to say *why* a thing behaves as it does, on the other hand, it is necessary to go beyond the facts themselves, and, as the facts form the total of our knowledge, *assume* that a certain structure, for example, is responsible for the behavior. But, since in our assumption we have gone *beyond the facts*, we cannot prove it to be either correct or false by *aid of the facts*. It is true, of course, that the assumption may satisfactorily account for the facts as we know them at the time, but we have no reason to believe that it is the *only* one that will account for them, or even that *it* will account for those which are yet to be discovered. In other words, the hypothesis at best enables us to see how the facts, or a certain number of them, *might* be explained; but it does not add anything of value to what has already been deduced from the facts themselves, nor does it lead more than they do to the discovery of new facts.*

This repetition of our standpoint and its advantages is quite necessary here, for no portion of chemistry is richer in hypothetical assumptions than that which includes the gaseous state, and in no place is a distinction between hypothesis and fact more essential. In order that we may always retain our standpoint, and devote ourselves exclusively to facts, therefore, we shall have to continually inquire as to *how* things occur, avoiding any assumption as to *why* they should occur as they do.

Although the gaseous state as such has but little importance in electrochemistry, it is absolutely essential that the electrochemist obtain a clear idea of its laws, if he is to understand the laws which have been found to govern the behavior of substances in solution. And certainly no one can question the value of these laws to

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* See Ostwald's Vorlesungen über Naturphilosophie, l.c.

the electrochemist, for, with but few exceptions, all electrochemical processes take place in solutions.

Since gases are characterized by an absence of form, i.e. occupy entirely any space in which they are present, their condition is dependent solely upon *external* influences. Of the variations which a gas may undergo, as the result of a change in these influences, the most important are those of volume, pressure, and temperature. Experiment shows, however, that *when the temperature is retained constant, the volume of the gas is the greater the smaller its pressure, and vice versa; and, so long as the volume (pressure) remains unchanged, the pressure (volume) is the greater the higher the temperature, and vice versa.* These laws are the generalization of the facts observed by several generations of investigators, and an exception to them is yet to be found.

In quantitative work, however, such purely qualitative laws are of little value, for they simply indicate the direction of the variation without at all showing its extent. And when altered to show the extent, they lose the absolute generality which distinguishes them, and hold true with accuracy only between certain limits.

Quantitative experiments on gases have resulted in the following conclusions: *When the temperature is retained constant, the volume is inversely proportional to the pressure* (Law of Boyle). *And retaining the volume (pressure) constant the increase in pressure (volume) per degree centigrade is* $^1/_{273}$ *of its value at 0° centigrade* (Law of Charles).

Starting with unit volume at 0°, and constant atmospheric pressure, then, and decreasing the temperature to $-273°$ centigrade, the volume of the gas will be reduced to zero *if the law of Charles holds at such a temperature.*

In other words, for each decrease of 1° the volume will be reduced $^1/_{273}$ of its original value, and at $-273°$ the loss in volume will be $^{273}/_{273}$, i.e., 1. If we consider $-273°$ centigrade as the zero of a new scale (the absolute zero), and employ centigrade degrees, calling the temperatures absolute temperatures, we can say—at 0° absolute (i.e., $-273°$ centigrade) the volume of a gas (as a gas) is zero, and its volume will increase per degree by $^1/_{273}$ of the value it would have at 273° absolute (i.e., 0° centigrade), and that increase will always be the same, independent of the actual temperature.

Expressing these relations mathematically we have

$$v \propto \frac{1}{p} \text{ (}T\text{ is constant),}$$

and $$v \propto T \text{ (}p\text{ is constant);}$$

i.e. $$v \propto \frac{T}{p},$$

or $$v = k\frac{T}{p},$$

and $$pv = kT.$$

But at 273° absolute (0° centigrade)

$$p_0v_0 = k273,$$

and by combination, eliminating the common constant **k**, we obtain

$$pv = \frac{p_0v_0}{273}T,$$

which gives the value of the product pv at any temperature (absolute) in terms of p and v at 273° absolute.

The term $\frac{p_0v_0}{273}$ is a constant, however, which depends for its value only upon the weight of gas occupying the volume v_0, and the units of volume and pressure chosen.

Considering v_0 as the volume of *1 gram* of gas, we have

$$pv=\frac{p_0v_0}{273}T=rT,$$

where, although the value of r, *the specific gas constant*, depends upon the units, it *is constant for any one gas.*

Regarding v_0 as the volume occupied by *1 mole* of gas, on the other hand, and designating it by V_0, we find

$$pV=\frac{p_0V_0}{273}T=RT,$$

where R, *the molecular gas constant, is the same for all gases*, for, by definition, page 10, 1 mole of gas always occupies the normal volume under standard conditions.

The difference in meaning of these two constants, r and R, accentuates the difference in standpoint of physics and physical chemistry. While the results of physics are always given for a specific quantity of substance, without regard to the similarities which chemistry has discovered to exist between the formula weights of all substances, physical chemistry employs physical methods from the chemical point of view, i.e. strives to discover general laws by applying both physics and chemistry to the facts observed.

Since a mole of any substance in the gaseous state occupies the same volume as 32 grams of oxygen, i.e. $32 \times 699.8 = 22393.6$ cubic centimeters, or nearly 22.4* liters, at 0° and 76 centimeters pressure, we can find the value of $R = \frac{p_0 V_0}{273}$ for the various units in which pressure and volume may be expressed. As the specific gravity of mercury is 13.6, the pressure of 76 centimeters is 1033.6 grams per square centimeter (i.e. 13.6×76), and we have

$$R = \frac{p_0 V_0}{273} = \frac{1033.6 \times 22400}{273}$$

$$= 84800 \text{ (}V\text{ in cc., }p\text{ in grams per sq. cm.)}$$

$$= 84800 \times 980.1 = 8.3 \times 10^{+7} \text{ (}V\text{ in cc., }p\text{ in dynes)}$$

$$= \frac{1 \times 22.4}{273} = 0.0821 \text{ (}V\text{ in liters, }p\text{ in atmospheres).}$$

This latter result, where p is in atmospheres, and v in liters, is expressed in so-called *liter-atmospheres*; 1 liter-atmosphere (L.A.) being the work done when the normal atmospheric pressure acts upon a square decimeter, through a decimeter.

A direct technical application of Boyle's law to the measurement of enclosed volumes inaccessible to liquids has recently been suggested by Rebenstorff (Chem. Ztg., 32, 570, 1908). Since, *at constant temperature*,

$$\frac{v_1}{v_2} = \frac{p_2}{p_1},$$

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* As the factor to transform grams to ounces (av.) is the same as that for the transformation of liters into cubic feet, 1 mole of gas *in ounces* (av.) occupies 22.4 *cubic feet* at 0° and 76 cms. of mercury pressure.

it follows, by a simple mathematical transformation, that

$$\frac{v_1 - v_2}{v_2} = \frac{p_2 - p_1}{p_1},$$

or

$$\frac{\Delta v}{v_2} = \frac{\Delta p}{p_1},$$

i.e., *the change in the volume of an enclosed gas is to the original* (*or final*) *volume, as the change in pressure is to the final* (*or original*) *pressure.*

If, for example, a burette holding, say 600 cc., is filled with water and connected to a tank full of air at atmospheric pressure, and the water allowed to run out slowly the new (final) volume will be equal to the original volume plus 600 cc., while the change in pressure will be equal to the weight of the column of water run out (height of water in cms. $\div 13.6 =$ cms. of Hg), and since Δv ($= 600$ cc.), Δp and $p_1 \left(= 76 - \frac{\text{height of water}}{13.6} \right)$ are known we can solve the above expression for v, the volume of the tank. Naturally, here, we must make sure that the temperature remains constant, if the result is to be accurate.

Another law which is of great value in considering the gaseous state is that of Dalton, according to which *each component of a mixture of gases exerts the same pressure in the system as it would exert were it alone present in the volume of the mixture.* In other words, the pressure of a system composed of several gases is an additive property.

Summarizing the gas laws in their mathematical forms, then, we have

$v_1 : v_2 :: p_2 : p_1$, or $p_1 v_1 = p_2 v_2 = \text{const.}$ (T is constant),

$p_1 : p_2 :: T_1 : T_2$ (v is constant),

$v_1 : v_2 :: T_1 : T_2$ (p is constant),

$pV = RT$

(where R is constant for all gases and depends in value upon the units of pressure and volume chosen), and

$$P = p_1 + p_2 + p_3 + \ldots,$$

where P is the total pressure of a mixture of gases and the terms p are the partial pressures of the components of the mixture.

As already mentioned, to secure quantitative results it is necessary to restrict the limits of the general laws holding for gases. Both these laws, viz. that of Boyle and that of Charles, hold rigidly, then, only between certain definite limits. In fact, stated as above, they hold *rigidly* only for *ideal* gases. It has been found, however, that the further a gas is removed from its liquefaction point, the more nearly ideal it is; i.e., the more accurately is its behavior represented by the laws. Indeed, the law of Boyle, as applied to the so-called permanent gases, gives very satisfactory results, except when the pressure is very high; as does the law of Charles, so long as the temperatures are not excessive.*

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* For hydrogen the product pV (or pv) at constant temperature increases steadily and regularly with an increase of pressure, and is expressed very accurately by the altered form of the equation $p(V-b) = \text{const.}$, where b is a constant. All other gases, on the other hand, starting with atmospheric pressure and constant temperature, give a value of pv, which first decreases with increased pressure, then passes through a minimum, and finally increases steadily. The relations, in such a case, can be followed by aid of Van der Waal's equation,

Dissociation.—By aid of the relation $pV = RT$ the so-called *equation of state for gases*, it is possible to obtain a slightly different form of definition for the formula (molecular) weight in the gaseous state. Instead of defining it as the weight which under like conditions will occupy the volume of 32 grams of oxygen, we may say *the formula weight of a gas is the weight which will give* V, *in* $\frac{pV}{T} = R$, *such a value that* R *is approximately equal to that calculated for oxygen.*

In actual practical work in the laboratory, however, it is better, for the reasons given there, to employ one of the definitions given on page 12, rather than either of the others already mentioned. According to this method we find

$$M = 32 \times \frac{\text{weight of 1 cc. of gas}}{\text{weight of 1 cc. of oxygen}},$$

or

$$M = 2 \times \frac{\text{weight of 1 cc. of gas}}{\text{weight of 1 cc. of hydrogen}},$$

the conditions of temperature and pressure for both gas and standard gas being the same.

For certain substances, however, the formula weight so determined is found to vary with the temperature and pressure, and in some cases to be equal to but one-half the sum of the combining weights of the con-

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i.e., $\left(p + \frac{a}{V^2}\right)(V - b) = \text{const.} \times T$, where a and b are constant values depending only upon the nature of the gas. In the case of ethylene, for example, the results by this formula agree very accurately with the experimentally determined ones up to a pressure of 400 atmospheres. ("Elements," 4th ed., 1909, pp. 34–38.)

stituents. Such a result at first glance would naturally lead one to object to the process of reasoning employed on page 9, and, indeed, without further knowledge of the substances behaving in this way, it would be impossible to defend its use. It is obvious, then, that either our definition of a formula weight in the gaseous state (p. 10) is incorrect in some cases, or that some process—common to these—is responsible for the abnormal results observed.

Further investigation of these substances, however, shows conclusively that our definition is correct in all cases, and that the abnormal results *are* due to a more or less complete decomposition of the substance, a *dissociation,* as it is called.

Of the substances for which such abnormal results are observed we may mention ammonium chloride (NH_4Cl), phosphorus pentachloride (PCl_5), and nitrogen tetroxide (N_2O_4) as typical examples, although many others might be cited. The formula weights (by definition) of these substances have each been observed to vary from the normal value represented by the formula to a minimum value which is one-half of this, the amount of the variation depending upon the temperature and pressure. In general, *the higher the temperature under constant pressure the lower the value, while at constant temperature the formula weight is the lower* (*one-half of the formula weight being the limit*) *the lower the pressure.*

The very fact that a general rule of this sort exists for substances behaving abnormally is evidence that it is not the definition of the formula weight which is at fault, but that some process occurring similarly in all these cases is responsible for a change in the formula weight itself. Indeed, later work, by which the actual presence of the products of the decomposition was shown, proved that the definition of a formula weight even in these cases is correct and that it was only our ignorance of the effects of temperature and pressure upon these substances which led us to infer otherwise. Instead of destroying the usefulness of one of our fundamental principles, then, these "abnormal" results have simply introduced to our attention a very important and common process, viz., that of dissociation.

In the three cases mentioned above the dissociation has been found to take place according to the following schemes, the symbol $\rightleftarrows$ being used to show that the reaction is reversible, i.e. that it goes in one direction or the other, depending upon the conditions:

$$NH_4Cl \rightleftarrows NH_3 + HCl,$$

$$PCl_5 \rightleftarrows PCl_3 + Cl_2,$$

$$N_2O_4 \rightleftarrows NO_2 + NO_2.$$

The presence of the NH_3, HCl, Cl, and NO_2 in these cases can be proven without difficulty. The gas which is evolved from ammonium chloride by heat, for example, can be shown to contain NH_3 and HCl by allowing it to diffuse through a porous diaphragm. Here the NH_3 being the lighter diffuses more rapidly than the HCl, and an excess of NH_3 is found on one side of the partition, while an excess of HCl remains on the other. The presence of chlorine in PCl_5, and NO_2 in N_2O_4, is even easier to show, for the dissociation can be followed by the eye, the chlorine imparting a green, the NO_2 a brownish red, color.

These methods, together with the many others, although proving conclusively that a decomposition (*dissociation*) does take place, are of little value in determining the extent to which it takes place, for at best they are but qualitative. For this purpose the simplest and most accurate method is based upon the density. It will be observed that in each of the cases above complete dissociation would transform one formula weight (mole) into two. The volume occupied by the two formula weights, however, will be double that which would contain, under like conditions, the formula weight of the undissociated substance, and the density (i.e. the weight of unit volume) after complete dissociation will be one-half what it would be without dissociation. When the dissociation is not complete we can also follow it and determine its extent from the two densities, i.e. with and without dissociation, although the relation is not so obvious.

Assume in a case such as the above that we start with 1 mole of the undissociated substance, and that this dissociates to the extent of $\alpha\%$. From the one mole before dissociation, then, we obtain $1+\alpha$ moles after dissociation, for we have $1-\alpha$ still undissociated, and α each of the two products, i.e. $1-\alpha+2\alpha=1+\alpha$ moles in total. Under like conditions, the volumes occupied by the substance before and after dissociation, then, will be related as $1:1+\alpha$; and the densities before and after will be related as $1+\alpha:1$, for the greater the volume produced by the dissociation of the original mole the smaller will be the density (weight of 1 cc.) of the system. In general, consequently, for all substances forming 2 moles from 1 by dissociation we have the relation

$$1:(1-\alpha)+2\alpha::d_d:d_u,$$

where d_d is the observed density after dissociation, and d_u is the density without dissociation, both being measured under the same conditions of pressure and temperature. The term d_u can, naturally, be obtained from the formula weight of the undissociated substance, i.e. is one-half the formula weight, when based upon hydrogen, or one thirty-second when based upon oxygen, one twenty-eighth when based on nitrogen, etc.

When one mole of substance produces three moles by complete dissociation, for example, the case of ammonium carbamate, i.e.,

$$NH_2CO_2NH_4 \rightleftarrows CO_2 + 2NH_3,$$

and α is the *degree of dissociation*, we have $(1-\alpha)+3\alpha : 1 :: d_u : d_d$. And, in general, where 1 mole falls into i moles by dissociation,

$$(1-\alpha)+i\alpha : 1 :: d_u : d_d,$$

or

$$\alpha = \frac{d_u - d_d}{(i-1)d_d},$$

from which α may be calculated without difficulty.

It is not to be assumed because we have restricted ourselves to these few typical examples that the process of dissociation is simply a scientific curiosity, for it is not only exceedingly important in itself, but is absolutely essential to things we shall have to consider later. Without knowing it, in fact, the reader has probably made use of the process of gaseous dissociation in qualitative analysis, for the Marsh test for arsenic depends solely upon it. The gaseous arsine, which is dissociated by its passage through the red-hot tube, re-unites in the colder portions, but, since the hydrogen diffuses more rapidly than the arsenic, an excess of the latter is left behind, and crystallizes upon the walls.

In addition to the influence of pressure and temperature upon the degree of dissociation of a gaseous substance, it has been found *that the introduction of one of the products of the dissociation into the system*, either before or after the process takes place, *always decreases the degree of dissociation of the substance.* Although the calculation of the effect of these three influences upon the dissociation can only be considered later, it may be mentioned here that a formula can be derived (the law of mass action) by which both the effect of pressure and that of the addition of a definite amount of a product may be calculated at constant temperature, and that another formula enables us to follow the influence of temperature.

The following tables will enable the reader to gather some idea of the effect of pressure and temperature upon the dissociation, and also make clear the calculation of α in the various cases.

DISSOCIATION OF NITROGEN TETROXIDE, N_2O_4.
(Density of $N_2O_4 = 3.18$; of $NO_2 + NO_2 = 1.59$; air $= 1$.)*

Temp.	Sp. Gr. of Gas.	Percentage Dissociation.
26°.7	2.65	19.96
35°.4	2.53	25.65
39°.8	2.46	29.23
49°.6	2.27	40.04
60°.2	2.08	52.84
70°.0	1.92	65.57
80°.6	1.80	76.61
90°.0	1.72	84.83
100°.1	1.68	89.23
111°.3	1.65	92.67
121°.5	1.62	96.23
135°.0	1.60	98.69
154°.0	1.58	100.00

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* The densities of hydrogen, oxygen, and air are related as 1 : 15.88 : 14.49, from which the densities in other units may be calculated.

DISSOCIATION OF PCl_5.

(Density $PCl_5=7.2$; $PCl_3+Cl_2=3.6$; air$=1$.)

Temp.	Density.	Percentage Dissociation.
182°	5.08	41.7
190°	4.99	44.3
200°	4.85	48.5
230°	4.30	67.4
250°	4.00	80.0
274°	3.84	87.5
288°	3.67	96.2
300°	3.65	97.3

DISSOCIATION OF N_2O_4.

(Equal Temperatures, Varying Pressures.)

Temp.	Pressure.	Density (air = 1).	Percentage Dissociation.
18°.0	279.0 mm.	2.71	17.3
18°.5	136.0 "	2.45	29.8
20°.0	301.0 "	2.70	17.8
20°.8	153.5 "	2.46	29.3

When 1 mole of gas is formed from a solid or liquid, against the constant pressure p, the work done is equal to p times the increase in volume. Since the volume of the solid or liquid is negligibly small, as compared to that of the gas, however, we may regard the total volume occupied by the gas as equivalent to the increase of volume. The work done, then, will be equal to $p\Delta V$, or, practically pV. But the product pV at constant temperature is constant, independent of the countless values of p and V from which it might be made up $\left(\text{for } p \propto \frac{1}{V}\right)$, and is equal in value *for 1 mole* to RT, in which R is a constant, energy, quantity. In calculating amounts of work of this kind, then, we shall always employ the right side of the equation $pV=RT$, for it shows the relations much more definitely and clearly than the other. We can also define molecular weight as a gas in this way. *The molecular weight of any substance as a gas is that weight which in going from negligible volume, at any temperature,* AGAINST ANY PRESSURE, *does the external work RT.* Thus to form n moles of gas at any temperature *against any pressure* always requires the work nRT, which will be given in the units employed for R, since T is a pure number.

If instead of forming one mole, as we suppose, the gas dissociates into others, the work involved will still be RT units for each *mole,* but nRT in total, where n is equal to the number of moles formed from one original mole. This value n may also be expressed in terms of the degree of dissociation, for, if this is α, and i moles are formed from one, n, the total number of moles, will be $(1-\alpha)+i\alpha$, and the work of formation from a liquid or solid will be $[(1-\alpha)+i\alpha]RT$ units.

We could also determine dissociation in this way, i.e., by determining the work done and finding the value of n as a difference, from which α, when i is known, can be found; but the method based upon the density as illustrated above is far simpler and decidedly more practical.

Partial pressures and concentrations.—For the description of a gaseous system composed either of a single gas or a mixture of gases it is essential that we have a convenient method of representing the amount of a gas present. This is not only necessary for the description of such a system, and for use in the formula (mentioned above) which shows the dependence of the degree of dissociation upon the pressure, and upon the amount of one of the dissociation-products that has been added to the system, but will also serve to simplify some of our later work.

Thus far we have used either the density of the gas or the volume (V) which contains 1 mole for this purpose, but these are not the only forms of expression, nor are they even the most convenient. We shall therefore consider briefly the other, better, methods for the definition of the amount of gas present in a system.

Since under definite conditions 1 mole of gas (by definition) occupies a definite volume, and 1 liter of this volume will contain a definite fraction of a mole, under those conditions, it is evident that any change in the system due to an alteration of the conditions can be accurately described by a statement of the change in *concentration, i.e., the change in the number of moles per liter.* But, at constant temperature, the concentration is proportional to the pressure, i.e., the greater the concentration the greater the pressure, and vice versa, so that it is obvious that a change in any gaseous system can also be accurately described by a statement of the change in pressure (or partial pressures in case the system is composed of several gases).

As these two terms, concentration and partial pressure, are to be used constantly in our later work, it will be necessary here to find the exact quantitative relation which exists between them. From the definition of the formula weight, however, remembering the laws of Boyle and Charles (p. 18), this relation follows directly, provided the laws continue to hold. For at 0° C. the concentration 1, *i.e. 1 mole per liter,* is equivalent to a pressure of 22.4 atmospheres $\left(p \propto \frac{1}{V}\right)$, and at any other absolute temperature T, the unit of concentration gives the pressure $22.4\frac{T}{273}$ atmospheres.

In order that the reader may become familiar with the use of these terms, we shall now consider a specific case of the system formed by dissociation. At 190° C., for example, we find that PCl_5 is 44.3% dissociated (p. 29), i.e., the reaction

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

goes toward the right until 44.3% of the PCl_5 originally present is decomposed and equilibrium is established. We have then a system composed of the three gases, PCl_5, PCl_3, and chlorine. Since the data in the table (p. 29) are given for atmospheric pressure, the total pressure after dissociation remains atmospheric and the volume increases. Starting with 1 mole of PCl_5, assuming no dissociation to take place, the volume would be $22.4\frac{273+190}{273}$ liters. But by the dissociation we lose 0.443 mole of PCl_5, and gain 0.443 of a mole of each of the products, PCl_3 and chlorine, hence the total volume *after dissociation* is $1.443 \times 22.4\frac{273+190}{273}$ liters, for the mole of PCl_5 has been transformed into $(1-0.443)+2\times0.443=1.443$ moles, the temperature and pressure remaining unchanged. The partial pressures in atmospheres, then, will be $\frac{1-0.443}{1.443}$ for PCl_5, and $\frac{0.443}{1.443}$ each for PCl_3 and chlorine, i.e., the number of moles of each, divided by the total number of moles in the system, and multiplied by the total pressure. And the concentrations, i.e., number of moles per liter, will be

$$\frac{1-0.443}{1.443\times 22.4\frac{273+190}{273}}=c_{\mathrm{PCl}_5},$$

$$\frac{0.443}{1.443\times 22.4\frac{273+190}{273}}=c_{\mathrm{PCl}_3}=c_{\mathrm{chlorine}},$$

i.e. the number of moles divided by the total volume in liters.

In case the volume remained constant, i.e., that the pressure increased by the dissociation (*assuming* the increase of pressure to have no effect upon the degree of dissociation) the final pressure would be 1.443 atmospheres. The partial pressures in atmospheres, then, would be $1-0.443$ for PCl_5, and 0.443 each for PCl_3 and chlorine. And the concentrations would be

$$\frac{1-0.443}{22.4\frac{273+190}{273}}=c_{\mathrm{PCl}_5}$$

and

$$\frac{0.443}{22.4\frac{273+190}{273}}=c_{\mathrm{PCl}_3}=c_{\mathrm{chlorine}}.$$

The relationship existing between V, p, and c is shown by the following almost self-evident equations:

$$p=22.4\frac{T}{273}c \text{ atmos.},$$

or

$$c=\frac{273p}{22.4T}=\frac{1}{V};$$

i.e., the pressure of 1 mole per liter at 0° (since in 22.4 liters it is 1 atmosphere) is 22.4 atmospheres, and at T° is $\frac{T}{273}\times 22.4$; while V, the volume of 1 mole, is the reciprocal of concentration, the number of moles per liter.

In a mixture of two gases if the total pressure of the N $(=n_1+n_2)$ moles is P, the partial pressures of the individual gases will be

$$p_1:P::N:n_1 \quad \text{and} \quad p_2:P::N:n_2,$$

i.e.,

$$p_1=\frac{n_1}{N}P \quad \text{and} \quad p_2=\frac{n_2}{N}P,$$

for the total number of moles N gives the pressure P and $\frac{n_1}{N}$ must be the fraction of the total pressure due to the gas present to the extent of n_1 moles.

It will be seen then that the concentration of any constituent, i.e., the number of moles per liter is given by the expression

$$c_{\text{constituent}}=\frac{\text{moles of constituent}}{\text{total volume}},$$

and the partial pressure by the expression

$$p_{\text{constituent}}=\frac{\text{moles of constituent}}{\text{total moles}}\times\text{total pressure}.$$

It is to be remembered, in this connection, that while so long as the volume of any system remains the same and no reaction takes place the concentration $\left(=\frac{\text{moles}}{\text{liters}}\right)$ remains the same, the partial pressure will vary if the temperature is changed. Thus 1 mole per liter remains 1 mole per liter at any temperature so long as the volume of the system does not change and no reaction takes place, but the pressure of 1 mole per liter at 0° under these conditions would be 22.4 atmospheres, while at 100° it would be $22.4\times\frac{373}{273}$ atmospheres. In short, partial pressure, even with unchanged volume, and no reaction taking place, varies with the temperature, while concentration remains constant.

CHAPTER III.

HEAT AND ITS TRANSFORMATION INTO OTHER FORMS OF ENERGY.

The first law of thermodynamics.—As has already, been mentioned, energy may be manifested in various forms. An amount of energy, then, may be expressed in either the so-called absolute units (erg, dyne, etc.), or in any of the units employed exclusively for one specific form of energy (coulomb, calorie, etc). This conception of energy is the one which has been commonly accepted since the time of J. R. Mayer (1841), who was the first to determine the factor necessary to transform energy expressed as heat into mechanical units, i.e., the so-called *mechanical equivalent of heat.* It is to be remembered here, however, that the word equivalent is used *only* in the sense that *if* heat is transformed into mechanical work we shall always obtain a definite number of mechanical units from each unit of heat (calorie) transformed, *and does not at all imply that heat is always transformed into work under all conditions, or that all the heat present will be transformed into work.* The principle governing the transfer of heat, and the relation existing between the heat transferred and that transformed into work, is to be considered below; here we shall only discuss the relation of the amount of heat actually transformed into mechanical work to the amount of work which results from the transformation.

Of the various methods for determining the mechanical equivalent of heat (Joule's, Rumford's, etc.), the most interesting in principle for our purposes is that of J. R. Mayer, which was the forerunner of all the others. This depends upon the difference observed when the specific heat of a gas is determined for variable or for constant volume. Since by definition the specific heat of a substance is the heat necessary to raise 1 gram of it 1° C. (from some one standard temperature), it is obvious that for gases two values will be found, one when the gas is allowed to expand under constant pressure, the other when the volume is retained constant. Naturally, *à priori*, there is no means of deciding whether these two values will be experimentally identical or not, unless we understand the difference in the process in the two cases. Experiment, however, shows the values to be different when work is done by the expansion, the one for constant pressure (i.e. where the volume increases) being the larger; while no difference from that at constant volume is observed when the expansion takes place without involving mechanical work, e.g. into an exhausted space. Mayer was the first to recognize that the only difference possible in these two experimental values is the amount of heat which is used in overcoming the resistance offered to expansion. From actually observed values, then, it was possible for him to calculate the exact value of a calorie in mechanical units. By experiments with air, for example, it is found that

$$c_p - c_v = 0.0692 \text{ cal.},$$

i.e., the amount of work necessary to expand 1 gram of air by the $^1/_{273}$ part of its volume at 0° C., against the pressure of the atmosphere, is equivalent to 0.0692 cal. Since 1 gram of air occupies 773.3 cc., it would occupy 773.3 cm. of a tube having a cross-section of 1 square centimeter. An increase in temperature of 1°, then, would involve an increase of 2.83 $\left(\text{i.e. } \frac{773.3}{273}\right)$ cm., and the weight of the atmosphere, $13.6 \times 76 = 1033.6$ grams per square centimeter, must be raised through this distance of 2.83 cm. But the work necessary to do this is $2.83 \times 1033.6 = 2928$ gram-centimeters, and hence

$$0.0692 \text{ cal.} = 2928 \text{ gram-centimeters,}$$

$$\text{i.e.,} \quad 1 \text{ cal.} = 42,300 \text{ gram-centimeters,}$$

which is *the mechanical equivalent of heat.**

It has been shown since Mayer's time that in general any form of energy can be transformed into any other form, and that in every case we obtain from each unit (which has been transformed) of the original form of energy a definite, constant number of units of the final form resulting from the transformation. Or, expressing it in another way, if we start with an amount of energy in the form *A* and transform it *completely* into the form *B*, and this *completely* into the form *D*, which is then transformed *completely* into the form *A* again, the original and final amounts of *A* will be identical. And when

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* Since the experimental error in determining the specific heat of a gas, particularly for constant volume, is not inconsiderable, this result is less accurate than later ones, determined in other ways, although all methods give sensibly the same result. The commonly accepted value of the mechanical equivalent of heat at present is *42,600 gram-centimeters*, so that we shall use it, in preference to the above value, in all our later calculations.

in any case the transformation is *not* complete, another kind of energy of the form Z_1, Z_2, etc., being produced to a slight extent, the final amount of A will be smaller than the original one by the sum of the amounts of Z_1, Z_2, etc., expressed in the same units as A. Or the final value of A plus the sum of the amounts of Z_1, Z_2, etc., after they are completely re-transformed into A, will be identical with the initial value.

These facts concerning the mutual transformation of the various kinds of energy are usually summed up in the form of a law which is known as the *first law of thermodynamics or energetics.* This law may be expressed most conveniently in one of the two following ways: *The energy of any isolated system is constant;* or, *a perpetual motion of the first kind is impossible, i.e. energy can neither be created nor destroyed.*

If a system is heated, then, i.e. absorbs energy from its environment, all the energy which it has gained must appear either in the form of the energy absorbed or in some other form, and the total amount of energy in the system will be equal to that which it contained originally plus that added, both being expressed in the same terms. A gaseous system, for example, when heated, will increase in temperature, and may also expand against a pressure, i.e. do external mechanical work. Expressed mathematically, then, the first law of energetics as applied to the system will lead to the relation

$$dE = dU + W,$$

where dE is the energy absorbed, dU is the increase of internal energy, and W is the external mechanical work involved in the expansion, all being expressed in the same kind of units. The term W, for a gas, however, we know to be equal to pdV (i.e. $=RT$ for each mole), hence we obtain

$$dE=dU+pdV,$$

which is the analytical expression of the first law of energetics.

Starting with this expression of the first law it is possible to derive a number of mathematical relations, which, although important for general purposes, are not absolutely essential for the object we have in view.* Two relations which are thus to be found will be valuable to us, however, so that we shall discuss them as though they were empirical facts, rather than the result of mathematical reasoning.

It will be remembered (p. 18) that we found the relation between the pressure and volume of a gas *under the condition that the temperature remains constant.* But if we compress a gas *rapidly* its temperature rises; and if we allow it to expand *rapidly* its temperature falls. Naturally, Boyle's law holds for the gas in these two cases, *after the temperature, in consequence of radiation, has attained its initial value;* but what is the relation between pressure and volume *immediately after* compression or expansion, i.e., before the temperature has become equalized? This question could still be answered by Boyle's law if we knew the temperature produced by the compression or expansion; but we do not. As the result of mathematical reasoning, however, this relation is found to be the following:

$$p_1:p_2::v_2{}^k:v_1{}^k,$$

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* "Elements," pp. 38–48.

where $k=\frac{c_p}{c_v}$, i.e. is the ratio of the specific heat of the gas at constant pressure to that at constant volume. When the temperature of the gas is allowed to change, as a result of the compression or expansion, then, we find the pressures inversely proportional to the k powers of tne volume, instead of to the volumes themselves (Boyle's law), as is observed when the change takes place so slowly that the heat lost or gained by radiation retains the temperature constant, or when the original temperature is once more regained.*

The value of this same term k † $\left(=\frac{c_p}{c_v}\right)$ for any gas has also been found empirically to vary with the number of

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* By a simple transformation, since $\frac{pV}{p_1V_1}=\frac{T}{T_1}$, where p, V, and T refer to an *isothermal*, i.e. a constant temperature (slow change), and p_1, V_1, and T_1 refer to an *adiabatic*, i.e. a varying temperature (rapid change), we also find the following relations:

$$\frac{T_1}{T}=\left(\frac{V}{V_1}\right)^{k-1} \text{ (when the pressure is retained constant),}$$

and

$$\frac{T}{T_1}=\left(\frac{p}{p_1}\right)^{\frac{k-1}{k}} \text{ (when the volume is retained constant).}$$

By aid of these two equations we can calculate the temperature produced by an adiabatic change of either pressure or volume. (See "Elements," pp. 46, 47.)

† k, in itself, is a physical constant, for it can be determined without any knowledge of the component terms c_p and c_v, as well as from the ratio of these. In fact, the direct determination of k from the velocity of sound in the gas, as measured in a Kundt tube, or by application of the formula $\left(\frac{p_1}{p}\right)=\left(\frac{v}{v_1}\right)^k$ (method of Clement and Desormes, "Elements," pp. 52, 53), is probably more accurate than the indirect method.

combining weights present in the formula weight, although we do not know why such a relation should exist, nor even the exact form of the relation which does exist. For example, it has been found that all substances which are "*monatomic*" *in the gaseous state, i.e., all substances whose formula weight according to the definition is identical with the combining weight, Hg, etc., give a value of k equal approximately to 1.67; and that those with two combining weights to the formula weight,* O_2, H_2. *etc., lead to the value 1.4.* This relation, purely, empirical as it is, is of very great value in those cases where no combination of the gas with other elements is known, and only the formula weight, from the density, can be determined. Thus for argon the formula weight is found to be 40, and although it is impossible to find the combining weight directly, since no combinations with argon have been found to exist, it is said that it must be 40, for by experiment the value of *k* is shown to be 1.67. This will explain how argon and similar gases, which are not known to combine with any element or elements, receive a value in the atomic weight table, although, by definition, atomic weights are in all cases *combining weights.* The ratio for "triatomic" gases is not so well established, but for ozone, O_3, $\frac{c_p}{c_v}$ has been found to be 1.29, while for H_2O and SO_2 the values 1.28 and 1.25 respectively have been observed.

One very important, absolutely general result of mathematical reasoning can be derived directly from our definition of formula weight. Since to form 1 mole of gas from negligible volume, at $T°$, the external work, by definition, is RT, and at $T+1$ would be $R(T+1)$, it is evident that the external work done when 1 mole of gas is heated 1° is equal to the difference between the work at $T+1$ and that at T. In other words, since the specific heat at constant pressure is greater than that at constant volume by the amount of external work done in expanding under the increase of temperature of 1°, we have

$$Mc_p - Mc_v = C_p - C_v = R(T+1-T) = R = 2 \text{ cals..}$$

where M is the formula (molecular) weight, and C_p and C_v are the formula (molecular) specific heats. *The formula specific heat at constant pressure, then, is always greater by 2 calories than the formula specific heat at constant volume.**

This relation $C_p - C_v = 2$ cal. again emphasizes the difference in point of view of physics and physical chemistry (p. 19), and is very valuable in the various calculations with specific heats, for, when we know c_p (or c_v) for a gas, and its formula weight, for example, we can readily find the value of c_v (or c_p). And, knowing k ($=\frac{c_p}{c_v}$, see foot-note, p. 38), and the formula weight, i.e., having no knowledge of the value of either c_p or c_v, we can calculate these values. Thus, for argon, we know that $k = \frac{c_p}{c_v} = 1.67$, and that $40c_p - 40c_v = 2$, hence $c_v = 0.075$ and $c_p = 0.124$.

By combining the two equations $M(c_p - c_v) = R$ and $\frac{c_p}{c_v} = 1.66$ we find that

$$Mc_p = \text{constant} \qquad \text{and} \qquad Mc_v = \text{constant}.$$

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* For a table of these values, see "Elements," p. 49.

In other words, for all monatomic gases the product $M \times c_p$ has a constant value independent of the nature of the gas. In the same way the product $M \times c_v$ is also constant, though of a different actual value. Similarly, all diatomic gases give a constant value for $M \times c_p$, and a constant, but different value, for $M \times c_v$, etc. This relation is often of convenience in calculating the specific heat of a gas (either c_p or c_v) when the molecular weight and either c_p or c_v of another gas of the same type (monatomic, diatomic, etc.) are known. The error at worst here, for diatomic gases, should not exceed a few per cent; so long as the ratio $\frac{c_p}{c_v}$ for them is practically identical.

A case which is similar to the dependence of specific heat upon the volume relations is the dependence of the heat evolved by a chemical reaction upon the volume relations of the system. In other words, certain reactions are observed to evolve a different amount of heat when the volume of the system is allowed to increase than when it is retained constant. Naturally, in such cases, the progress of the reaction itself must involve a change in volume, for it has been observed that a reaction is unaffected by changes in volume when the initial and final substances, under like conditions, occupy the same volume, i.e., the reaction is unaffected unless the change in volume which we bring about affects the two sides differently. Thus the volume of the system has no influence whatever upon the direction of, or the heat evolved by, the gaseous reaction

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

for we have two formula weights of substance on each side and hence (by definition) the volume of each side, under like conditions, must be the same and influenced equally. A general rule in this connection as to the effect of a change of volume upon the *direction* (not the heat evolved) of a reaction is the so-called *principle of Le Chatelier*, which may be expressed as follows: *Any change from the exterior in the factors governing the reaction always causes the system to react in the direction favored by the change.* Thus in the reaction

$$N_2O_4 \rightleftarrows NO_2 + NO_2,$$

for example, decreased volume will cause the reaction to go toward the right to a smaller degree than before, i.e., since, in going toward the right, an increase in volume is involved, decreased volume favors the reaction going in the reverse direction and involving a decrease in volume.

Although this shows the effect of external conditions upon the *direction* of a reaction, it does not give us any idea of the effect upon the heat evolved, except that it must necessarily be different, because the reaction takes place to a smaller extent, owing to the decreased volume. The point alluded to above, however, was the effect of constant volume or constant pressure, *when the reaction still continues to take place normally and to its full extent.* Here, as will be seen immediately, it is only a question of the loss of heat due to external work performed in expanding, or of the absorption of heat due to the work done upon it when the volume decreases. Starting with the reaction

$$\underbrace{2H_2 + O_2}_{\text{Gaseous.}} = \underbrace{2H_2O}_{\text{Liquid.}} + 2 \times 67484 \text{ cal.}$$

at 18° and constant volume, for example, we can readily calculate the value under constant pressure, for 3 moles of substance in the gaseous state are transformed by the reaction into 36 grams (about 36 c.c.) of liquid water. At constant pressure, that of the atmosphere, for example, the volume of the system would decrease from $3 \times 22.4\frac{291}{273}$ liters to 36 c.c., and heat, equivalent to the work done upon the system during this reduction of volume, will be *absorbed.* In case the reaction took place in the opposite direction, i.e., liquid water were decomposed into gaseous oxygen and hydrogen, this same amount of heat would be *lost* under constant pressure, for the system would have to perform work in expanding. Since the work in either case would be equal to the product of pressure and volume, i.e. equal to RT or $2T$ cal. for each mole of gas, the difference in heat evolved in the two cases would be $3 \times 2T$ calories. And this work will depend in value only upon the temperature, *and will be independent of the pressure or volume of the gas* (p. 30).

Expressing this mathematically, then, we have

$$Q_p = Q_v - n \times 2T \text{ cal.},$$

where n is the number of moles of gas *formed* in excess of those originally present; and is negative when gas is absorbed. Q_p will always be larger than Q_v, then, when a gas is absorbed by the reaction, i.e., when the volume decreases; otherwise Q_v will be the larger.

A constant volume condition, it will thus be seen, is a no-external work condition; while constant pressure means that work is done either by or upon the system.

The second law of thermodynamics.—Thus far, in considering the first law of thermodynamics or energetics, we have only made use of the principle, based upon experience, that *when* a quantity of energy disappears at any place, a precisely equal quantity (in the same terms) of energy appears simultaneously elsewhere. And this condition was fulfilled in all the things we discussed. We must now consider another, also empirical, principle relating to energy and its transformation, the so-called *second law of thermodynamics.* This principle may be expressed in the form, *a perpetual motion of the second kind is impossible, i.e., heat cannot be made to go from a colder to a warmer body without the expenditure of work.*

As has already been mentioned (p. 13), the transfer of heat is conditioned by the temperature, i.e., the intensity factor of heat energy. But the simple transfer of heat does not always result in the appearance of mechanical work. Here, consequently, we must consider the questions as to how heat is to be transferred that work may result from the transference, and how the amount of work resulting depends upon the amount of heat transferred—for we know that although all forms of energy may be completely transformed into heat, the reverse transformation is never complete. It will be seen, then, that we are only to discuss the second law of thermodynamics in order that we may obtain a general and absolutely essential rule for our later work, and not from the standpoint of pure thermodynamics.

The transformation of heat into mechanical work takes place only through the medium of a gaseous body. Thus by absorbing an amount of heat a gas expands, performing external work, until its temperature, which must be higher than that of the environment, is reduced to this. By this process heat at a high temperature is absorbed by the gas and is partly transformed into mechanical work, i.e., until the temperature of the gas has fallen to that of the environment. No further transformation of that amount of heat is possible, then, for heat cannot go from one body to another (second law) when both are at the same temperature.

The relation between the amount of heat absorbed in any process and the consequent maximum amount of mechanical work resulting can be derived by aid of the following cycle, composed of assumed, ideal processes:

1. Assume an ideal gas, enclosed in a cylinder with a movable piston, at a certain temperature and pressure. Imagine the cylinder to be placed upon a heating-bath at the temperature T_1, allowing the volume to increase at a constant pressure which is just greater than that of the atmosphere. By the expansion the gas will cool, but so long as it remains on the heating-bath it will absorb heat, retaining the temperature constant. If this heat absorbed is Q_1, the initial volume is v_1, and its final one v_2, the temperature being T_1, the work done will be equal to $\int_{v_1}^{v_2} pdv$, and expressing both in the same units we have, since $p = \frac{rT}{v}$ (p. 20),

$$dQ_1 = rT\frac{dv}{v}$$

or

$$Q_1 = rT_1 \log_e \frac{v_0}{v_2}.$$

The gas is next allowed to expand adiabatically away from the heating bath until the temperature falls to T_2. For this, the new volume being v_3, we have the relation (p. 39)

$$\frac{T_1}{T_2}=\left(\frac{v_3}{v_2}\right)^{k-1}.$$

3. Next the pressure is increased until the volume is decreased to v_4, heat to the amount Q_2 being removed, so that the temperature remains constant at T_2. The work done here by the gas is $-\int_{v_3}^{v_4} pdv$, and we have

$$Q_2=rT_2\log_e\frac{v_3}{v_4}.$$

4. Finally the gas is compressed adiabatically until the original volume v_1, and the original temperature T_1, are reached. For this we have the relation

$$\frac{T_2}{T_1}=\left(\frac{v_1}{v_4}\right)^{k-1}.$$

We have thus carried the gas through a series of ideal changes, and have finally the same conditions as those with which we started. The amount of heat Q_1 has been absorbed at the higher temperature T_1, and a smaller amount Q_2 has been evolved at a lower temperature T_2, and the rest has been transformed into work; i.e., Q, the amount of work produced (in terms of heat), is equal to Q_1-Q_2, for the amount of heat Q_2 has simply been transferred from T_1 to T_2.

The relation between Q_1 and Q_2, then, is obviously the following:

$$\frac{Q_1}{Q_2}=\frac{rT_1\log_e\frac{v_2}{v_1}}{rT_2\log_e\frac{v_3}{v_4}},$$

but

$$\frac{v_2}{v_1}=\frac{v_3}{v_4},\quad \text{i.e., } \log_e\frac{v_2}{v_1}=\log_e\frac{v_3}{v_4};$$

hence

$$\frac{Q_1}{Q_2}=\frac{T_1}{T_2},$$

i.e., *the amounts of heat absorbed and liberated are proportional to the absolute temperatures of the processes.*

Since $Q=Q_1-Q_2$ is the heat transformed into work, we have, then,

$$\frac{Q_1-Q_2}{Q_2}=\frac{T_1-T_2}{T_2},$$

and

$$\frac{Q_1-Q_2}{Q_1}=\frac{T_1-T_2}{T_1}.$$

From these two equations we may conclude that in reversible processes, the work done, or to be done, by the transformation of heat into work is to the amount of heat absorbed at the temperature T_1 *(or liberated at* T_2*) as the temperature interval through which the heat has fallen (or must fall) is to the absolute temperature* T_1 *(or* T_2*).*[*]

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[*] The reader who does not follow the mathematical reasoning is advised at least to become thoroughly familiar with the laws in italics, as well as the three last formulas, for they are vital in some of our later work.

Examples of the use of this law will be found later in the chapters on " Solutions " and " Electrochemistry."

It will be observed from the above that *it is only at the absolute zero that all heat will be transformed into work*, for when $T_2=0$, Q_2 will be zero, and $Q_1-Q_2=Q_1$.

In its second form this general rule is that which is used in engineering work to find the efficiency of heat-engines. Thus, at best, an engine working with a boiler temperature of 200° C., the temperature of the condenser being 50° C., will have an efficiency of $^{150}/_{473}=0.317$ $\left(=\frac{T_1-T_2}{T_1}\right)$, i.e., assuming no heat to be lost either by radiation or by the work used in overcoming friction, such an engine would transform 31.7% of the heat absorbed into work.

CHAPTER IV.

SOLUTIONS.

The formula (molecular) weight in the liquid and solid states.—Most of that which we have found to hold true for gases is directly applicable to substances in the state of solution; and even a cursory glance at the contents of this chapter will convince one of it, and justify the time we have devoted to the discussion of gaseous systems—all unnecessary, as this may have appeared at first sight. Before discussing this similarity of behavior, however, it would first seem necessary to consider something of the general relations of the other two states (liquid and solid) in which the substances composing the solution may have previously existed, i.e., of the components of the system. But experience shows that such a knowledge is not essential, for much more is known of the laws governing the behavior of solutions than of those regulating that of either liquids or solids. In fact, the behavior of a solution differs so utterly from that of the pure, liquid, solvent, that it may be followed without any further knowledge of the behavior of the solvent than that comprised in the few and well-known physical facts with which we assume familiarity. The only purely chemical relation to be considered, indeed, for either liquids or solids, is the definition of the formula weight, and this is only necessary that we may be able to follow the changes in the formula weight as the substance passes through the various possible phases of its existence, i.e., the gaseous, liquid, solid, and dissolved states.

The formula weight in the gaseous state, as we have already observed, may be defined in several ways; and all definitions will lead to the same result, for all are based upon the same fundamental fact, although expressed in other terms. Thus we may say, *the formula weight of a substance in the gaseous state is that weight which will occupy, under like conditions, the same volume as 32 units of weight of oxygen;* or, *is the weight which when multiplied by the difference in the specific heats under constant pressure and at constant volume (i.e., $c_p - c_v$) will give the value 2 calories;* or, *is the weight of the gas which in going from negligible volume, against any pressure, does external work equal to RT units of energy.* And still other definitions could be given. In short, then, the formula weight in the gaseous state is a very definite conception, and can be readily determined experimentally.

In the liquid state,* on the other hand, we have only one general definition for the formula weight, and this depends upon the so-called surface tension of the liquid, i.e., upon the force in dynes necessary to form a liquid surface with an area of 1 square centimeter. The surface tension of a liquid can be found indirectly from the height to which the liquid ascends in a capillary tube of known radius, and is equal to one-half the product of the height (in centimeters), into the radius (also in centimeters) into the specific gravity, i.e., the surface

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* For further information as to the liquid state, see "The Elements," pp. 60–99.

tension = $^1/_2$ hrs. According to this definition, *the formula weight of a liquid is that weight in grams which gives such a surface that its increase, due to a heating of 1° C., involves the surface work of 2.12 ergs;* in other words, *the temperature coefficient of the formula (molecular) surface tension (i.e., the temperature coefficient of the tension of the surface of 1 mole) is always the same, independent of the nature of the substance.** This definition, it will be observed, is very similar to one of those given above for gases, except that surface energy is involved in place of volume energy.

There is one question which may arise here, which, if not answered, can lead to confusion; it is, How was this definition obtained originally? Naturally, we may not go very deeply into this matter here, but at any rate the empirical origin of the definition may be pointed out. By assuming the formula weight to be the same in the liquid as in the gaseous state, the factor 2.12 ergs was found to remain constant for a large number of substances. The natural inference, then, was that this value (2.12) is typical of the formula weight, and that any variation from it, when the gaseous formula weight is assumed, shows that the formula weight changes as the substance goes from the gaseous to the liquid state. Using this same plan, other methods decidedly more restricted in their scope have been developed, and as the same discrepancy for any one substance is shown by all, our conclusion is considered to be justified.

It must be acknowledged that our definition of formula weight in the liquid state is very much less satisfactory than that for the gaseous state, but unfortu-

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* Morgan and Stevenson have shown that the same is true for the temperature coefficient of the weight of a drop of the liquid which falls from a definite tip. "Elements," pp. 92–95.

nately we find the relations for the solid state * still less satisfactory, for as yet it has been impossible to find any definition for the formula weight in the solid state. It is true that at first glance it would seem that the law of Dulong and Petit—that the combining (atomic) weight of an element (excepting carbon, boron, and silicon) when multiplied by its specific heat always gives the approximately constant value 6.34—would suffice for this purpose, since the sum of the combining weights, i.e. the formula weight, multiplied by the specific heat of the compound should give approximately the same value as is obtained when 6.34 is multiplied by the number of combining weights in the formula weight. But a moment's thought shows that this relation is only of value in that it insures uniformity in the choice of the combining ratio to be used as the combining (atomic) weight; in other words, at best, it is only another method for fixing the combining (atomic) weight of an element without the necessity of knowing or studying the compounds which it may form (see pages 4 and 40), and has nothing to do with fixing the formula weight of the compound. Thus analysis shows the existence of two chlorides of mercury, the simplest formulas, using at least one combining weight of each element, being $HgCl$ and $HgCl_2$, but the application of the law of Dulong and Petit does not enable us to state whether the formula weight in the solid state is $HgCl$ or Hg_2Cl_2,† etc., any more than the analytical result does. And the same is true for the other chloride. It is only because the

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* For further information on this state, see "Elements," pp. 100–115.

† For $HgCl$ we have $(200+35.5)\ 0.052=12.25$; for Hg_2Cl_2 $(400+71)\ 0.052=24.5$; while $2\times 6.34=12.68$, and $4\times 6.34=25.36$.

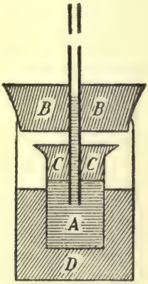
formulas Hg_2Cl_2 and $HgCl_2$ (and not Hg_2Cl_4) are found under certain conditions in the gaseous state that they are *assumed* in the solid state. In all reactions involving solids, then, it is only the actual weight of the reacting substances which is essential, and the very fact that we cannot define formula weight in the solid state shows its utter lack of chemical or physical influence. If at any time this should be changed, and it appear that the formula weight does exert an influence experimentally, naturally all our difficulty would disappear, for then a definition could at once be derived from observations of this influence.

The molecular weight of a dissolved substance, in contrast to that of a liquid or a solid, plays a very important rôle indeed, and is just as definite in its meaning as that in the gaseous state. Indeed, it will almost appear to the reader, after his perusal of the following pages, that the formula weight is *the* significant and fundamental conception in the consideration of dissolved substances; and certainly its paramount practical importance is decidedly striking, especially when contrasted with the slight importance of, and impossibility of defining chemically, the formula weight in the liquid state, and its apparent utter lack of either chemical or physical influence in the solid state.

Osmotic pressure.—It is a well-known fact that, when a solution is carefully superimposed upon another containing a different amount of the substance, diffusion takes place, and that this diffusion is so directed that the entire system finally becomes homogeneous. There is, then, a tendency for the substance in solution to become uniformly distributed throughout the volume of liquid accessible to it. Following the plan we have adopted, i.e. considering only the facts and avoiding all hypothesis, we shall study the facts of this phenomenon, and the general relations to be derived from them, without at the same time trying to picture their cause, or to explain their origin, by hypothesis.

The facts of diffusion may be summed up by the following statement: A system composed of a substance dissolving in a solvent, or of two solutions of different strength, one being superimposed upon the other, behaves as though there existed an attraction between the substance and the solvent, which ultimately produces a uniform concentration of the dissolved substance throughout the entire system. It is to be noted here that this is not in any way an assumption, but simply a description of the behavior of the system as we observe it.

The difference in concentration of the two liquids in contact has been observed to influence very largely the force of diffusion and in such a way that the greater the concentration-difference the greater will be the force of diffusion. To find the quantitive relation existing between the amount of dissolved substance in the solution and the force of diffusion into the pure solvent, however, it is necessary for us to find a method of measuring the force of diffusion. Naturally, such a measurement would not be difficult if we could obtain a partition, to be placed between the solution and the pure solvent, which would allow passage to the solvent and not to the solute, for then we could simply measure the force with which the pure solvent goes through the partition. At first glance the difficulty of obtaining such a partition, i.e. one which in the case of water and an aqueous sugar solution, for example, will allow water, but not the dissolved sugar, to pass through, seems absolutely insurmountable. It is not so, however, for such *semipermeable films*, as they are called, are very widely distributed in nature, and can also be readily prepared by artificial means. In the first class, for instance, we find the protoplasm of which living organisms are made up, while of the second, a good example is a film of copper ferrocyanide, as formed by the reaction of copper sulphate and potassium ferrocyanide.



By aid of a copper ferrocyanide film, permeable to water but not to sugar and many other substances, Pfeffer was able to measure the apparent attraction between substance in solution and the pure solvent, the *osmotic pressure*, as it is called. The principle of Pfeffer's apparatus is illustrated by the figure above. The cylinder *A*, closed at the bottom, is of porous clay and is intended to support the semipermeable film. This film is prepared by filling the porous cup with a solution of potassium ferrocyanide and allowing it to stand for a day in a solution of copper sulphate. In this way the pores of the cup are filled with the precipitated copper ferrocyanide, which, although permeable to water, is not so to the dissolved substance.

To make a measurement with this apparatus the cup so prepared is filled with the solution to be studied and the rubber stopper *CC* inserted in such a way that the solution rises a short distance in the measuring-tube. The cell is next immersed in water and retained in position by the cork *BB*. The liquid is now observed to rise very slowly in the tube until equilibrium is finally attained, i.e., until the weight of the liquid in the tube just counteracts the pressure with which the water enters the cell. Since the entrance of water into the cell decreases the concentration of the solution within it, the actual measurements are usually made by aid of a mercury manometer, so arranged that the change in volume is negligible. In this way the pressure observed is that which just prevents the entrance of water into the original solution, diluted only to an exceedingly small extent, and not, as in the above description, into one diluted by an amount of water equal in volume to the liquid which rises in the tube.*

From the experiment, then, we know that a certain definite pressure is necessary to prevent water going into the porous cell to dilute the solution contained in it. *This is what we shall call osmotic pressure. Whenever we use this term, consequently, it is without any assumption as to the cause of the pressure, and is merely expressive of the experimental fact that it is necessary to exert a pressure in order to prevent pure solvent flowing through a semipermeable film to dilute the solution, which is surrounded by it.*

It will be noted here that we do not consider what

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* For experimental details of very accurate measurements, where the pressures rise as high as 25 atmospheres, see Morse and Frazer, Am. Chem. Jour., 34, 1, July 1905.

osmotic pressure really is, but what we mean by the word osmotic pressure. This again emphasizes our standpoint. By defining each concept in terms of experiment, and studying the facts of the phenomenon, asking only *how* it takes place and *never why*, we may always be certain that our knowledge is based upon facts alone, and is perfectly free from any trace of hypothesis.

Pfeffer's results showed that this osmotic pressure increases with the amount of substance dissolved, and for any one concentration *is proportional to the absolute temperature of the solution.* The numerical values for various sugar solutions at 15° C., as found by Pfeffer, are given below, c being the percentage of sugar, and p the pressure, in centimeters of a column of mercury, which will just preserve equilibrium between the water and the solution, i.e. will just prevent water flowing through the semipermeable film.

c	p	p/c
1	53.8	53.8
1	53.2	53.2
2	101.6	50.8
2.74	151.8	55.4
4	208.2	52.1
6	307.5	51.3
1	53.5	53.5

The principal difficulty experienced by Pfeffer was the breaking down of the film under the pressure exerted, which, naturally, allowed the solution enclosed to escape and so led to a smaller result than would otherwise have been obtained. Such an action can always be detected, however, by testing the pure solvent for sugar; and, indeed, the presence of this was always observed when the stronger solutions were measured, and was the reason why the 6% concentration was the highest employed.

From Pfeffer's observations, as given above, it is quite evident that, within the experimental error, there exists a general relation between concentration and osmotic pressure, for the term p/c is practically constant, at constant temperature. But c, the number of grams of solute in 100 grams of solution, is obviously the reciprocal of the volume of solution, v, containing 1 gram of solute, i.e., $c=\frac{1}{v}$. We have, then, however, in place of $p/c=$ constant, the relation

$$pv = \text{constant},$$

and further, since p is proportional to the absolute temperature, T, i.e., $p=0$, when $T=0$, we may write

$$pv = \mathit{constant} \times T.$$

This equation is so strikingly similar to the one already derived for gases (pp. 19 and 20) that it at once suggests an analogy between the *behavior* * of a substance in solution and one in the gaseous state, and makes the determination of the *value* of the constant a point of extreme interest. Since for the gaseous state we have found the constant R (in $pV=RT$) to be a constant for all substances, when the volume V is that occupied by the formula weight (i.e., the combining weight of an element multiplied by some small whole number, or the sum of the combining weights of the elements composing a compound), it is but natural to think that some such analogous result may be found for substances in solu-

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* It is to be remembered here that experiment shows the analogy in behavior, and does not justify the assumption that the *reason* for the behavior is the same. Although it has been possible *by aid of hypothesis* to formulate a kinetic theory (i.e., in one sense of the word a hypothesis) of gases, all efforts to do likewise with liquids or solutions have been futile.

tion. Such a result, however, would lead immediately to a definition of formula weight in solution, if such a conception exist, for it would show that the formula weight exerts an easily observed influence upon the physical behavior of the solution. And its importance would probably not be restricted to osmotic pressure alone, for presumably then the physical behavior of a solution *in other respects* would also be influenced by the formula weight, and we could employ the definitions for formula weight so obtained not only as definitions, but, knowing the formula weight, could also calculate the exact behavior in these other respects of any substancce dissolved in a solvent.

In order to find whether the constant in our equation has any definite relation to that for gases, however, it is necessary to calculate it for one formula weight in the dissolved state. Here, naturally, arises the question as to what the formula weight in solution is, for as yet we have not derived any definition of it. Let us assume temporarily that sugar has the same formula weight in solution as it is generally *assumed* * to have in the

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* It will be observed after a survey of chemical compounds that many formulas are employed which cannot be proven experimentally. Under the atomic hypothesis it was usually assumed that the formula of a compound was that simple relation which would give at least one atom of the substance present to the smallest extent, and would lead to a whole number of atoms of the other constituents. Or, from the hypothesis-free standpoint, would involve a whole number of combining weights of each constituent. This, naturally, is but following out the consequences of the choice of hydrogen (or $^1/_{16}$ oxygen) as the basis of the combining weights. But in either case the assumption of a formula weight without experimental foundation is not justified. In the case of sugar the structure, the products of decomposition, etc., have led to the formula $C_{12}H_{22}O_{11}$, and we *assume* without direct experimental evidence that this would also be the formula in the gaseous state if no decomposition took place.

other states, viz., $C_{12}H_{22}O_{11}$, and calculate the constant on the assumption that the v in our equation is the volume of solution in which this formula weight (342 grams) is dissolved.

Pfeffer found for a 1% solution of sugar (i.e., 342 grams in 34,200 c.c.) at 0° an osmotic pressure of $49.3 \times 13.6 = 671$ grams per square centimeter; hence

$$\frac{p_0 V_0}{273} = \text{constant} = \frac{671 \times 34200}{273} = 84200,$$

i.e., assuming that sugar has the formula $C_{12}H_{22}O_{11}$ in solution we find that the *osmotic* constant is identical, within the experimental error, with the *gaseous* constant (p. 21) which would be obtained if sugar in the gaseous state had the same formula.

This same constant has also been obtained for many other organic substances, using the customary formula weights (p. 60) (many of which *can* be confirmed by aid of the gaseous density), and we may say in general that it enables us to find the formula weight from the observed osmotic pressure, or, knowing the formula weight, to calculate the osmotic pressure. It is true that we find in many cases that this constant is only obtained when the formula weight in solution is taken as some small multiple of that in the gaseous state, but in every such case it can be experimentally shown, by a method given below, that the formula weight undergoes a change when the substance goes out of that solvent in which its behavior seems abnormal, into another in which it is normal, i.e., in which the assumption of the gaseous formula weight in solution leads to the above constant. Naturally, direct osmotic pressure observations with solvents other than water cannot be made with the ferrocyanide film, but it has been possible to find other substances which are permeable to other solvents and yet not to dissolved substances. Thus vulcanite and rubber have been found permeable to ether and not to alcohol, so that it is possible to measure the pressure with which ether goes through the film to dilute a solution of alcohol in ether. Pressures of this kind have been observed up to 50 atmospheres, but no very accurate measurements have been made.*

From the fact that the osmotic constant is identical with the gas constant, both calculated for the volume containing 1 mole, it is evident that the equation $pV=RT$ is applicable to both the dissolved and gaseous conditions, p being the osmotic pressure in the one case and that of the gas in the other, while in both cases V is the volume occupied by 1 mole and R is a constant depending in value only upon the units chosen. This fact may also be expressed in other ways. For example, we may say that *the pressure necessary to just prevent pure solvent flowing through a semipermeable film to dilute a solution is the same as would have to be exerted upon the amount of substance contained in the solution if it were in the gaseous state, at the same temperature and occupying the same volume, to just prevent it expanding; provided, of course, that the formula weight is the same in both states.* Or, *with the same proviso as to formula weight*, as van't Hoff originally announced the law, *the osmotic pressure of a substance in solution is the same pressure as that amount of substance would exert were it in the gaseous state at the same temperature and occupying the same volume.* Pos-

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* See Raoult, Zeit. f. phys. Chem., 27, 737, 1895.

sibly a better form of this law, and certainly one that is more general, is as follows: *The osmotic pressure exerted by 1 mole of substance in solution is the same as the gaseous pressure exerted by 1 mole, provided the conditions of temperature and volume are identical.*

Based upon experiments with comparatively weak solutions, then, we may define the formula weight in the state of solution. And naturally the possible forms of expression are similar to those for the gaseous state. *The formula weight in the dissolved state is that weight which in the volume of approximately 22.4 liters of solvent will exert the osmotic pressure of 1 atmosphere at 0°, or a corresponding pressure at another temperature or volume;* or *is the weight which occupies such a volume of solvent that R in the equation* $R=\frac{pV}{T}$ *will have approximately the value of 84,800 when p is expressed in grams per square centimeters and V in cubic centimeters.*

One other thing has been observed in working with these comparatively weak solutions, i.e., that the osmotic pressure is independent of the nature of the semipermeable film. We may say, then, from this, and the fact that the nature of the solvent has no influence upon the pressure, provided the formula weight is the same in all solvents, *the osmotic pressure exerted by 1 mole in any solvent is a constant so long as the temperatures and the volumes of the solvents are alike.*

All our conclusions thus far have been drawn from experiments upon comparatively weak solutions, and, indeed, up to a very recent date all our knowledge of osmotic pressure was derived from such experiments as have been mentioned (together with very many others), where the concentration never exceeded a certain small value. Naturally, this left much uncertainty as to our quantitative law for osmotic pressure, and to the limits within which the observed values of formula weights held. One point in particular here is the question as to which volume, that of solution or of solvent, is to be considered as V in $pV = RT$. For experimentally it has been impossible to tell which should be chosen owing to the fact that the two volumes would be practically identical for such dilute solutions as we have considered.

All doubt on these and many other points connected with osmotic pressure, however, have been removed very recently by the brilliant work of Morse and his students,* who have measured directly, and with very great accuracy, the osmotic pressures of sugar solutions up to a concentration of 342 grams of sugar in 1 liter of water. Their results, a summary of which is given in the following tables, show that everything said above for dilute solutions holds true for the more concentrated solutions of sugar, *if the volume V in $pV = RT$ is taken as that of the pure solvent.*†

This interpretation of volume simplifies the laws of osmotic pressure very considerably, for, according to it, the osmotic pressure of a mole of substance in a liter of any solvent is the same, independent of the possible expansion or contraction caused by the solution; while if the volume of the final solution were the significant conception, the osmotic pressure would only be the same when the changes in volume caused by solution are the same in extent and direction. Whether other substances will lead

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* Am. Chem. Jour., 34, 1; 36, 1, and 39; 37, 324, 425, 558; 38, 175.

† *In all of the above laws and definitions, then, this volume is to be taken when the solution in question is so strong that its total volume is appreciably different from that of the pure solvent.*

OSMOTIC PRESSURES OF CANE SUGAR.*

Weight Normal Concentration.	Temperature of Solution.	Observed Osmotic Pressure Ostmosphere.	Theoretical Gas Pressure at same TemperatureAtmospheres.	Difference between Osmotic and Gas Pressure.	Molecular Weight Calculated from Osmotic Pressure.	Mean Molecular Weight for each Concentration.
0.1	24°.06	2.51	2.42	+0.09	327.85	325.21
	24°.23	2.55	2.43	+0.12	322.56	
0.2	20°.90	4.72	4.79	−0.07	344.96	341.87
	21°.38	4.78	4.80	−0.02	344.90	
	21°.77	4.81	4.81	0.00	339.74	
0.3	21°.67	7.24	7.21	+0.03	338.37	338.29
	19°.88	7.20	7.16	+0.04	338.20	
0.4	21°.63	9.64	9.61	+0.03	336.73	338.12
	22°.15	9.69	9.63	+0.06	337.50	
0.5	22°.62	12.06	12.06	0.00	339.59	337.89
	23°.70	12.23	12.10	+0.13	336.19	
0.6	24°.38	14.74	14.55	+0.19	335.32	335.24
	24°.10	14.70	14.55	+0.15	336.07	
	24°.24	14.77	14.54	+0.23	334.32	
0.7	23°.64	16.95	16.94	+0.01	339.39	339.45
	23°.90	16.96	16.93	+0.03	339.50	
0.8	23°.60	19.30	19.35	−0.05	339.50	339.78
	23°.69	19.39	19.36	+0.03	340.48	
0.9	24°.79	21.82	21.86	−0.04	340.19	339.51
	24°.76	21.91	21.86	+0.05	338.82	
1.0	23°.56	24.42	24.19	+0.23	336.39	339.56
	24°.58	23.98	24.28	−0.30	342.72	
		Final mean of mol. weight				337.49
H=1		Theoretical mol. weight				339.60

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* In these tables the volumes of 2 grams (not 2.02) of hydrogen is taken as *V* and is equal to 22.265 liters.

OSMOTIC PRESSURES OF GLUCOSE.

Weight Normal Concentration.	Temperature of Solution.	Observed Osmotic Pressure, Atmospheres.	Theoretical Gas Pressure at same Temperature, Atmospheres.	Difference between Osmotic and Gas Pressure.	Molecular Weight Calculated from Osmotic Pressure.	Mean Molecular Weight for each Concentration.
0.1	24°.10	2.39	2.42	−0.03	181.4	180.62
0.1	25°.10	2.42	2.43	−0.01	179.83	
0.2	24°.10	4.76	4.85	−0.09	181.77	181.94
0.2	24°.93	4.77	4.86	−0.09	182.10	
0.3	22°.20	7.12	7.22	−0.10	181.38	181.06
0.3	23°.48	7.17	7.25	−0.08	180.73	
0.4	26°.90	9.70	9.78	−0.08	180.21	180.62
0.4	26°.60	9.65	9.77	−0.12	181.02	
0.5	21°.86	12.07	12.03	+0.04	178.12	179.35
0.5	24°.17	12.00	12.12	+0.12	180.57	
0.6	22°.57	14.56	14.46	+0.10	177.62	179.62
0.6	22°.40	14.32	14.40	−0.08	180.42	
0.6	22°.30	14.29	14.45	−0.16	180.83	
0.7	22°.26	16.82	16.85	−0.03	179.18	179.63
0.7	25°.43	16.96	17.04	−0.08	179.55	
0.7	22°.70	16.75	16.88	−0.13	180.16	
0.8	23°.00	19.27	19.31	−0.04	179.16	179.76
0.8	23°.28	19.16	19.33	−0.17	180.39	
0.8	23°.64	19.25	19.35	−0.10	179.73	
0.9	23°.80	21.64	21.80	−0.16	179.87	179.99
0.9	22°.58	21.49	21.70	−0.21	180.49	
0.9	23°.10	21.63	21.74	−0.11	179.60	
1.0	22°.20	24.12	24.08	+0.04	178.46	179.04
1.0	22°.60	24.00	24.11	−0.11	179.60	
1.0	22°.10	24.03	24.07	−0.04	179.07	

H = 1. Molecular weight glucose = 178.74. Mean calculated molecular weight = 180.08.

to a similar law, and whether still more concentrated solutions of sugar will continue to follow this law (contrary to gases, where high pressures fail to give a constant when multiplied by the volume), are questions for the future. At any rate, the authors have so perfected their method that after a short time we should have a very complete quantitative knowledge of osmotic pressure, and be able to state exactly the limits within which the laws that we know will hold. Until that time, then, we may consider the laws above as binding, for they can be indirectly confirmed by other methods.

Since our definitions show the osmotic pressure of 1 mole of substance in a certain volume, it is simply a matter of calculation to find the formula weight from the osmotic pressure observed for a solution containing a known amount of substance. In general, we have the proportion

$$M : 22.4 \frac{T}{273} :: W : P,$$

where $22.4 \frac{T}{273}$ is the osmotic pressure in atmospheres of a solution of M grams in 1 liter of solvent,* and W is the number of grams in 1 liter of solvent which gives an osmotic pressure of P atmospheres. For example, at 0° C., a 2% solution of sugar, i.e., about 20 grams to 1 liter of water, gives an osmotic pressure equal to 101.6 cms. of Hg,

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* Since 1 mole in 22.4 liters of solvent gives an osmotic pressure of 1 atmosphere at 0°, and $p = \frac{1}{V}$, 1 mole in 1 liter of solvent would give a pressure of 22.4 atmospheres, or at $T°$ $22.4 \frac{T}{273}$ atmospheres.

hence the formula weight of sugar can be found from the proportion

$$M:22.4::20:\frac{101.6}{76},$$

i.e., $$M=335.$$

Just as we found a definition of formula weight in the gaseous state from the work done by expansion (pp. 29–30), we can also find one adapted to the dissolved state from the work necessary for the removal of solute, against the osmotic pressure, from the solution. Imagine a cylinder provided with a semipermeable piston, water being above it and a solution below. If work is done upon the piston, i.e. if it is lowered into the solution, pure solvent will be removed from below it to the mass of solvent above. And since $pV=RT$, the work necessary to remove the amount of solvent which has previously contained 1 mole will be equal to RT. In other words, *the formula weight in solution is that weight which can be separated from the solvent by the work* RT, or, what is the same thing, *is the weight which was previously dissolved in the volume of solvent requiring* RT *units of work to remove reversibly from the solution.* Any method, then, by which solvent can be removed from a solution will serve as a method of defining formula weight (as freezing, boiling, etc.).

In addition to the method of measuring osmotic pressure which was described above, there is one that is so simple and at the same time so striking that a short description of it will possibly make the conception more clear in the reader's mind. If in a moderately strong solution of copper sulphate we place a drop of a strong solution of potassium ferrocyanide, it is immediately surrounded by a semipermeable film of copper ferrocyanide. We have, then, a semipermeable film of copper ferrocyanide surrounding a strong solution of potassium ferrocyanide. Since the ferrocyanide is stronger than the copper sulphate (i.e., contains a greater number of formula weights per liter), water will flow *into* the bubble with a greater force than it will flow outward, and this can be proven by the swelling of the bubble and the formation of dark streaks in the copper sulphate solution, which is concentrated by the removal of water. If the copper sulphate drop is placed in the potassium ferrocyanide, the opposite effect is observed, i.e., water flows outward from the bubble, and this decreases in size. By this method, then, it is always possible to show an equal number of formula weights to the liter, for, under such conditions, no change in the size of the bubble can result. And, naturally, the formula weights need not be of the same substance, i.e., other things may be added to the weaker solution until no change in the size of the bubble is observed. After such an addition, then, we can conclude that the sum of the original number of moles to the liter of the weaker solution and those added is equal to the original number of moles in the stronger solution.

Vapor pressure.—It has been known for many years that the vapor pressure of a liquid is always depressed when substance is dissolved in it. It was not until 1887, however, that Raoult applied chemical conceptions to the physical facts, and obtained general results. Proceeding in a way similar to that used in finding a definition of formula weight based on osmotic pressure, *and always using the formula weight of the solvent as found in the gaseous state*, Raoult found that *the vapor pressure of a solution is related to that of the pure solvent as the* *number of moles of solvent is to the total number of moles in the system, i.e., of solvent plus solute.* Our definition of formula weight in the dissolved state by aid of vapor pressure, then, is not quite as simple as that based upon osmotic pressure, for it necessitates a knowledge of the formula weight of the solvent when in the gaseous state. *The formula weight in the dissolved state is that weight which when dissolved in 99 moles of any solvent depresses its vapor pressure 1%.* And, so far as we know, the formula weight by this definition agrees in each case with that found from osmotic pressure.

Expressed in the form of an equation, the above relation between the vapor pressures and the number of moles may be written

$$\frac{p'}{p}=\frac{N}{N+n},$$

where p' is the vapor pressure of the solution, p that of the pure solvent, $n\left(=\frac{w}{m}\right)$ is the number of moles of dissolved non-volatile substance, and $N\left(=\frac{W}{M}\right)$ is the number of moles of solvent *calculated from the gaseous formula weight.* This relation can also be written in other forms, i.e., can readily be transformed into

$$\frac{p-p'}{p}=\frac{n}{N+n},$$

or

$$\frac{p-p'}{p'}=\frac{n}{N}.$$

This latter form is very useful for the determination of the formula weight of a dissolved substance, the other forms being better adapted for the calculation of *vapor pressure* from known concentrations. Thus experiment shows that a solution of 2.47 grams of ethyl benzoate in 100 grams of benzene has a vapor pressure of 742.6 mm. of Hg, while pure benzene shows 751.86 mm., both at 80° C. Since $w=2.47$, $M=78$ (i.e., gaseous C_6H_6), $W=100$, $p'=742.6$, and $p=751.86$, we find from $\frac{p-p'}{p'}=\frac{n}{N}$ that $m=154$, while the formula in the gaseous state, $C_6H_5COOC_2H_5$, leads to the value 150.*

Boiling-point.—Since the vapor pressure of a solution is lower than that of the pure solvent, and the boiling-point is that temperature at which the vapor pressure becomes equal to the atmospheric pressure, the boiling-point of a solution must be higher than that of the pure solvent. Just as general relations were found for the vapor pressure and osmotic pressure, so they have been found for the boiling-point. In few words, it has been found that *1 mole of a non-volatile substance dissolved in 1000 grams of a solvent gives a definite, constant, increase of the boiling-point, which depends in value only upon the nature of the solvent and is independent of the nature of the dissolved substance.* This constant number of degrees for any one solvent we shall designate as $K_{\text{b.p.}}$ *The formula weight of any substance in the dissolved state, then, is that weight which in 1000 grams of the solvent will increase its boiling-point* $K_{\text{b.p.}}$ The value of

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* For the vapor pressure of a system of two non-miscible liquids, as well as for those cases where both solvent and solute are *volatile*, see "Elements," pp. 133, 158–167.

$K_{\text{b.p.}}$ for a solvent must consequently be known before it is possible to define a formula weight in that solvent.

Although this value $K_{\text{b.p.}}$ can be found by direct observation when the formula weight is known, i.e., by finding the effect on the boiling-point of a small amount in 1000 grams of solvent, and then calculating this weight to the formula weight, it can also be found by calculation, i.e., by using the conception of osmotic pressure. In this case we separate, as vapor, the solvent from the solution, and the amount of work necessary for this must be equal to that necessary for an osmotic separation (p. 66). Since to separate 1 mole of substance from 1000 grams of solvent requires osmotic work, by definition, equal to $2T$ calories; and the separation of this weight of solvent as vapor, calling the latent heat of evaporation w_e would require the thermal work $1000w_e$, we can now apply the second law of thermodynamics and obtain a general equation by which $K_{\text{b.p.}}$ can be calculated. If the osmotic work is to be done simply by the transformation of heat, it is quite evident that the heat must be absorbed at a higher temperature than T, the boiling-point of the pure solvent, and just so much higher that the heat available, i.e., the heat of evaporation of the pure solvent at T, $1000w_e$ can do the work $2T$ calories. We have, then, page 51:

$$\frac{2T}{1000w_e}=\frac{\Delta T}{T},$$

or

$$\Delta T_{\text{b.p.}}=\frac{0.002T^2_{\text{b.p.}}}{w_e}=K_{\text{b.p.}}$$

The boiling-point constant, the increase of the boiling-point of any solvent due to the presence of 1 mole of sub-

stance in solution in 1000 grams of solvent, is equal to 0.002 times the square of the absolute boiling-point of the solvent, divided by its heat of evaporation for 1 gram.

Some values of $K_{\text{b.p.}}$, as found by experiment (they agree with the calculated ones), are as follows: Benzene, 2.67; chloroform, 3.66; carbon disulphide, 2.37; ether, 2.15, water, 0.52, carbon tetrachloride 4.8, ethyl alcohol, 1.15; methyl alcohol, 0.88, etc.

Since the increase of the boiling-point is known for a solution containing 1 mole in 1000 grams, the molecular weight of a substance in solution, or the increase of the boiling-point caused by the solution of any amount of substance, can be found by aid of a simple proportion.

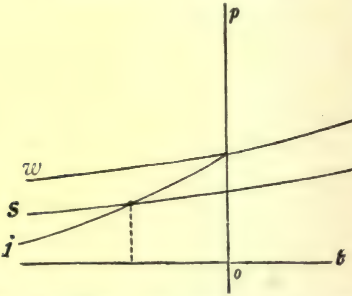
We have, in general,

$$M : K_{\text{b.p.}} :: W : \Delta t,$$

where M is the formula weight, $K_{\text{b.p.}}$ is the increase when M grams are present in 1000 grams of solvent, and Δt is the increase for W grams in 1000 of solvent. Knowing any three terms, then, the other one may be readily calculated.

This value $K_{\text{b.p.}}$ is one-tenth the value of the conventional *molecular increase of the boiling-point*, which refers to 1 mole in 100 grams, and is much to be preferred as it can always be readily verified by experiment, which is not possible for the conventional value.

Freezing-point.—The fact that the vapor pressure of a solution is lower than that of the pure solvent necessitates the depression of the freezing-point of a solvent in which substance is dissolved, i.e., causes pure solvent to separate from the solution by freezing at a *lower* temperature than is observed for the pure solvent. This relationship, perhaps, is not so obvious as is the one for the boiling-point, but a glance at the figure below will make it quite clear. Here *ww* is the vapor-pressure curve for water, *ss* that for the solution, and *i* that for ice. At the point $t = 0°$ C., ice and *water* have the same vapor pressure, and consequently are in equilibrium. The *solution* and ice, however, will only be in equilibrium at the temperature corresponding to the point of intersection of their curves, so that the freezing-point of the solution must always lie below that of the pure solvent, if its vapor pressure does. And the more substance there is in solution the lower will be the curve *ss*, and the lower the freezing-point, i.e., the point of intersection.



Exactly as with the boiling-point, it has been found that *1 mole of substance dissolved in 1000 grams of any solvent will depress the freezing-point of this* $K°_{\text{f.p.}}$, *where the value of* $K_{\text{f.p.}}$ *depends only upon the nature of the solvent. And just as the boiling-point law holds only when pure solvent and no solute separates, i.e., where the solute is non-volatile, so here this law only holds when it is pure solvent which separates in the solid state.** One thing is

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* In case these conditions are not fulfilled, it is still possible to get

to be observed especially in regard to freezing. If the liquid is overcooled and solid is caused to separate by stirring, it is to be remembered that the freezing-point observed is not that of the original solution, but of the stronger solution which is produced by the loss of the solvent solidifying, for the freezing-point of a solution is that temperature at which it exists in equilibrium with the solid solvent.

The value of $K_{\text{f.p.}}$ can be determined here in a similar way to that used for $K_{\text{b.p.}}$ in the boiling-point, and can also be calculated by an analogous method of reasoning. Since to remove 1 mole of any substance from 1000 grams of solvent requires, as given above, the work $2T$ calories; while to separate the substance by freezing it out would require the thermal work $1000w_{\text{f}}$ calories (where w_{f} is the latent heat of fusion of 1 gram), we can proceed as before to apply the second law of thermodynamics. If the work of separation were to be done solely by the transformation of heat into work it is evident that the heat must be evolved at a lower temperature than T, and just so much lower that the heat available, $1000w_{\text{f}}$, at T can do the work $2T$ calories. We have, then, as above

$$\frac{2T}{1000w_{\text{f}}}=\frac{\Delta T}{T},$$

or

$$\Delta T_{\text{f.p.}}=\frac{0.002T^2_{\text{f.p.}}}{w_{\text{f}}}=K_{\text{f.p.}}$$

The freezing-point constant, the depression of the freezing-point of any solvent due to the presence of 1 mole of substance in solution in 1000 grams, is equal to 0.002 times the square of the absolute freezing-point of the solvent divided by its heat of fusion for 1 gram. This constant, $K_{\text{f.p.}}$ is also one-tenth the value of the conventional value of the *molecular lowering of the freezing-point* (referring to 100 grams of solvent), and is to be preferred for the reasons given above.

Values of $K_{\text{f.p.}}$ are as follows: Acetic acid, 3.88; benzene, 4.9; phenol, 7.5; water, 1.86, etc.

Here, also, we have the general relation

$$W : K_{\text{f.p.}} :: W : \Delta t,$$

where M grams in 1000 grams of solvent produce a depression of $K_{\text{f.p.}}$ in the freezing-point and W grams in the same weight leads to a depression of $\Delta t°$. And, just as above, when any three of these are known the fourth may be calculated.

Considering the four relations above we find then that *osmotic pressure depends upon the number of moles of substance per liter of solvent, the vapor pressure upon the number of moles of substance in a number of moles of solvent, and the freezing-point depression and boiling-point increase upon the number of moles of substance per 1000 grams of solvent.* And since knowing the density we can find the weight of 1 liter of solvent, and knowing its molecular weight as a gas we can find the number of moles of solvent equal to 1 liter or 1000 grams, it is easily possible to find from any one of the four above results the other three. Thus, suppose a water solution gives an osmotic pressure of 1 atmosphere at 0°, and assuming the formula weight to be independent of temperature, we wish to find the freezing-point, boiling-point, and vapor pressure of the solution. Since 1 mole in 1 liter of water or any other solvent at 0° gives an osmotic pressure of 22.4 atmospheres, in a solution with an osmotic pressure of 1 atmosphere we must have x moles per liter, the value of x being determinable from the proportion

$$22.4 : 1 :: 1 : x.$$

The boiling-point of this solution, then, if the solvent be water, will be $(x \times 0^\circ.52) + 100^\circ$, and the freezing-point $-(x \times 1^\circ.86)$; while the vapor pressure will be p' in

$$\frac{p'}{p} = \frac{\frac{1000}{18}}{\frac{1000}{18} + x},$$

where p is the vapor pressure of pure water at 0°. If the solvent is not water, then, of course, it would be necessary first to transform the x moles per liter into the number of moles per 1000 grams, by aid of the density of the solvent, and employ this value in the place of x for the freezing- and boiling-point; and to use this as well as its molecular weight, in the place of 18, to find the vapor pressure.

Or, if the vapor pressures of solvent and solution are given, we can first find the ratio of moles of solute to moles of solvent (based on the gaseous formula weight) from $\frac{p - p'}{p'} = \frac{n}{N}$, and then calculate, for example, the number of moles dissolved in 1 liter of water (i.e., where $N = \frac{1000}{18} = 55.5$).

It will be seen from what has been said above that a solution as we have considered it can be defined as follows: *A solution is a liquid mixture which changes its properties when a portion has been separated by either boiling or freezing.* Thus the constant boiling solution of hydrochloric acid in water is not a solution in this sense, for on boiling, it distils over unchanged, and that which is left has the same properties (vapor pressure and boiling-point) as the original solution.

Coefficient of distribution.—One exceedingly important relation has been observed as to the distribution of a substance between two non-miscible solvents. This relation, indeed, is the one mentioned above (p. 61), by which the change in the formula weight during transition from one solvent to another is detected. When a solution is agitated with an equal volume of another solvent, which can dissolve the solute, but does not form a homogeneous mixture with the first solvent, it is found that the distribution in the two layers is either the same for all original concentrations of solute in the first solvent, or differs with that concentration. Thus when, by our definitions, the formula weight is the same in the two solvents (succinic acid dissolved in water and shaken with ether, for example) the ratio of the concentrations in the two layers is independent of the original amount dissolved in the first solvent. When the formula weights, by definition, differ in the two solvents, however, the ratio depends upon the original concentration, and in such a way, as we shall see later, that it is possible for us to calculate the relation of the formula weight in one to that in the other.

This relation is not restricted to a solution containing one solute, for it has been observed that when several solutes are present each is distributed as if it alone were present, and its behavior is entirely unaffected by the others.

Electrolytic dissociation or ionization.—In obtaining our definitions of formula weight, as given above, we have assumed in each case, as a temporary supposition, that the formula weight in the dissolved state is identical with that in the gaseous state. In this way a constant relation has been observed for a large number of substances and our temporary assumption is justified. Sooner or later, in all cases, however apparently abnormal results (the formula weight being greater than that in the gaseous state) are observed, and it becomes necessary to decide whether the definitions so obtained are incorrect, or whether in these abnormal cases there is not some specific influence which has not been considered. Since as a rule these abnormalities disappear when the substance is dissolved in another solvent, the relation then being the same as for substances which behave normally in all solvents, the only conclusion possible is *that the definitions for formula weight in all these cases are correct, and that the apparently abnormal results are really due to a change in the formula weight.* This conclusion, indeed, is the only one possible in such cases, for all definitions of formula weight in solution, independent of the principle upon which they are based, give sensibly the same formula weight when carried out with the same degree of accuracy.

In other cases, and these form a very large class composed of inorganic salts, bases, and acids, the same question as was considered above also arises, but here the formula weight (by definition) appears *smaller* than the gaseous formula weight. Again the abnormality may be due to incorrect definition, or to the fact that a specific action causes the formula weight to change. And again here we find that the solvent has a great influence, i.e., in some solvents abnormal results are observed, while in others the behavior is quite normal (according to definition). Thus Arrhenius observed that *all those substances, and only those, which give abnormally large osmotic pressures in solution are capable of conducting the electric current, and if they are dissolved in other solvents, in which they behave normally, they lose this power.*

Arrhenius determined the electrical conductivity of such solutions in terms of molecular conductivity; the molecular conductivity of a solution being defined as the reciprocal of the resistance (in ohms) of the volume of liquid which contains one formula weight of the substance, i.e., the weight of the generally accepted formula, the electrodes being 1 cm. apart and large enough to contain between them the entire amount of solution. This value, naturally, is not found directly, but is calculated from that value found for a centimeter cube of the solution. (See Chapter VII.) In this way, always having 1 mole (according to the accepted formula) between the electrodes, he found that the more dilute the solution the greater is the molecular conductivity. In many cases, indeed, he was able to reach such a dilution that the molecular conductivity attained a maximum value, which is unaffected by further dilution. This molecular conductivity at infinite dilution, as it is called, is designated by the term μ_{∞}, that value for any dilution V being designated by μ_v

From this it is apparent that the solution undergoes some kind of a change as the result of dilution; and the investigation of such solutions at various dilutions shows, indeed, that the formula weight (according to definition) also changes with the dilution, the formula weight decreasing to a minimum, constant value, which for binary electrolytes is one-half the formula weight of the substance dissolved. We may conclude, then, that the breaking down of the formula weight of a substance in a solution is very intimately connected with the power it possesses of conducting the electric current.

These facts formed the starting-point of what is known at present as the "theory of electrolytic dissociation."

As this theory to-day is much misunderstood by many, and is the subject of much speculation on the part of others, it will be necessary for us to consider carefully just what is fact and what assumption, and to see clearly which portions are hypothetical and which are destined to remain under any hypothesis or lack of hypothesis; in other words, which are experimental facts. It may be said, however, that that which is hypothesis in this theory is unessential, as far as the use of the data is concerned, and the only hypothesis present, as we shall consider it, is that inherent in the terminology, which is a relic of the atomistic hypothesis and utterly beyond our power either to prove or disprove.

The salient facts which have been grouped in this theory, for it is a theory in the sense that it is a law of nature holding between certain limits, although these are not as yet definitely fixed, are as follows:

(1) The molecular conductivity of certain substances in water is found to increase up to a maximum, constant value, and this increase is the result of dilution.

(2) Those solutions which conduct the current also give abnormal osmotic pressures, freezing-points, boiling-points, and vapor pressures; in other words, the formula weight (according to the above definitions) decreases with increased dilution, and finally reaches a minimum value, which, for binary electrolytes, is one-half the accepted formula weight of the substance.

(3) Those substances which in water conduct the current and give abnormal osmotic pressures, depressions of the freezing-point and vapor pressure, and increases of the boiling-point, give normal values when dissolved in other solvents in which they do not conduct.

(4) The nearer the value of μ_v is to that of μ_∞, the more abnormal the value of the osmotic pressure, etc. (formula weight), of the solution. And the solution for

which μ_∞ is found also gives the maximum osmotic pressure, i.e., the minimum formula weight.

(5) The molecular conductivity of a solution at infinite dilution is an additive value, i.e., is equal to the sum of the conductivities of the substances of which it is composed. The meaning of this is as follows: The molecular conductivity at infinite dilution of, for example, potassium chloride plus that of nitric acid minus that of potassium nitrate is found to be equal to that of hydrochloric acid. In other words,

$$\mu_{\infty \mathrm{KCl}} + \mu_{\infty \mathrm{HNO_3}} - \mu_{\infty \mathrm{KNO_3}} = \mu_{\infty \mathrm{HCl}}.$$

For this to be true, and it is true in general for all substances, it is necessary that the molecular conductivity of such a substance in solution be the sum of two values which are independent each of the other. Chlorine, for example, as the constituent of an electrolyte, at the dilution giving μ_∞, has the same conducting effect when part of a compound with one element as it has when combined with any other. It is possible, then, to find the value of μ_∞ for any binary electrolyte when the values for the elements composing it are known. In other words, the conductivities of the solution as produced by the presence of any element can be calculated; and from these values, by summation, the value of μ_∞ for any binary electrolyte can be found.

(6) When a solution is electrolyzed, the products of electrolysis appear instantaneously at the electrodes so soon as the circuit is completed. This indicates (since the solvent, water, does not conduct beyond a very small extent) that whatever does carry the current through the liquid is charged with electricity even before the current is applied, for the conduction is due to the dis-

solved substance, and the speed of movement of the substance can be measured, so that it is no question of matter being electrically charged at one electrode before carrying this charge bodily through the solution to the other. (See Chapter VII.) Further, it is observed that the same amount of electricity, 96,540 coulombs, is necessary for the separation of one equivalent weight (in grams) of any element; in other words, that 96,540 coulombs of electricity are transported through the liquid with each equivalent weight (in grams) of an element. (Faraday's Law, see Chapter VII.)

(7) The properties of electrolytes are found to be the sum of the properties of the products observed during electrolysis. Thus any solution giving off chlorine on electrolysis, excluding secondary reactions, will precipitate silver from its solution as the chloride. And if chlorine cannot be produced in any way by the electrolysis, silver will not be precipitated as chloride from its solutions. And, on the other hand, silver is only precipitated by chlorine when contained in a solution from which silver can be deposited by the current by primary action.

The catalytic effect of acids on the inversion of sugar as well as on the decomposition of methyl acetate is found to be proportional to the ratio $\frac{\mu_v}{\mu_\infty}$ for the acid; and when a large amount of a salt of this acid is added to the acid this effect is decreased. But this is only true when the salt added is an electrolyte.

All copper solutions, when very dilute, show the same blue color, and this also depends upon the ratio $\frac{\mu_v}{\mu_\infty}$, and can also be changed, as the effect of acids was above, by the addition of a large amount of an electrolyte which contains the same acid radical as the copper salt in question.

Further, when the colored copper solution is superimposed upon a colorless solution of another salt, the blue color boundary is observed to move with the current, i.e., to the cathode, where copper is deposited. Hence the substance which is moved in this direction contains only copper, the negative radical separating at the anode. In other words, copper in solution, when it conducts the current, is blue.

8. Observation shows that when an element is separated on one electrode, anode or cathode, it is always separated on that one by primary action; in other words, the sign of the electricity transported by an element is always the same. And unless an element in the pure state, when dissolved in water, reacts with the water it does not conduct the current. This circumstance is assumed to be due to the fact that only one kind of electricity could be carried by the substance, and hence it produces no conduction.

The question now arises as to what theory can be found to correlate these facts and observations so that the generalization thus obtained may be employed to foresee other facts, and applied to other observations, that they, in their turn, may be elucidated and generalized. By the word theory, then, we do not mean a hypothesis, in which something not observed is added to the facts to "explain" them, but only a generalization of observed facts. In other words, what law of nature, holding within definite, if small, limits, can be obtained from the above experimental facts when considered together?

The generalization which has been made from these facts is known as the theory of electrolytic dissociation, and, considering those portions which are free from hypothesis and fulfil the above conditions, in other words, omitting the hypothetical portions which it has attained since the time of its inception, we find in it, within certain limits, a definite law of nature.

The principal points of this theory are summarized below in brief form, and will each be expanded in the later portions of the book.

A substance in solution, which conducts the electric current, is dissociated or ionized into its constituents, and these constituents, when secondary actions are excluded, appear at the electrodes during electrolysis. The extent of the ionization or dissociation in any solution being given at the dilution V (number of liters in which 1 mole, according to the accepted formula, is dissolved) by the ratio $\frac{\mu_v}{\mu_\infty}=\alpha$.

These products of ionization or dissociation are charged with electricity, 96,540 coulombs being carried by the gram equivalent of any element (see (6) above). A further proof of this charged state of ionized matter is given by the fact that not only is the current carried by a solution dependent upon the number of gram equivalents transported, but, as we shall see later, any other means of depositing the constituents of the solution upon the electrodes liberates an amount of electricity which depends also upon the number of gram equivalents deposited. And all cells in order to give a current must contain electrolytes, i.e., solutions which are ionized.

Since a solution which by conductivity is shown to be completely ionized, or practically so, leads to a formula weight, by osmotic pressure or any of the other methods, of one-half the value expressed by the formula weight, then, from the case of hydrochloric acid in solution, where we can designate the process by the equation

$$HCl = H^{\cdot} + Cl',$$

the formula weight of the hydrogen and chlorine in the ionic state, according to our definition of formula weight, must be synonymous with the combining weight.

The ionic state, then, is an allotropic form of the ordinary state of the constituents, and differs from that in being charged with electricity, in having less energy than when in the gaseous state, and in always being transformed into the ordinary state on the loss of its charge of electricity.

Since the constituents in the case already mentioned, and in general in all cases, show a formula weight (by the definitions) which is the same as the combining weight, it is possible to determine α, the degree of ionization, by osmotic-pressure, etc., measurements, or from the average formula weight of the substance in solution, as determined by osmotic pressure or any of the other methods. If, for example, we start with one formula weight of hydrochloric acid in a solution, and α moles of it are ionized, the total number of moles will consist of $(1-\alpha)$ of un-ionized HCl and α moles each of $H^{\cdot}$ and Cl' (where the dot indicates positive electricity as the charge and the accent negative). The total number of moles in the volume of the solution will go then from 1 to $(1-\alpha)+2\alpha$, i.e. $1+\alpha$, and the ratio of osmotic pressure when entirely un-ionized to that when partially ionized will be the same as this. In other words, if the formula weight in a certain volume *should* give the osmotic pressure p_0, it will give, when ionized to the extent α, the pressure $p' = (1 + \alpha) p_0$. Since the number of moles (by definition) shown by the same weight is thus increased, the formula weight will be smaller, and the relation between the two values of the formula weight will be $M'(1 + \alpha) = M$, where the M refers to substance if it were un-ionized, i.e., is the accepted formula weight of the substance, and M' is the formula weight (by definition) observed in the dissolved state.

Just as with gaseous dissociation, the ionization of a substance in solution is affected by the presence of one of the products of the ionization, and later, when we consider the quantitative effects for gases, we shall study the quantitative effect for substances in solution.

Owing to the fact that the constituents produced by the ionization of a substance in solution are called ions (in the Faraday sense of charged atoms) it is usually assumed that ionized matter also has an atomic structure. As this is hypothesis, if we are to follow our plan, we must either use the word with an altered meaning or employ another word *representing the same facts* in its place. *We shall use the word ionization here only in the sense that it is expressive of the experimental relation* $\frac{\mu_v}{\mu_\infty}$, *and employ the expression ionized matter to designate all that is ever legitimately included in the word ion, i.e., all the facts and none of the hypotheses.*

Summarizing our argument, the application of the experimental definitions of formula weight in solution (derived as given above) indicates that certain substances are decomposed in certain solvents, the fraction decomposed being α in the expressions $M'(1 + \alpha) = M$ (according to any of the methods) and $\alpha = \frac{\mu_v}{\mu_\infty}$, and increasing with the dilution up to the value which gives $M=2M'$. This is, of course, only true for substances giving at the maximum dilution a formula weight of one-half the generally accepted one; in general the fraction decomposed can be found from $[(1-\alpha)+i\alpha]M'=M$, where at the maximum dilution $i=\frac{M}{M'}$. That this is really the result of a decomposition, and not merely the failure in these cases of the definitions of formula weight in solution, is evidenced by the above facts and many others, given later. And that this ionized matter which is formed is electrically charged is also not to be doubted, as well from the above facts as from the general agreement of the results by electrical and other methods.

It is always to be remembered, then, that when we speak of ionization we mean something which can be defined in terms of experiment, and is free from hypothesis. And the same is true of ionized matter, so long as we do not assume for it a certain structure such as is naturally assumed in the impression made by the expressions "an ion" or "the ions."

Later we shall find that starting with this conception for a simple substance we can derive other experimental definitions, not only for ionization, but also for the amount of any one definite kind of ionized matter which is present with any number of other kinds.

One fact may be mentioned here which indicates what a very marked difference dilution makes in the behavior of a substance, and which decidedly supports the conclusions we have just drawn. Although hydrochloric acid is more volatile than hydrocyanic acid, it has been observed that from a mixture of the dilute acids (0.1 molar of HCl) it is possible to distil the HCN quantitatively (provided the dilution of the HCl is retained at about this value by the frequent replacement of the water lost). In the light of the above theory the difference between the two acids in solution is that while $\frac{\mu_v}{\mu_\infty}$ is nearly equal to 1 for HCl, it is very small for HCN. In other words, HCl is composed principally of the ionized constituents $H^{\cdot}$ and Cl', which cannot produce HCl gas without going through the state HCl in solution, and that is prevented by the nearly constant dilution which is retained during the distillation. Any gaseous substance, then, which in solution is largely ionized is more difficult to distil from the liquid than an un-ionized or less ionized one. The HCN, being dissolved and retained in this state in solution, can be expelled readily just as any other gas which undergoes no great change in solution. This method, indeed, was discovered as the result of such theoretical reasoning, and it is but one example of the many practical applications of the above generalization.*

It is not to be imagined that the facts mentioned above are the only ones leading to these conclusions, for later, throughout our work, we shall find occasion to consider other things which will confirm each of the steps leading to the final conclusion. In other words, it is not to be thought that the whole theory has been described in this place, or that, because some of the points mentioned are not clear, the theory itself is to be condemned, for many of the points can only be brought out after considering certain other methods which will enlarge our horizon. It may be said, however, that these further aids but

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* For details of the separation see Richards and Singer, Am. Chem. J., 27, 205, 1902.

confirm and make more evident the truth of the conclusions we have arrived at. At the same time we must not forget that we have been speaking of this subject as lying within certain limits, and so cannot expect our conclusions to hold outside of these, nor to condemn them because they do not. The relation of substances in non-aqueous solvents to a certain extent is different, and consequently these conclusions could not be expected to hold. As a matter of fact, the conduction relations for these solutions are so utterly different from the aqueous ones that it would be impossible to attempt to consider them together in the light of our present knowledge. All of these points will be discussed more fully later, however, and the limits stated, within which our conclusions in general will hold. It is to be remembered, though, that simply because our theory does not hold for solutions in certain non-aqueous solvents (solutions which show no similarity in behavior to the aqueous ones, and which may or may not be solutions as we consider them, but may involve an entire rearrangement of the composition of the solvent, or solute, or both), it should not be considered as false and of little use, for the two kinds of systems are so different that it would be impossible to imagine from our present knowledge that both are subject to the same laws.

The values for α, the degree of ionization, for a few electrolytes are given below for varying conditions. These are the values as found from the ratio of molecular conductivities, since that method is apparently the most delicate one which we possess for this purpose.

Naturally, instead of first finding the formula weight in solution, by aid of one of the practical definitions, and then calculating α from the relation of this value to the generally accepted formula weight, we can find

DEGREES OF IONIZATION.

V	$AgNO_3$ 25° α	*V*	$AgNO_3$ 60° α
16	0.828	16	0.841
64	0.899	64	0.909
512	0.962	512	0.964
	40°		HCl 25° α
16	0.832		
64	0.904	2	0.876
512	0.965	16	0.955

V	HBr 25° α	HI 25° α	*V*	KCl 25° α	NaCl 25° α	NH_4Cl 25° α	LiCl 25° α
2	0.897	0.895	2	....	0.737	.....	.....
4	0.932	0.926	10	0.86	0.842	0.852	0.803
8	0.950	0.945	100	0.94	0.937	0.94	0.907
16	0.965	0.963	1000	0.98	0.982	0.979	.....
			10000	0.993	.....	.....	.....
			16667	0.996	.....	.....	.....

directly the number of moles present, when we have started with 1 formula weight (the accepted value) in a certain volume of liquid. If the commonly accepted formula weight in a certain volume should give the osmotic pressure P, and the substance is ionized, the observed osmotic pressure would be $[(1-\alpha)+i\alpha]P$, and the vapor pressure would be that calculated for $n[(1-\alpha)+i\alpha]$, where n is the number of moles which would be present without ionization. In a corresponding way, also, the boiling-point of a solution containing 1 accepted formula weight in 1000 grams of solvent would be $[(1-\alpha)+i\alpha]K_{\text{b.p.}}$, higher than the pure solvent, and the freezing-point would be depressed by $[(1-\alpha)+i\alpha]K_{\text{f.p.}}$ The freezing-point depression produced by the dissociation of 1 accepted formula weight in 1000 grams of solvent can thus be used to find the ionization as follows: A 0.0107 molar solution of KOH (assuming this formula) depresses the freezing-point 0°.0388. If it were un-ionized, it could only depress the freezing-point by an amount equal to

$$1:1.86::0.0107:x,$$

where x equals 0.0199, but it depresses it actually 0°.0388, hence we can find α by aid of the proportion

$$1:1+\alpha::1.86:0.0388,$$

i.e., $\alpha=0.95$, the solution is 95% ionized into $K^{\cdot}$ and OH'.

Calculation of ionization in general.—Certain relations have been observed connecting the extent of the ionization of salts of the same type, and those of different types, which are very convenient approximations. Thus Noyes and Melcher (Carnegie Publication, No. 63, 29) show the *following rough proportionality between the* UN-IONIZED *fraction of a salt at any concentration and the product of the valences of its ions.* In the table below, under *A*, are given the mean values of the percentage of un-ionized salt $100(1-\alpha)$ for the neutral salts of several types at the concentration 0.04 moles per liter and for the one-one salts at 0.08 moles per liter, and under *B* are given the ratios of these values to the product of the valences (V_1, V_2) of the ions.

V_1V_2	Moles per Liter.	18°		100°		156°		218°		281°		306°	
		A	B	A	B	A	B	A	B	A	B	A	B
1×1	0.04	12	12	15	15	17	17	20	20	25	25	31	31
1×1	0.08	15	15	18	18	21	21	25	25	31	31	39	39
1×2	0.04	28	14	34	17	40	20	15	25	65	32	74	37
2×2	0.04	55	14	68	17	81	20	93	23	..	..	..	..

Examples of the three types illustrated here are KCl (1×1), $BaCl_2$ (2×1), and $MgSO_4$ (2×2). When the comparison is made at the same equivalent concentration here (i.e., the 0.08 for the 1×1), the principle seems to hold satisfactorily, even at the high temperature when the ionized portion is reduced to 26% for the 1×2 salt and to 7% for the 2×2 salt.

Another and similar relation is given by Bodländer, with Storbeck and Eberlein (Zeit. f. anorg. Chem., 31, 19, and 39, 195). According to this *the ionization of any salt is equal to that for a 1×1 salt, at the same* EQUIVALENT *dilution, raised to a power equal to the product of the valences of the ions of the salt, of which the ionization is to be determined.* Examples of this relationship are given in the tables below, all dilutions being *equivalent normal*,

Dilution (liters per equivalent)	100	20	10	2
α (ionization of KCl)	0.94	0.88	0.85	0.78
α^2	0.88	0.77	0.73	0.61
α for $BaCl_2$	0.87	0.77	0.74	0.60

Liters per equivalent	KCl	Na_2SO_4		$K_3Fe(CN)_6$		$K_4Fe(CN)^6$		$Na_6C_{12}O_{12}$	
	α	α'	α^2	α'	α^3	α'	α^4	α'	α^6
32	0.90	0.81	0.81	0.75	0.74	0.67	0.67	0.50	0.55
64	0.93	0.86	0.87	0.80	0.80	0.74	0.74	....	....
128	0.95	0.90	0.90	0.85	0.85	0.81	0.81	0.65	0.73
256	0.96	0.92	0.92	0.89	0.89	0.87	0.87	....	....
512	0.97	0.94	0.94	0.92	0.92	0.91	0.89	0.74	0.83
1024	0.98	0.96	0.96	0.95	0.94	0.94	0.93	0.89	0.89

Here α is the actually determined value, α^2, α^3, α^4, and α^6 being the values of α for KCl raised to a power in each case equal to the product of the valences of the ions formed from the salt. Thus we have $2Na^{\cdot}$ and SO_4'' (1×2); $3K^{\cdot}$ and $Fe(CN)_6'''$ (1×3); $4K^{\cdot}$ and

$Fe(CN)_6^{IV}$ (1×4); and finally 6Na· and $C_{12}O_{12}^{VI}$ (1×6); the concentrations for the $^1/_{32}$ normal being $^1/_2(^1/_{32}Na_2SO_4)$; $^1/_3(^1/_{32}K_3Fe(CN)_6)$; $^1/_4(^1/_{32}K_4Fe(CN_6))$; and $^1/_6(^1/_{32}Na_6C_{12}O_{12})$. Whether this relationship holds at other temperatures and for other salts is apparently not as yet known; if it does it is certainly a very valuable relation.

The thermal relations of electrolytes. — *Two salt solutions which are so dilute that the ratio* $\frac{\mu_v}{\mu_\infty} = 1$ (p. 83) *do not evolve or absorb heat when mixed, provided no chemical reaction takes place between them.*

This fact was first observed by Hess and has been confirmed by all observers since.

Another experimental fact observed to hold for solutions of electrolytes is as follows: *When an acid is neutralized by a base, both being in so great a dilution that for each* $\frac{\mu_v}{\mu_\infty} = 1$, *which is also true for the salt formed, the heat evolved is equal to 13,700 cal. and is independent of the nature of the base and acid used or the salt formed, so long as this latter at that dilution fulfills the condition* $\frac{\mu_v}{\mu_\infty} = 1$.

These facts, taken in connection with those mentioned above (pp. 76–90) and the conclusions arrived at there, are not so startling as one might imagine at first glance. Since for the acid and base we have the relation

$$\mu_{\infty \text{acid}} - \mu_{\infty \text{base}} - \text{constant} = \mu_{\infty \text{salt}},$$

where the constant is independent of the nature of either the acid or the base.

and, since the salt is observed to have a formula weight (by definition) equal to one-half the generally accepted formula weight, i.e., is completely ionized according to all the possible methods of measurement, it is quite certain that it is made up of the substances previously composing the acid and base *in the same state as that in which they existed in them.* In other words, expressing the chemical equation in accord with the experimental facts above, we have

$$H^{\cdot}+A'+M^{\cdot}+OH'+nH_2O=A'+M^{\cdot}+(n+1)H_2O,$$

where n represents the number of moles of water (H_2O) present in the system before the reaction.

Since the conductivity shows the constituents of the salt (the two kinds, + and −, of ionized matter) to be present in the same form they were in originally, the only portion of the reaction which could possibly involve heat is the formation of water from ionized hydrogen ($H^{\cdot}$) and ionized hydroxyl (OH'). As we know that hydrogen and hydroxyl in the ionized state can exist together to but an infinitesimal extent (for pure water conducts only very slightly), the following conclusion is certainly justified: *When an acid unites with a base (at any rate in the condition in which we have assumed them) the cause of the reaction is the inability of ionized hydrogen to exist in the presence of ionized hydroxyl beyond an exceedingly small amount, and the heat of the neutralization (for this case) is that heat which is evolved during the formation of water from its constituents in the ionized state in this way, i.e., 13,700 cals. for each mole of* $H^{\cdot}$ *and* OH' *(by definition) forming one mole of* H_2O.

By a method which we shall consider later (Chapter VI) it is possible not only to show the presence of, but to calculate accurately, the heat involved in the ionization of a substance. When the acid and salt are completely ionized, for example, and the base but slightly, it is possible to show just how much extra heat (either positive or negative) is involved by the further ionization of the base. For the partly ionized base must increase in ionization as its ionized OH′ is used up, since the more dilute the solution of the base the greater, up to a certain point, is its ionization.

If both the acid and the base are but partly ionized the result will differ still more, for heat will be absorbed or evolved by the further ionization of both of these. In general, we shall have, then, if the salt, also, is not completely ionized, i.e., if more heat is liberated by its undissociated product being formed,

$$q=x-w_3(1-\alpha_3)+w_2(1-\alpha_2)+w_1(1-\alpha_1),$$

where

α_1 = ionization of the acid, w_1 = its heat of ionization;
α_2 = " " the base, w_2 = " " " "
α_3 = " " the salt, w_3 = " " " "
x = heat of association of 1 mole of ionized H˙ with 1 mole of ionized OH′ to form 1 mole of un-ionized H_2O;

i.e., *the heat generated by the neutralization of an acid by a base is equal, for each mole of water formed, to 13,700 cal. plus the heat evolved by the amount of un-ionized salt formed plus the sum of the heat evolved in the completion of the ionizations of the acid and the base.* The heat evolved by the *association* of the salt is of course equal to $-w_3(1-\alpha_3)$ which is the heat of *dissociation.*

Naturally, the negative value of the heat of association of ionized $H^\cdot$ with ionized OH' is the heat of ionization of water, i.e., the heat necessary to form 1 mole of ionized $H^\cdot$ and 1 mole of ionized OH' from water.

Later we shall consider this relation more in detail, i.e., after we have studied the method to be used for the measurement of the heat of dissociation.

It is obvious from the above that the thermal properties of electrolytes are additive when they are in such a dilution that they fulfill the condition $\frac{\mu_v}{\mu_\infty}=1$; and when not in this condition the change in the thermal effect depends upon the amount of heat involved in causing them to attain this state.

When a precipitate is formed in such a solution (i.e., when a chemical reaction takes place, which was excluded above) it is often possible to find its heat of formation just as we found that of water above. An example of this is the following:

$$\begin{aligned} &Ag^\cdot Aq+NO_3'Aq+Na^\cdot Aq+Cl'Aq \\ &\qquad =AgClAq+Na^\cdot Aq+NO_3'Aq+15{,}800 \text{ cals.} \end{aligned}$$

or

$$Ag^\cdot Aq+Cl'Aq=AgClAq+15{,}800 \text{ cals.}$$

i.e., when 1 mole of un-ionized AgCl is formed in a solution from the ionized silver and ionized chlorine 15,800 calories are evolved. Conversely, if 1 mole of AgCl were dissolved, this amount of heat would be absorbed, i.e., the heat of solution of a substance is equal to the negative value of the heat of precipitation.

Although it is not always possible, we can find the heat of formation in solution in still another way. The principle of this is as follows: By electrical measurements it has been possible to find the amount of heat involved when 2 grams of gaseous hydrogen form 2 grams of ionized hydrogen in solution. This value is approximately equal to 4 J,* but since there is some uncertainty about its exact value, it is usual to assume it equal to zero. Later, then, when this value has been accurately determined, the results found in this way can be readily recalculated. From this value, by dissolving a metal in a completely ionized acid, i.e., by the substitution of metal in the ionized state for the hydrogen, which is evolved as a gas from that state, we can observe directly the heat of formation of the ionized metal from massive metal. By then determining the heat of solution of a completely ionized salt of this metal, the heat due to the negative radical in the ionized state can be determined readily, for the heat of solution of the salt is equal to the sum of the heats of ionization of the constituents, of which we assume that of hydrogen to be zero.

In this way the table given below has been prepared by Ostwald. In order to find the heat of formation of a salt it is only necessary to obtain the sum of the heats due to the kinds of ionized matter into which it decomposes, taking into account the valence of the ionized matter as indicated by the dots for the electro-positive and the accents for the electro-negative substances.

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* One joule (j) = 10^7 ergs = 0.2391 cal., i.e., 1 cal. = 4.183 j. A unit a thousand times as great as j is designated by J, and we find 1 J = 239.1 cal. = 10^{10} ergs, i.e., 1 cal. = 0.004183 J.

Cathion Matter.	J = joules × 10³.		Anion Matter of	J = joules × 10³.	
Hydrogen	$H^{\cdot}$	+ 0	Hydrochloric acid	Cl'	+ 164
Potassium	$K^{\cdot}$	+259	Hypochlorous acid	ClO'	+ 109
Sodium	$Na^{\cdot}$	+240	Chloric acid	ClO_3'	+ 98
Lithium	$Li^{\cdot}$	+263	Perchloric acid	ClO_4'	− 162
Rubidium	$Rb^{\cdot}$	+262	Hydrobromic acid	Br'	+ 118
Ammonium	$NH_4^{\cdot}$	+137	Bromic acid	BrO_3'	+ 47
Hydroxylamine	$NH_4O^{\cdot}$	+157	Hydriodic acid	I'	+ 55
Magnesium	$Mg^{\cdot\cdot}$	+456	Iodic acid	IO_3'	+ 234
Calcium	$Ca^{\cdot\cdot}$	+458(?)	Periodic acid	IO_4'	+ 195
Strontium	$Sr^{\cdot\cdot}$	+501	Hydrosulphuric acid	S''	− 53
Aluminium	$Al^{\cdot\cdot\cdot}$	+506		HS'	+ 5
Manganese	$Mn^{\cdot\cdot}$	+210	Thiosulphuric acid	S_2O_3''	+ 581
Iron	$Fe^{\cdot\cdot}$	+ 93	Dithionic acid	S_2O_6''	+1166
	$Fe^{\cdot\cdot\cdot}$	− 39	Tetrathionic acid	S_4O_6''	+1093
Cobalt	$Co^{\cdot\cdot}$	+ 71	Sulphurous acid	SO_3''	+ 633
Nickel	$Ni^{\cdot\cdot}$	+ 67	Sulphuric acid	SO_4''	+ 897
Zinc	$Zn^{\cdot\cdot}$	+147	Hydrogen selenide	Se''	− 149
Cadmium	$Cd^{\cdot\cdot}$	+ 77	Selenious acid	SeO_3''	+ 501
Copper	$Cu^{\cdot\cdot}$	− 66	Selenic acid	SeO_4''	+ 607
	$Cu^{\cdot}$	− 67(?)	Hydrogen telluride	Te''	− 146
Mercury	$Hg^{\cdot}$	− 85	Tellurous acid	TeO_3''	+ 323
Silver	$Ag^{\cdot}$	−106	Telluric acid	TeO_4''	+ 412
Thallium	$Tl^{\cdot}$	+ 7	Nitrous acid	NO_2'	+ 113
Lead	$Pb^{\cdot\cdot}$	+ 2	Nitric acid	NO_3'	+ 205
Tin	$Sn^{\cdot\cdot\cdot}$	+ 14	Phosphorous acid	HPO_3'	+ 603
			Phosphoric acid	PO_4'''	+1246
				HPO_4''	+1277
			Arsenic acid	AsO_4'''	+ 900
			Hydroxyl	OH'	+ 228
			Carbonic acid	HCO_3'	+ 683
				CO_3''	+ 674

These numbers hold only for the case that the ionized matter is in very dilute solution, i.e., Aq should be added to the symbol of each kind. For stronger solutions, in which the ionization is not complete, other amounts of heat are involved which, unless allowed for, will lead to incorrect results.

The equations

$$Na = Na^{\cdot} + 240\ J$$

and

$$Cl_2 = Cl'_2 + 2 \times 164\ J$$

mean that by the transformation of the accepted formula weight of metallic sodium into the ionized state 240 J are evolved, and for the change of the formula weight of chlorine gas into two formula weights of ionized chlorine (by definition, p. 84) 2 × 164 J are liberated.

CHAPTER V.

CHEMICAL MECHANICS.

The law of mass action.—In considering such a reaction as

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

or any other reversible, gaseous process which finally attains a state of equilibrium, the question naturally arises, In which direction, and to what extent, will the reaction go, when we start, for instance, with a certain amount of the three gaseous constituents, HI, I, and H?

From the purely chemical point of view the above equation simply provides that *if* we start with 1 mole of hydrogen and 1 mole of iodine, and *if* these unite completely, 2 moles of hydriodic acid gas will be formed; or *if* we start with 2 moles of hydriodic acid gas, and this is completely decomposed, we shall obtain 1 mole each of hydrogen and iodine. As to what portion of the hydrogen and iodine will unite to form hydriodic acid, or what portion of a definite original amount of hydriodic acid will decompose to form hydrogen and iodine, or what will take place if all three substances are mixed together, we are utterly ignorant, failing further information than that contained in the chemical equation.

The answers to these questions can only be obtained by the application of a very general law which was first announced by Guldberg and Waage in 1864. The qualitative form of this *law of mass action* is as follows: *Chemical action, at any stage of the process, is proportional to the active masses of the substances present at that time, i.e., to the amounts of each present in the unit of volume.*

In this form, however, the law of mass action is of but little practical use. It will be necessary, then, for us to derive a quantitative expression of it, and thus to obtain it in such a form that it may be applied to our needs in answering questions similar to those above.

Imagine a reaction of the type

$$n_1A_1+n_2A_2 \rightleftarrows n_1'A_1'+n_2'A_2'$$

having taken place in a closed vessel and to have attained a state of equilibrium in which we have the partial pressures p_1, p_2, p_1' and p_2'.

Assume, further, that it is possible to insert each of the substances on the left against its gaseous or osmotic pressure, p_1, p_2, and to remove each of the products, as they are formed, from the gaseous or osmotic pressure p_1', p_2' to the original external pressure p_0, and that this insertion and removal is isothermal and reversible.

Since by such a series of operations we would do work on one side $(-)$, and obtain work $(+)$ from the other, the sum of the two amounts (regarding the signs) would give us an expression for the work $(+$ or $-)$ which is done *by the system itself* during the transformation, at constant temperature, of n_1 moles of A_1 and n_2 moles of A_2 to n_1' moles of A_1' and n_2' moles of A_2', the initial and final pressures being the same, viz., p_0. And this in its turn would lead to the expression of the quantitative relation existing between the active masses of the constituents at equilibrium, i.e., to the relation we seek.

Since the work required to change the osmotic or gaseous pressure of 1 mole of substance from p_0 to p_1 is given by the expression $RT \log_e \frac{p_1}{p_0}$,* that for n_1 moles will be $n_1 RT \log_e \frac{p_1}{p_0}$. For n_2 moles of A_2 we have, then, the corresponding expression $n_2 RT \log_e \frac{p_2}{p_0}$. The sum of these two terms is the work done, i.e. lost, by us in the process. The gain of work for us then for this stage is

$$-RT\left(n_1 \log_e \frac{p_1}{p_0} + n_2 \log_e \frac{p_2}{p_0}\right).$$

By the removal, as they are formed, of n_1' moles of A_1' and n_2' moles of A_2', the amount of work (a gain for us) is

$$RT\left(n_1' \log_e \frac{p_1'}{p_0} + n_2' \log_e \frac{p_2'}{p_0}\right).$$

In total, then, our gain in work in transforming n_1 moles of A_1 and n_2 moles of A_2 into n_1' moles of A_1'

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* Work $= Vdp = \frac{RT}{p}dp = RT\int_{p_0}^{p_1}\frac{dp}{p} = RT\log_e \frac{p_1}{p_0}$.

and n_2' moles of A_2' at constant temperature, the initial and final pressure being p_0, is

$$W=RT\left(n_1' \log_e \frac{p_1'}{p_0}+n_2' \log_e \frac{p_2'}{p_0}-n_1 \log_e \frac{p_1}{p_0}-n_2 \log_e \frac{p_2}{p_0}\right),$$

or

$$\begin{aligned}W=&RT(n_1 \log_e p_0+n_2 \log_e p_0-n_1' \log_e p_0-n_2' \log_e p_0)\\&+RT(n_1' \log_e p_1'+n_2' \log_e p_2'-n_1 \log_e p_1-n_2 \log_e p_2).\end{aligned}$$

But, as we simply wish to get the relation which depends upon the pressures in the reaction at equilibrium, and the pressure p_0 has nothing to do with this, we can assume p_0 to be 1, and obtain, since the first term is equal to zero,

$$W=RT(n_1' \log_e p_1'+n_2' \log_e p_2'-n_1 \log_e p_1-n_2 \log_e p_2).$$

As the processes of insertion and removal are assumed to be isothermal and reversible, this work, W, must be *the maximum work which can be done by the reaction*, and hence must be a constant at any one temperature.

We have, then,

$$W=\text{constant}=RT \log_e \frac{p_1'^{n_1'} p_2'^{n_2'}}{p_1^{n_1} p_2^{n_2}},$$

anc since if the logarithm is a constant the expression itself must be a constant, and since T and R are also constants,

$$\text{Constant}=K_p=\frac{p_1'^{n_1'} p_2'^{n_2'}}{p_1^{n_1} p_2^{n_2}},$$

or, since pressure and concentration are proportional,

$$K_c=\frac{c_1'^{n_1'} c_2'^{n_2'}}{c_1^{n_1} c_2^{n_2}},$$

where the relationship between K_p and K_c can be readiiy found as follows: Since $c=\frac{1}{V}=\frac{p}{RT}$ (where p in atmospheres and R in liter atmospheres leads to V as the liters containing 1 mole and c to moles per liter),

$$K_c=\frac{\left(\frac{p_1'}{RT}\right)^{n_1'}\left(\frac{p_2'}{RT}\right)^{n_2'}}{\left(\frac{p_1}{RT}\right)^{n_1}\left(\frac{p_2}{RT}\right)^{n_2}}=(RT)^{n_1+n_2-n_1'-n_2'}K_p.$$

The constant for concentrations is equal to that for pressures multiplied by RT raised to a power equal to the difference between the number of moles originally present and those finally present in the chemical equation. Calling the sum of the initial moles Σn and that of the final moles $\Sigma n'$ we have

$$K_c=K_p(RT)^{\Sigma n-\Sigma n'}.$$

When the reaction is similar to $2HI=H_2+I_2$, i.e., when we have the same number of moles on each side (two in this case), $\Sigma n-\Sigma n'$ becomes zero, and hence K_c will be equal to K_p.

The constant (K_p or K_c) is known as the *constant of equilibrium.*

We may express the *law of mass action* as follows, then: At equilibrium *the product of the pressures (concentrations) of the substances on the right (final ones), each raised to a power equal to the number of formula weights reacting, divided by the product of the pressures (concentrations) of the substances on the left (initial ones), each* *raised ta a corresponding power, is a constant for any one reaction at any definite temperature.**

It must be remembered that *to apply the law of mass action to a reaction the chemical equation is to be expressed in moles,* for both pressures and concentrations depend upon the number of moles present. Thus in case of the reaction

$$H_2+O=H_2O,$$

we would first have to transform the equation into the form

$$H_2+\tfrac{1}{2}O_2=H_2O$$

before applying the law of mass action.

The variation of this constant, K_p or K_c, with the temperature is to be considered later, after we have studied the application of this most important and general law.

Equilibrium in gaseous systems.—For gases we can most conveniently use the form of the law of mass action which refers to partial pressures. We have, then, for the equilibrium of a gaseous chemical system

$$K_p=\frac{p_1'^{n_1'}p_2'^{n_2'}\dots}{p_1^{n_1}p_2^{n_2}\dots}.$$

An illustration of the application of this formula is given by the gaseous reaction

$$2HI=H_2+I_2.$$

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* In case the reader cannot follow this derivation he should at any rate memorize this law and thoroughly understand the meaning of the two mathematical forms of it.

The reaction, whatever the original amounts, will only progress until the pressure of H is p_1 that of I is p_2, and that of HI is p, where

$$\frac{p_1 p_2}{p^2} = K_p,$$

K_p being a constant depending only upon the temperature and the nature of the reaction. This reaction has been studied by Bodenstein, who found by experiment that K_p at 444°C. is equal to 0.02012.

If we heat hydriodic acid, then, to this temperature it is possible to calculate, from the original quantity the amounts of hydrogen, iodine, and undecomposed hydriodic acid present at equilibrium when the temperature is 440°, for under these conditions $p_H = p_I$.

If we have a mixture of H, I, and HI, of which the partial pressures are respectively a, b, and d, and wish to find in which direction and to what extent the reaction will go at 440°, we proceed as follows: Let x represent the unknown partial pressure of H lost to form HI, where x may be positive or negative; then, according to the chemical equation $2HI = H_2 + I_2$, we shall have *at equilibrium*, as the partial pressure of HI,

$$p_{HI} = d + 2x;$$

as that of H uncombined,

$$p_H = a - x,$$

and of I uncombined,

$$p_I = b - x.$$

And x must have such a value (i.e., the reaction must go so far) that *at equilibrium* it will just satisfy the equation of the law of mass action for the reaction at 440°, i.e.,

$$K_p = 0.02012 = \frac{(a-x)(b-x)}{(d+2x)^2}.$$

Knowing the values of a, b, and d, in this system it is then possible to solve the equation for x, and to find how and how far the reaction will go. For example, in this case, if x is found to be positive in value, the reaction will go toward the left, as we have assumed; if negative, in the opposite direction.

There is one thing to be said of the solution of such equations. There are two possible values of x; which is to be taken? It will be found in this case, as, indeed, in all others, that only one value is in accord with the existing data, so that it alone could be taken. For instance, if the positive value of x is larger than a or b, it would lead to an absurdity, for it would show a negative value for H or I, and the other value is the correct one. In cases of equations of a higher degree, where more than two roots exist, this same rule is to be followed. A possible case here is to have two values of the same sign, but one smaller than the other. There can be no question in such a case, however, for if the reaction would be in equilibrium after the smaller change had occurred, it could not go out of this state to attain the equilibrium shown by the greater value, hence the lower value is to be taken as the correct one.

Here we have used the partial-pressure form of the law of mass action; we could use the other just as well, however, for it will be observed that the constant factor which would transform pressures to concentrations, $c=\frac{p}{22.4\times\frac{T}{273}}$, is eliminated, since we have the same number of formula weights (2) on each side of the equation $2HI=H_2+I_2$. For this reason the constant, K, for this reaction, as for all others *with the same number of formula weights on both sides*, has the same value for concentrations, pressures, volumes under standard conditions, or any other terms in which the amounts may be expressed, so long as they are proportional to the formula weights.

A further effect of this condition of equal volume on the two sides is that the direction of the reaction is perfectly independent of pressure (Le Chatelier's theorem, p. 42); and Lemoine has shown this to be true for the decomposition of HI for pressures ranging from 0.2 to 4.5 atmospheres.

In using concentrations in place of partial pressures it is always to be remembered that the concentration (i.e., moles per liter) is the actual number of moles present divided by the total volume (see pp. 32–33). An example will perhaps make this clearer. In the reaction $A=2B+D$, at equilibrium, we have 0.1 mole of A, 0.3 of B, and .05 of D in 10 liters at atmospheric pressure and 0°. Starting with 0.5 mole of A, 0.1 of B, and 0.4 of D, in 22.4 liters, find direction and extent of the reaction.

Here we must first find the constant of equilibrium for the data given at equilibrium. Since we have 0.1 mole of A in 10 liters, the concentration of A, at equilibrium, is $\frac{0.1}{10}$, of B $\frac{0.3}{10}$, and of D $\frac{0.05}{10}$;

hence $$K_c=\frac{\left(\frac{0.3}{10}\right)^2\left(\frac{0.05}{10}\right)}{\left(\frac{0.1}{10}\right)}.$$

Assuming that x moles of A are formed by the reaction, the final volume will be $[(0.5+x)+(0.1-2x)+(0.4-x)]22.4$ liters, the temperature remaining constant at 0°, i.e., $(1-2x)22.4$ liters. The concentrations at equilibrium, then, will be $\frac{0.5+x}{(1-2x)22.4}$ moles per liter of A, $\frac{0.1-2x}{(1-2x)22.4}$ of B, and $\frac{0.4-x}{(1-2x)22.4}$ of D; hence the value of K_c, as found above, is to be equated to these values in the following way:

$$K_c=\frac{\left(\frac{0.1-2x}{(1-2x)22.4}\right)^2\left(\frac{0.4-x}{(1-2x)22.4}\right)}{\left(\frac{0.5+x}{(1-2x)22.4}\right)},$$

and the sign of x will show the direction of the reaction, and the numerical value its extent (p. 110).

Since according to the law of mass action the *concentration* is to be raised to a power, *it is the whole fraction representing it which is to be so treated, i.e., the number of moles per liter.*

When applied to the equilibrium resulting from a gaseous dissociation the constant of the law of mass action is usually designated as *the constant of dissocia-*

tion. From it, it is possible, just as above, to calculate the degree of dissociation from a certain amount of the dissociating substance, or how much of the products, when present alone, or with the substance, will unite to form the substance itself. And, conversely, we can calculate K_c or K_p for each of the substances for which data was given on pages 28 and 29, and the values will be dependent only upon the *temperature, the units employed* (i.e., c or p), *and nature of the substance.*

When, as is the case here, we know α, the degree of dissociation of the substance, we can proceed as follows: For the reaction $PCl_5 \rightleftarrows PCl_3 + Cl_2$, for example, we have for concentrations the relation $K = \frac{c_{PCl_3} \times c_{Cl}}{c_{PCl_5}}$.

Starting with 1 mole of PCl_5, which, if undissociated, would occupy V' liters at atmospheric pressure, with α as the degree of dissociation, the concentrations, where V is the final volume, i.e., $(1+\alpha)V'$, at the same temperature and pressure, are as follows: For PCl_5 $\frac{1-\alpha}{V}$, for PCl_3 $\frac{\alpha}{V}$, and for chlorine $\frac{\alpha}{V}$, *all at equilibrium;* hence K, which we wish to determine, is to be found from

$$K_c = \frac{\alpha^2}{(1-\alpha)V} \quad \left(\text{i.e., } \frac{\alpha}{V} \times \frac{\alpha}{V} \div \frac{1-\alpha}{V}\right).$$

At 250° for PCl_5 $\alpha = 0.8$ (p. 29) and, since the pressure is atmospheric, 1 mole must be present in $22.4 \frac{273+250}{273}$ liters; this is equal to the term V' above. V, then, is equal to $(1+0.8)\left(22.4 \frac{273+250}{273}\right)$, and we have as the dissociation constant for PCl_5 at 250°

$$K_c = \frac{(0.8)^2}{(1-0.8)(1+0.8)22.4\frac{273+250}{273}}.$$

From the value thus obtained we could then calculate the direction and extent of the reaction at 250° when we start with definite amounts of the three constituents, or the value of α for a different V, i.e., when the pressure is other than atmospheric. This value will only hold for the temperature of 250°, however.

A physical idea of the dissociation constant, as found for concentrations, can be obtained by aid of the formula $K_c = \frac{\alpha^2}{(1-\alpha)V}$. Assuming that α is equal to 0.5, i.e., that the degree of dissociation is 50%, for a reaction by which 1 mole is transformed into 2, we find that $K_c = \frac{(0.5)^2}{(0.5)V}$, or $2K_c = \frac{1}{V}$. *The dissociation constant of such a reaction, then, when multiplied by 2 is equal to the reciprocal of the final volume resulting from the dissociation of 1 mole into 2 to the extent of 50%.* This volume is that in which 1 mole of the original substance must be placed in order that at that temperature it may dissociate to the extent of 50% into two others. Since $\frac{1}{V}$, the reciprocal of the volume produced by the dissociation of 1 mole, is equal to C, the concentration in moles per liter, we also have $2K = C$. An example of the use of this relation is given by the reaction $N_2O_4 \rightleftarrows NO_2 + NO_2$, for which $K_c = \frac{\alpha^2}{(1-\alpha)V} = 0.0138$ (calculated from $p = 182.69$ mm.,

$d_d = 1.894$, $d_u = 3.18$, i.e. $\alpha = 0.69$ and $V = 111$, all at 49°.7). Nitrogen tetroxide, then, should be 50% dissociated at a concentration of $2 \times 0.0138 = \frac{1}{V} = C$ moles per liter, or at a dilution of 1 mole in 36.3 liters. Experiment shows that at this temperature $\alpha = 0.493$ at the dilution 1 mole in 40 liters, which, considering the single value from which K is determined, and the evident small error in the experimental observations, is a satisfactory agreement.

A similar definition could also be deduced for the reaction $A = 2B + D$, where $K_c = \frac{\alpha^3}{(1-\alpha)V^2}$, although the above simpler one suffices for a physical idea of the dissociation constant.

It is to be noted here that the product of the substances on the right of the equation has always been placed in the numerator of the fraction giving the value of K (p. 106). This arrangement, of course, is optional, so long as it is retained the same. In the one case the value of K_c or K_p will simply be the reciprocal of that of the other.

In speaking of dissociation (p. 28) it was mentioned that the addition of one of the products of dissociation to the system, or their previous presence over the dissociating body, decreases the extent of the dissociation. That this must be true according to the law of mass action is made obvious by the consideration of any definite case.

Supposing, for example, in the case of phosphorus pentachloride, the space over it contains chlorine prior to the dissociation. Since the ratio $\frac{c_{Cl} \times c_{PCl_3}}{c_{PCl_5}}$ must be a constant, less of the PCl_5 will dissociate, for less of it, with the chlorine already present, will suffice to cause the ratio to attain the value it must possess at that temperature.

Or to take another case, suppose that 0.1 mole of B (p. 104) were introduced into a vacuum, and the substance A allowed to dissociate into this, arrangement being made by a movable piston, for example, so that the final pressure would be atmospheric. What would be the effect of this 0.1 mole of B upon the dissociation of A, the temperature being 0°? If the amount of A when undissociated were 1 mole, the volume occupied by it and the 0.1 mole of B would be 1.1 (22.4). Assume the dissociation to give rise to x' moles of B, then the number of moles of B in the final volume would be $(0.1+x')$, and since the final volume will be $0.1+\left(1-\frac{x'}{2}\right)+\frac{3}{2}x'$, i.e. $1.1+x'$, times the original one, we have

$$c_B=\frac{0.1+x'}{(1.1+x')22.4}, \qquad c_A=\frac{1-\frac{x'}{2}}{(1.1+x')22.4},$$

$$c_D=\frac{\frac{x'}{2}}{(1.1+x')22.4},$$

and

$$K_c=\frac{\left(\frac{0.1+x'}{(1.1+x')22.4}\right)^2\left(\frac{\frac{x'}{2}}{(1.1+x')22.4}\right)}{\frac{1-\frac{x'}{2}}{(1.1+x')22.4}},$$

where the value of K_c was found above (p. 112). This x' is smaller than the value (x) which would be obtained from 1 mole of A in the pure state, occupying the same volume (i.e., $(1.1 + x')$ 22.4 litres) at the same temperature. And the difference between them is the depression of the dissociation, in terms of B, due to the addition. Since for every mole of A lost, two of B are formed, $\frac{x - x'}{2}$ gives the decrease of the dissociation of A (in moles) due to the presence of the 0.1 mole of B.

The addition of an *indifferent* gas, either before or after the dissociation, to a system composed of a dissociating substance and its products, has no effect upon the degree of the dissociation, *so long as the total volume is unchanged*, for then the partial pressures (and concentrations) remain unaltered. *An increase of volume, on the other hand, such as was allowed to take place above, no matter what its cause, results in an increase in the degree of dissociation. When due to the addition of an indifferent gas, this is the only effect, and the nature of the gas is without influence. When due to the addition of one of the constituents, however, it is partly compensated by the depressing effect of this upon the dissociation,* according to the law of mass action, and it is possible to cause the one influence to just compensate the other, so that no change in the dissociation is to be observed as the result of the addition with an increase of volume.*

A somewhat more complicated case of the application

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* The value of x' above is larger than it would have been if the volume were not allowed to increase, as can be seen by substituting 22.4 in the denominators in place of $(1.1 + x')22.4$. The very expansion of volume, without the presence of B, would cause the dissociation to increase.

of the law of mass action to homogeneous gaseous systems is given by the dissociation of carbon dioxide, according to the scheme

$$2CO_2 = O_2 + 2CO.$$

If at equilibrium at any definite temperature the partial pressures are p for CO_2, p_1 for oxygen, and p_2 for CO (where these come from the CO_2), then for that temperature

$$K_p = \frac{p_1 p_2^2}{p^2},$$

and if oxygen is already present from an exterior source to the pressure a, the decrease in the pressure of carbon monoxide due to its effect upon the dissociation can be readily calculated. We have, then, when the *volume* is retained constant,

$$K_p = \frac{(p_1 + a - x)(p_2 - 2x)^2}{(p + 2x)^2},$$

from which x can be calculated (p. 110). $p_2 - 2x$ will then give the partial pressure of carbon monoxide, and $p + 2x$ that of carbon dioxide, in the presence of a of oxygen, the constant remaining as above.

For carbon dioxide at atmospheric pressure and 3000°, $\alpha = 0.4$, i.e., 0.5 of the total pressure (0.5 of an atmosphere) is due to CO_2, 0.33 to CO, and 0.17 to oxygen, consequently $K_p = 0.704$.

The constant for CO_2 may also have a different value;

it is that which is obtained from the formula

$$CO_2 = \tfrac{1}{2}O_2 + CO,$$

and is equal to $K_p' = \frac{\sqrt{p_1 p_2}}{p}$, which, with the above data, leads to the value $K_p = 0.272$.

Naturally, what was said of the arrangement of the ratio expressing K also holds here. Either constant may be used for this temperature, provided we always use the same form of relation.

This is also true for the reaction

$$N_2O_4 \rightleftarrows NO_2 + NO_2, \quad \text{or} \quad N_2O_4 \rightleftarrows 2NO_2,$$

which may be written by the α formula either as

$$K_c = \frac{\alpha^2}{(1-\alpha)V} \quad \left(\text{i.e., } \frac{\alpha}{V} \times \frac{\alpha}{V} \div \frac{1-\alpha}{V}\right),$$

or

$$K_c' = \frac{4\alpha^2}{(1-\alpha)V} \quad \left(\text{i.e., } \left(\frac{2\alpha}{V}\right)^2 \div \frac{1-\alpha}{V}\right).$$

And one form must be selected and retained.

Thus far in our consideration of gaseous equilibrium we have applied the law of mass action only to systems composed exclusively of gases. Other systems exist, however (i.e., those made up of a liquid or a solid which evolves a gas or a number of gases), to which the law of mass action can be applied with great success. And the application is usually much simpler in such cases, for it is a well-known experimental fact that a liquid or a solid gives a definite, constant gaseous pressure at any one temperature, and that the amount of liquid or solid has no further effect so long as it produces sufficient gas to cause the pressure to be attained in that volume. A similar action is observed when we saturate a solution with a substance, for so long as sufficient solid is present to saturate the solution an excess will not supersaturate it. The active mass of the solid, in applying the law of mass action, then remains constant in value, and its effect can be included in the constant of equilibrium. Thus in the reaction

$$\text{solid CaCO}_3 \rightleftarrows \text{solid CaO} + \text{gaseous CO}_2,$$

although the pressures π_1 and π_2, due to the gaseous $CaCO_3$ and CaO, p being that of CO_2, can be given in the equation

$$K_p = \frac{\pi_2 p}{\pi_1},$$

a constant value will also be found by employing the simpler form

$$K_p' = p.$$

For since at any one temperature π_1 and π_2 remain constant p must also be constant, i.e. the equilibrium at any one temperature depends only upon the pressure of CO_2 produced, and this is shown to be true by experiment.

In the same way it has been shown that equilibrium in the reaction

$$\text{solid NH}_4\text{HS} \rightleftarrows NH_3 + H_2S$$

is present when $K_p'\pi = p_1p_2$, or, in the simpler form, when $K_p' = p_1p_2$. And in the reaction

$$\text{solid } NH_4OCONH_2 \rightleftarrows 2NH_3 + CO_2,$$

when $K_p\pi = p_1^2p_2$, or when $K_p' = p_1^2p_2$. And both of these results are confirmed by experiment.

These relations, just as those for homogeneous systems, hold also after the addition of one of the products of dissociation, or when one of the products is initially present, in the space into which the solid is to sublime and dissociate. *Contrary to the case of homogeneous equilibrium* (p. 110), *however, an increase of volume has no effect upon the equilibrium, so long as the solid (or liquid) phase is present,* for the dissociation pressure is dependent, in such a system, only upon the temperature and nature of the system.

Equilibrium in liquid systems.—The reaction

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

it has been observed, reaches the state of equilibrium when we have present $\frac{1}{3}$ mole of acid, $\frac{1}{3}$ mole of alcohol, $\frac{2}{3}$ mole of ester, and $\frac{2}{3}$ mole of water, provided we start with 1 mole of each of the two constituents (either acid and alcohol, or ester and water).

This reaction goes very slowly at ordinary temperatures, but when it reaches the above final state it remains in it indefinitely. If we designate by v the volume (in liters) of the system, and start with 1 mole of acid, m moles of alcohol, and n moles of ester (or water), then in the state of equilibrium, after x moles of alcohol have been decomposed, we shall have $\frac{m-x}{v}$ moles per liter of alcohol, $\frac{1-x}{v}$ of acid, $\frac{x}{v}\left(\text{or } \frac{n+x}{v}\right)$ of ester, and $\frac{n+x}{v}$ $\left(\text{or } \frac{x}{v}\right)$ of water. And, applying the law of mass action, we obtain

$$K_c = \frac{(n+x)x}{(1-x)(m-x)}.$$

In the special case of equilibrium above, however, $m=1$, $n=0$, $x=\frac{2}{3}$; hence

$$K_c = \frac{(\frac{2}{3})^2}{\frac{1}{3}\times\frac{1}{3}} = 4.$$

This value of K_c is one of the few which are practically independent of temperature. At 10° it is found that 65.2% of the acid and alcohol undergoes change, while at 220° the decomposition is but 66.5%.

This equation has been tested by experiment with very satisfactory results. *It has been found, also, that by using a large amount of acetic acid to a small amount of alcohol, or vice versa, the formation of ester and water is almost complete, as it should be by the law of mass action.* In the same way a large amount of water upon a small quantity of ester causes the latter to be almost completely transformed.*

Amylene in contact with acid forms an ester, according to the equation

$$CH_3COOH + C_5H_{10} \rightleftarrows CH_3COO(C_5H_{11}).$$

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* For results of experiments, see "Elements," p. 264.

If x is the amount of ester formed when equilibrium is established, v is the volume of the system, and 1 mole of acid is used for a moles of amylene, at equilibrium we shall have $\frac{a-x}{v}$ moles per liter of amylene and $\frac{1-x}{v}$ of acid left, while $\frac{x}{v}$ moles per liter of the ester will be formed;

hence
$$K_c=\frac{xv}{(a-x)(1-x)}.$$

The value for K has also been experimentally determined in this case and was found to be $\frac{1}{0.001205}$, the value of the constant in the reciprocal form $K_c=\frac{(a-x)(1-x)}{xv}$ being 0.001205.*

When a solid goes into solution its action is apparently analogous to its transformation into the gaseous state. A saturated solution, thus, in contact with the solid at any temperature will still be saturated. We have, then, by the law of mass action, for any one temperature,

$$K_c\pi=c$$

or

$$K_c=c,$$

where c is the concentration of solid in solution and varies with the temperature. If the solid in going into solution dissociates (non-electrolytically) into other substances, an addition of one of these should cause less substance

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* See "Elements," p. 265.

to dissolve. This has been proven by Behrend for a solution of phenanthrene picrate in absolute alcohol, in which a decomposition into phenanthrene and picric acid takes place to a large extent.

By the law of mass action

$$Kc = c_1 c_2,$$

where c = undissociated phenanthrene picrate, c_1 = free picric acid, and c_2 = free phenanthrene—all expressed in moles per liter. For any one temperature c must be constant, since the solution is saturated; hence

$$c_1 c_2 = \text{constant}.$$

It is obvious that this will also enable us to find the conditions of the equilibrium attained when a substance is distributed between two non-miscible solvents (p. 74). *When the formula weight is the same in both solvents,* we shall have $K_c = \frac{c_2}{c_1}$, where, since $c_2 = \frac{w_2}{M}$, and $c_1 = \frac{w_1}{M}$, *the ratio of the concentrations in grams* $\left(\frac{w_2}{w_1}\right)$ *per liter must also remain constant, independent of the original concentration of substance.*

In case the formula weight in one solvent is n times that in the other ($A_1 = nA_2$), we shall have $K_c c_1 = c_2{}^n$, where c_1 would be equal to nc_2 if all A_1 were transformed into A_2. Since $c_1 = \frac{w_1}{M_1}$, $c_2 = \frac{w_2}{M_2}$, and $M_1 = nM_2$, $K_c c_1 = c_2{}^n$ can also be written in the form $\frac{M_2{}^n}{M_1} K_c = \frac{w_2{}^n}{w_1}$, where w_1

and w_2 are the weights in grams in a certain volume. But, as $\frac{M_2^n}{M_1}$ is a constant so long as the ratio of the formula weights does not change with the dilution, we may include the constants $\frac{M_2^n}{M_1}$ and K in a new constant, and say, *when the formula weight in one solvent is always n times that in the other* (*at the dilutions in question*), *the ratio of distribution in the form* $\frac{w_2^n}{w_1}$ *will remain constant, independent of the original dilution.* An illustration of this is given by the distribution of benzoic acid between benzene (w_1) and water (w_2), the values of $\frac{w_2}{w_1}$, for various original concentrations, being 0.062, 0.048, and 0.030, while those of $\frac{w_2}{\sqrt{w_1}}$ (which must be constant if $\frac{w_2^2}{w_1}$ is), for the same dilutions, are 0.0305, 0.0304, and 0.0293, the differences lying well within the experimental error. The formula weight of benzoic acid in benzene, then, must be twice that in water, a fact which has been confirmed by aid of the definition of formula weight in solution, as based upon freezing-point depression.

The effect of temperature upon the equilibrium-constant.—Wherever a change in temperature changes the equilibrium, and does not alter the nature of the equilibrium, i.e., does not cause the disappearance of any of the constituents of the previous equilibrium, it is possible, knowing certain factors, to find the effect upon the constant of equilibrium. This relation, which can be readily derived from the law of mass action and the second law of thermodynamics,* we shall regard as given and simply consider its typical applications. The differential form of the equation obtained is

$$\frac{d}{dT}(\log_e K_p) = -\frac{q_p}{RT^2},$$

or

$$\frac{d}{dT}(\log_e K_c) = -\frac{q_v}{RT^2},$$

where q_p is the heat *evolved* at constant pressure (and consequently is *negative in sign when heat is absorbed*), and q_v is the heat evolved at constant volume (see pp. 46, 47) by the reaction.

To integrate this expression it is necessary to assume that q itself is independent of the temperature. This will undoubtedly be practically true for small temperature intervals; for larger ones, however, we must be satisfied to obtain q as the value for the temperature which is the mean of the two extreme temperatures.

By integration, under the above assumption, we find

$$\log_e K_{p'} - \log_e K_p = \frac{q_p}{R}\left(\frac{1}{T'} - \frac{1}{T}\right),$$

and

$$\log_e K_{c'} - \log K_c = \frac{q_v}{R}\left(\frac{1}{T'} - \frac{1}{T}\right),$$

which, using ordinary logarithms and solving for q, is transformed into

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* See "Elements," pp. 270, 271.

$$q_p = \frac{2 \times 2.306\,(\log K_{p'} - \log K_p)\,TT'}{T - T'}\text{ cals.*},$$

or

$$q_v = \frac{R \times 2.306\,(\log K_{c'} - \log K_c)\,TT'}{T - T'},$$

where 2.306 is the reciprocal of the modulus of the system of logarithms.

The heat evolved by a reaction at $\frac{T+T'}{2}$, *under constant pressure (external work) conditions, i.e.,* q_p, *can be calculated from the equilibrium constants for pressures* ($K_{p'}$ *and* K_p) *at the two temperatures* T' *and* T; *or, knowing* q_p *and* K_p *at one temperature we can calculate* $K_{p'}$ *at the other.*

The heat of reaction at $\frac{T+T'}{2}$ *and constant volume (no external work) conditions, i.e.,* q_v, *can be calculated in a similar manner from the equilibrium constants for concentrations,* K_c' *and* K_c, *at* T' *and* T.

The value of q in these relations is for the reaction of which the K values are expressive. Thus in the reaction

$$2A = B + C,$$

the heat would be for two moles of A if $K = \frac{B \times C}{A^2}$ were used; and for one mole of A if the K values used were $K = \frac{\sqrt{B}\sqrt{C}}{A}$.

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* This second form of the equation is to be preferred for the actual calculations, although the other is simpler in form.

One consequence of this formula is of special importance. *If q is zero, the value of K does not change as the result of a variation in the temperature; and of course if K is constant at various temperatures q must be equal to zero.* Thus the reaction between acid and alcohol, mentioned above (p. 122), the mutual transformation of optical isomers, and a number of others, are found neither to absorb nor generate heat, nor to suffer a displacement of equilibrium, i.e. a change in the value of K, by a change in temperature.

We shall now consider the method of applying this equation for various purposes to various equilibria.

Vaporization.—The condition regulating the equilibrium between a liquid and its vapor is the pressure or concentration of the latter (pp. 119–120), and this depends upon the temperature. We have then

$$K_p = p \quad \text{and} \quad K_{p'} = p'.$$

Regnault found for water that at $T = 273$, $p = 4.54$ mms. of Hg, and at $T' = 273 + 11.54$, $p' = 10.02$ mms. of Hg; we have then, for 18 grams of water, since R refers to one mole,

$$q_p = \frac{2 \times 2.306 \,(\log 10.02 - \log 4.54)\, 273 \times 284.5}{273 - 284.5}$$
$$= -10670 \text{ cals.},$$

while direct experiment shows that 10854 cals. are absorbed by the evaporation of 18 grams of water vapor.

Dissociation of solids.—When a solid dissociates into gases, the equilibrium is conditioned by the concentration or pressure of the latter. In the reaction solid $\mathrm{NH_4HS}=H_2S+NH_3$, where the partial pressures of H_2S and NH_3 are p_1 and p_2, that of the gaseous $\mathrm{NH_4HS}$ being negligibly small and constant, and the total pressure P, then

$$\pi K_p'=\left(\frac{P}{2}\right)^2 \quad \text{and} \quad \pi' K'_{p'}=\left(\frac{P'}{2}\right)^2;$$

and $\pi K'p$ and $\pi' K'_{p'}$ can be used for $K_{p'}$ and $K'_{p'}$ in the ratio if π does not vary greatly with the temperature.

Since at $273^\circ+9^\circ.5$, $P=175$ mms. of Hg, and at $273^\circ+25^\circ.1$, $P'=501$ mms. of Hg, we have

$$q_p=\frac{2\times 2.306\left[\log\left(\frac{501}{2}\right)^2-\log\left(\frac{175}{2}\right)^2\right]282.5\times 298.1}{282.5-298.1}$$
$$=-22740 \text{ cals.},$$

while direct experiment, under constant pressure (external work) conditions, leads to the absorption of 22800 cals. per mole of $\mathrm{HN_4HS}$ dissociating.

This formula may also be applied to the dissociation of salts containing water of crystallization into gaseous water and the dehydrated or partially dehydrated salt.

Solutions of solids.—In this case the equilibrium depends only upon the concentration of solid substance in the solution and the temperature; we have, then,

$$K_c=c, \quad K_{c'}=c',$$

where c and c' are the concentrations of a saturated solution at the temperature T.

van't Hoff found by experiment with succinic acid in water that for $T=273$, $c=2.88$ moles per liter; and for $T'=273+8.5$, $c'=4.22$ moles per liter.

For 1 mole, then, $q=-6900$ cals., while Berthelot found -6700 cals. by direct experiment.

Ionization of solids in solution.—If a substance is very slightly soluble, and the solution consists principally of ionized matter with very little undissociated substance, the heat of dissociation must be the same as the heat of solution, i. e., equal to the negative value of the heat of precipitation from the two kinds of ionized matter. Thus for AgCl we have

$$AgCl = Ag^{\cdot} + Cl'.$$

If the solubility at $T=c$, and $T'=c'$, in moles per liter, then, since 2 moles of the ionized matter are formed from 1 mole of the salt, we have,

$$K_c = c_{ag^{\cdot}} \times c_{cl'} = c^2_{salt},$$

and

$$K_{c'} = c'_{ag^{\cdot}} \times c'_{cl'} = c'^2_{salt},$$

and since at $T=273+20$, $c=1.10\times10^{-5}$, and for $T'=273+30$, $c'=1.73\times10^{-5}$; $q=-15900=-159K$.

For the negative heat of precipitation we found (p. 93) $-158K$, which is an excellent agreement. We have assumed the ionization to be complete here, and the fact that the heat results agree cannot but be considered as confirmatory of our assumption.

Dissociation of gaseous bodies.—Under constant, atmospheric, pressure the gas N_2O_4 dissociates into NO_2 according to the scheme

$$N_2O_4 \rightleftarrows 2NO_2,$$

and the following results are observed $T=273+26.1$, $\alpha=0.1986$, $T'=273+111.3$, $\alpha=0.9267$. Since here the total pressure is one atmosphere, the partial pressures are

$$p_{N_2O_4}=\frac{1-\alpha}{1-\alpha+2\alpha}\times 1 \text{ atmos.}$$

and

$$p_{NO_2}=\frac{2\alpha}{1-\alpha+2\alpha}\times 1 \text{ atmos.}$$

For K_p and $K_{p'}$, then, we have the values

$$K_p=\left(\frac{2\alpha}{1+\alpha}\right)^2 \bigg/ \frac{1-\alpha}{1+\alpha}=\frac{4\alpha^2}{1-\alpha^2},$$

$$K_{p'}=\left(\frac{2\alpha'}{1+\alpha'}\right)^2 \bigg/ \frac{1-\alpha'}{1+\alpha'}=\frac{4\alpha'^2}{1-\alpha'^2};$$

hence

$$q_p=\frac{2\times 2.306\left(\log\frac{4\times 0.9267^2}{1-0.9267^2}-\log\frac{4\times 0.1986^2}{1-0.1986^2}\right)299.1\times 384.3}{299.1-384.3}$$

$= -12260$ cals. per mole of N_2O_4.

Velocity of a chemical reaction.—As up to the present we have only considered the equilibrium which is attained after the reaction has come to rest, we must now consider very briefly the laws governing its progress toward this end. Since chemical action at any time, according to the mass-law (p. 98), is proportional, for constant temperature, to the active masses of the substances present, i.e. to those portions which are free to act, then, when we have two substances reacting, the concentrations being a_1 and a_2 moles per liter,

$$\frac{dx}{dt}=k(a_1-x)(a_2-x),$$

where x is the fraction of a mole of each which decomposes in the time t. The term k in this equation is known as the *speed constant* of the reaction, and is constant at any one temperature for any value of x in the reaction in question.

Suppose we have the reversible reaction

$$A_1+A_2 \rightleftarrows A_1'+A_2',$$

which after a time attains a state of equilibrium in which all four products are present. The relative amounts of these are dependent upon the value of K for this reaction at this temperature, i.e. are fixed by the relation

$$K=\frac{c_1'c_2'}{c_1c_2}.$$

If we start with a_1 moles of A_1 and a_2 moles of A_2, then

$$\frac{dx}{dt}=k(a_1-x)(a_2-x).$$

But if we start with a_1' moles of A_1' and a_2' of A_2',

$$\frac{dx'}{dt}=k'(a_1'-x')(a_2'-x'),$$

where $\frac{dx'}{dt}$ is the velocity in the opposite direction.

Starting with the substances on either side, then, those on the other will exert an ever-increasing influence upon the velocity due to the initial substances, and this velocity must decrease continually. Finally, however, equilibrium will be attained and the ratio of the amounts on the two sides will remain constant, i.e., the reaction as a whole will cease, and any motion which exists will be so compensated by a contrary one that it will not appear.

Imagine we start with a_1 moles of A_1 and a_2 moles of A_2. The total velocity due to these at any one time will be

$$\frac{dX}{dt}=\frac{dx}{dt}-\frac{dx'}{dt}=k(a_1-x)(a_2-x)-k'(x)(x),$$

and at equilibrium, i.e. where $\frac{dX}{dt}=0$,

$$k(a_1-x)(a_2-x)=k'x^2,$$

or

$$\frac{k}{k'}=K=\frac{x^2}{(a_1-x)(a_2-x)},$$

i.e., *the equilibrium constant, K, of any reversible reaction is equal to the ratio of the speed constants of that reaction for the two directions.*

This has been proven to be true for a number of cases. For the system acid-alcohol (p. 114) it was found for a certain strength acid that $k=0.000238$ and $k'=0.000815$, from which $K=\frac{k}{k'}=2.92$, while direct experiment gave $K=2.84$.

All this is only true, however, when the reaction takes place isothermally, i.e., when the heat liberated or absorbed is removed or supplied so that no change in the temperature results, for the constants k and k' are dependent upon the temperature.

In general the application of this formula is very much simplified by the fact that most reactions are almost complete in one direction, so that the second term will be so small that it may be neglected. We have, under these conditions,

$$\frac{dx}{dt}=k(a_1-x)(a_2-x).$$

In all these cases the values on the right are obtained by subtracting the loss from the concentration of the original substance and having as many such terms as there are formula weights of substance. Thus for the reaction $A=2B+D$ we would write

$$\frac{dx}{dt}=k(c_B-x)(c_B-x)(c_D-x).$$

This is simply custom (see pp. 108 and 112), for we could also write it

$$\frac{dx'}{dt}=k'(c_B-2x)^2(c_D-x),$$

and although the k' value would be different, it would still be a constant.

Reactions of the first order. Catalysis.—For convenience we shall divide all reactions into orders. Thus a reaction of the first order is one in which but one substance suffers a change in concentration. This definition is to be further restricted, in that for the first order it is necessary that the equation show but 1 formula weight of substance changing its concentration.

Cane-sugar in water solution is transformed in the presence of acids almost completely into dextrose and lævulose; it is inverted. The speed of the reaction is very small and increases with the amount of acid added.

The progress of the reaction may be observed by aid of the polariscope. The uninverted portion revolves the plane of polarization to the right, while the two products revolve it to the left.

This process was first measured by Wilhelmy (1850), and it has played an important rôle in the history of chemical mechanics.

The process follows the scheme

$$C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$$

whether acid is used or not, for the concentration of the latter does not change during the reaction. According to the law of mass action the speed is proportional to the amounts of sugar and water. The latter, however, is present in such an excess that its action may be regarded as constant. The speed of reaction, then, is proportional to the amount of sugar present, and we have a reaction of the first order, i.e. the relation is

$$\frac{dx}{dt}=k(a-x),$$

where for $t=0$, $x=0$, and k is the *inversion constant*, which depends only upon the temperature. By integration this becomes

$$-\log_e(a-x)=kt+\text{constant},$$

or, since for $t=0$, $x=0$,

$$\log_e(a)=\text{the constant},$$

$$k=\frac{1}{t}\log_e\frac{a}{a-x};$$

in other words, a constant fraction of the total amount of sugar is inverted in each unit of time.

The meaning of the constant k in words is as follows: *Its reciprocal value multiplied by the natural logarithm of 2 gives the time in minutes which is necessary for the transformation of one half the total amount of substance, provided the products of the reactions are removed as soon as they are formed and the substances replaced as they are used.* This is shown by the substitution of $\frac{a}{2}$ for x. Further, for all reactions of the first order, *this constant k is independent of the original concentration of the substance.*

Another reaction of the first order is the formation of alcohol and acid from an ester with water. For example, the reaction

$$CH_3COOC_2H_5+H_2O \rightleftarrows CH_3COOH+C_2H_5OH.$$

And here just as above we find a constant value for k in the formula.

Both these reactions are examples of the process which is known as *catalysis;* that is, the action of a substance in hastening the change of a substance without at the same time being decomposed itself. In both these cases the hydrogen in the ionized state (by definition) is the catalytic agent. *And it has been shown for more dilute solutions that the catalytic action is strictly proportional to the concentration of ionized $H^{\cdot}$, as found (by definition) by aid of any of the possible methods.* In strong acid solutions, however, this exact proportionality does not obtain, for reasons which as yet are not thoroughly understood. *At any rate, the method as it stands enables us to define the concentration of ionized $H^{\cdot}$ in the weaker solutions of acid.*

Reactions of the second order. — Here two formula weights of substance suffer a change in concentration during the reaction, i.e., the constant depends upon the concentration of two substances. We have then

$$\frac{dx}{dt}=k(a-x)(b-x),$$

or $$-\frac{1}{a-b}[\log_e(b-x)-\log_e(a-x)]=kt+\text{constant}.$$

And, since when $t=0$, $x=0$, the constant is

$$-\frac{1}{a-b}(\log_e b-\log_e a);$$

i.e., $$k=\frac{1}{(a-b)t}\log_e\frac{(a-x)b}{(b-x)a}.$$

If we use equivalent amounts of the two substances, then $a=b$, and we have

$$\frac{dx}{dt}=k(a-x)^2,$$

or

$$k=\frac{1}{t}\frac{x}{(a-x)a}.$$

In a reaction of the second order k is inversely proportional to the original concentration.

An example of such a reaction is

$$CH_3COOC_2H_5+NaOH=CH_3COONa+C_2H_5OH,$$

or, when written as an ionic reaction,

$$CH_3COOC_2H_5+Na^{\cdot}+OH'$$
$$=CH_3OO'+Na^{\cdot}+C_2H_5OH,$$

for a base acts in such a case with an effect proportional to its content (by definition) of ionized OH'. In other words, *the velocity of saponification is proportional to the concentration of ionized OH' present, and independent of the radical from which it is split off.*

For *weak* bases, i.e. those which are but slightly ionized (NH_4Cl, for example, where α in a $^m/_{40}$ solution is 0.0269, as compared to 0.972 for KCl), the salt formed, by its depressing effect upon the ionization of the base * (p. 85), for $C_2H_3O_2Na$ is very largely ionized,

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* It is a well-known experimental fact that a substance which is but slightly ionized is influenced to a greater extent by a given concentration of a substance containing a common kind of ionized matter, than one which is considerably ionized. For the calculation of this influence, see Chapter VI.

is found to influence the constancy of k, but this can be allowed for in the calculation, as we shall see later. Thus at 24°.7 a $^{m}/_{40}$ solution of KOH gives k a value of 6.41; hence k, for a like solution of any other base, must be equal to $\frac{\alpha}{0.972}\,6.41$, where α is the percentage present of ionized OH′ in the solution of that base in presence of the salt found. This α is a value that we can find when we know the ionization of the salt formed. *In short, then, from the speed of saponification of a base, knowing that produced by a definite concentration of ionized OH′, it is possible to define and determine the concentration of ionized OH′.*

Although reactions of the third order, as well as still higher, are also known, and have been investigated, their importance for our purposes is very slight, and consequently they need not be considered here. And for the consideration of those reactions which are incomplete, as well as of those which are non-homogeneous, and the discussion of the effects of temperature upon the speed of a reaction, the reader must also be referred elsewhere.*

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* "Elements," pp. 293–299.

CHAPTER VI.

EQUILIBRIUM IN ELECTROLYTES.

Organic acids and bases. The Ostwald dilution law.—The application of the law of mass action to gaseous equilibria, as well as to those existing in solutions of non-electrolytes—in short, to chemical equilibria—has shown that it is a general law of nature, holding between very wide limits. The question which naturally arises here, then, is, Can the law of mass action also be applied to those equilibria composed of the ionized and unionized portions of a substance in solution? In other words, Is the law of mass action the principle governing the amounts of these portions which can exist together in equilibrium? It is the purpose of this chapter to answer this question so far as is possible from our present knowledge of the facts.

The conductivity ratios $\frac{\mu_v}{\mu_\infty}$, as well as the methods for determining the average molecular weight, where these can be carried out with sufficient accuracy, show that a water solution of acetic acid is ionized according to the following scheme:

$$CH_3COOH \rightleftarrows CH_3COO' + H^{\cdot}.$$

From this equation, applying the law of mass-action, we obtain

$$K=\frac{c_{CH_3COO'}c_{H^{\cdot}}}{c_{CH_3COOH}}=\text{constant},$$

or (see page 106)

$$K=\frac{\alpha^2}{(1-a)V}=\text{constant},$$

which is known as the *Ostwald dilution law*, for it gives the relation of ionization to dilution.

Substituting the ratio $\frac{\mu_v}{\mu_\infty}$ for α at various dilutions, Ostwald found K to be constant, with a value at 25° of 1.8×10^{-5}. From the value of K at any temperature, then, it is possible, by solving for α, to find the degree of ionization at any dilution or at any concentration at that temperature, for $c=\frac{1}{V}$. We find thus that

$$\alpha=\sqrt{KV+\frac{K^2V^2}{4}}-\frac{KV}{2},$$

where K is the *equilibrium, dissociation, or ionization constant, or the so-called coefficient of affinity, of the acid.*

Further than this, when K is known for any temperature it is possible to find α, at any dilution, in the presence of an acid or salt with ionized matter in common ($H^{\cdot}$ or CH_3COO'). And, just as in the case of gaseous dissociation, we always find a smaller dissociation in the presence of the products arising from an exterior source. Naturally the calculation here is similar to the other (pp. 108–109). For example, we have

$$K=\frac{(c_{H^{\cdot}}+x-y)(c_{CH_3COO'}-y)}{(c_{CH_3COOH}+y)},$$

where x represents the concentration of ionized $H^{\cdot}$ due to other substances, $c_{H^{\cdot}}$ and $c_{CH_3COO'}$ are the concentrations due to the acid in the absence of other substances, and y is the concentration of each ($H^{\cdot}$ and CH_3COO') lost, i.e., uniting to form un-ionized CH_3COOH, as the result of the presence of x moles of ionized $H^{\cdot}$. The concentrations of $H^{\cdot}$ and CH_3COO', now arising from the acid, are equal, then, to $(c_{H^{\cdot}}-y)=(c_{CH_3COO'}-y)$, and the un-ionized acid concentration is $(c_{CH_3COOH}+y)$.

Indeed, everything which we found above (pp. 101–110 to hold true for gaseous dissociation, with the one exception mentioned below, also holds true for the relation of ionized and un-ionized portions of a substance, of the type of acetic acid, in solution. And, as a rule, the results are simpler to calculate, for the volume change of the system is so small as to be negligible.

We can also define the *ionization constant* in terms similar to the definition of the *gaseous dissociation constant* (p. 107). Thus by multiplying K for acetic acid by 2 we obtain 0.000036 as the concentration in moles per liter of a solution of acetic acid, which would be 50% ionized, i.e., a solution of 1 mole of acid in 27777.5 liters of water.

All organic acids when treated in this way give a constant value for the expression $\frac{\alpha^2}{(1-\alpha)V}$. This is the difference between gaseous and electrolytic dissociation equilibria, at least when the latter is for an organic acid. *The acid, whether it be mono, di, or polybasic, always ionizes as a monobasic acid up to the dilution at which* $\alpha=0.5$. This means that, assuming the acid to ionize simply into the two products $H^{\cdot}$ and the negative radical (i.e., for the calculation of μ_{∞}), which may also contain replaceable hydrogen, a constant is obtained so long as the ionization in this way is 50% or less. Beyond that point the ionized $H^{\cdot}$, due to a breaking down of the negative ionized radical containing replaceable hydrogen, is great enough in concentration to influence the constant, which begins to vary. Above the dilution at which $\alpha = 0.5$ the second and following replaceable hydrogens begin to appear in the ionized state, and must be taken into account; and at infinite dilution, if it were possible to attain it, the polybasic acid would be composed of all the replaceable hydrogen in the ionized state, together with the negative radical, without replaceable hydrogen, as the negatively charged ionized matter.*

The ionization constants at 25° C. for a few organic acids are given below; these are for the first equivalent of ionized $H^{\cdot}$, i.e., give results which agree with experiment up to a dilution at which $\alpha = 50\%$.

IONIZATION CONSTANTS OF ORGANIC ACIDS AT 25° C.

	$K \times 10^5$		$K \times 10^5$
Propionic	1.34	Malic	39.5
Isobutyric	1.44	Fumaric	93
Capronic	1.45	Tartaric	97
Butyric	1.49	Salicylic	102
Valerianic	1.61	Orthophthalic	121
Acetic	1.80	Monochloracetic	155
Camphoric	2.25	Malonic	158
Anisic	3.20	Maleic	1170
Phenylacrylic	3.55	Dichloracetic	5140
Succinic	6.65	Oxalic	10060 (±)†
Lactic	13.8	Trichloracetic	121000 (±)†
Glycollic	15.2		
Formic	21.4		

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* For the calculation of the amount of the 2d and 3d equivalents of ionized $H^{\cdot}$ at any dilution, see Smith, Zeit. f. phys. Chem., 25, 144, and 193, 1898, and Wegscheider, Sitzungsber. d. Akad. d. Wissenschaft., 111, 441–510, 1902; McCoy, J. Am. Chem. Soc., 30, 688–694; Chandler, ibid., 694–718.

† These two acids are so largely dissociated that a small error in α

The value of K at 18° for a few other acids, some of which are inorganic, but characterized by their small ionization, and by obeying the law of mass action, are given by Walker and Cormack,[*] the value of acetic acid being given for comparison.

Name.	$K \times 10^{10}$.	Per Cent Ionization in a 0.1 Molar Solution.
Acetic acid (25°), $CH_3COO'—H^{\cdot}$	1,800,000	1.3
Carbonic acid, $H^{\cdot}—HCO_3'$	3,040	0.174
$H^{\cdot}—CO_3''$	0.6[†]	......
Hydrogen sulphide, $H^{\cdot}—HS'$	570	0.075
Boric acid, $H^{\cdot}—H_2BO_3'$	17	0.013
Hydrocyanic acid, $H^{\cdot}—CN'$	13	0.011
Phenol, $H^{\cdot}—C_2H_5O'$	1.3	0.0037

In the case of the addition of a salt with an ion in common to an organic acid (pp. 141–142) the following will be seen at once to be true. If the degree of dissociation of a salt with an ion in common with an acid is d, and n is the number of moles per liter of salt present, then the equation of equilibrium of the acid will become

$$(nd+\alpha)\alpha = KV(1-\alpha).$$

For very weak acids we can generalize this as follows: α, the degree of dissociation of the acid, is very small in presence of the salt, so that α in comparison to 1 and

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affects K to a large degree. For a list containing a very large number of other acids, see Zeit. f. phys. Chem., 3, 418–20, 1889, or Kohlrausch and Holborn, Leitvermögen der Elektrolyte, pp. 176–193.

[*] Trans. Chem. Soc., 77, 8, 1900.

[†] McCoy, Am. Chem. Journ., 29, 455, 1903.

nd may be neglected. Since *d* for salts is almost independent of the dilution, we have

$$n\alpha = KV,$$

$$\alpha = \frac{KV}{n},$$

i.e., *the dissociation of a weak acid in presence of one of its salts is approximately inversely proportional to the concentration of the salt.*

The case of the partition of a base between two acids depends to a certain extent upon their ionization constants. This partition takes place when there is not enough base present to saturate both acids. The final mixture consists of water, undissociated salt, and the dissociated and undissociated portions of the acids. The equilibrium is the same as that which would be attained by the mixture of the salt of the one acid with the other acid. The affinity of each acid for the base will depend upon the percentage of ionized $H^{\cdot}$ which it possesses, i.e., the one containing the larger quantity will unite with the larger amount of the base.

For weak acids it is possible to formulate a general law regarding the partition and the ionization constants. In this case α is so small that it may be neglected in $1-\alpha$; hence we have $KV=\alpha^2$, i.e., $\alpha=\sqrt{KV}$. And for the two acids at the same dilution

$$\sqrt{K}=\alpha, \sqrt{K'}=\alpha', \quad \text{or} \quad \frac{\alpha}{\alpha'}=\frac{\sqrt{K}}{\sqrt{K'}}.$$

The coefficient of partition of two acids, then, is propor-

tionate to the ratio of their degrees of dissociation at the given volume, or for WEAK *acids to* $\frac{\sqrt{K}}{\sqrt{K'}}$.

This coefficient is independent of the nature of the base, and depends only upon the two acids.

For the partition of an acid between two bases the coefficient depends similarly upon the two bases, and is independent of the nature of the acid. If α is the degree of ionization of one base, and α' that of the other, we shall find for them, when weak, just as for acids, that $\frac{\alpha}{\alpha'}=\frac{\sqrt{K}}{\sqrt{K'}}$, and the same generalization holds true.

In order that a base may be divided equally between two acids it is necessary that they be isohydric, i.e., it is necessary that $Kv=K'v'$. An example of such isohydric solutions, i.e. two which contain the same concentration of ionized $H^{\cdot}$, is acetic acid at a dilution of 8 liters, and hydrochloric acid at one of 667 liters. These two solutions may be mixed in all proportions without any change in the ionization resulting; and when mixed in equal volumes, if treated with a small quantity of base, equal amounts of chloride and acetate will be formed.

All these conclusions for organic acids hold also for the organic bases, as well as for some inorganic ones. The ionization constants for these when binary are naturally found from the relation

$$K=\frac{c_{M^{\cdot}}\times c_{OH'}}{c_{MOH}},$$

where $M^{\cdot}$ is the positive and OH' the negative kind of ionized matter. The value of K for a few bases is given on page 147.

Urea	(40°.2)	$K = 0.0037 \times 10^{-11}$
Acetamide	(40°.2)	0.0033×10^{-11}
Acetanilide	(40°.2)	0.0044×10^{-11}
Aniline	(25°)	5.4×10^{-10}
p-Toluidine	(40°.2)	20.7×10^{-10}
m-Nitraniline	(40°.2)	4×10^{-12}
p- "	(40°.2)	1×10^{-12}
o- "	(40°.2)	0.01×10^{-12}
Ammonium hydrate, $NH_4^{\cdot}$—OH'	(25°)	23×10^{-6}
Methylamine	(25°)	5×10^{-7}
Dimethalamine	(25°)	0.074×10^{-5}
Trimethylamine	(25°)	0.0074×10^{-5}
Propylamine	(25°)	0.047×10^{-5}
Isopropylamine	(25°)	0.053×10^{-5}
Isobutylamine	(25°)	0.034×10^{-5}

An interesting relation has been found by Osaka to exist between the concentration of H' ion (or OH') in a weak acid (or weak base) when it is 50% neutralized by a strong base (or strong acid). If the acid (or base) is very slightly ionized and the salt practically completely ionized, we have

$$HA + {}^1/_2Na^{\cdot} + {}^1/_2OH' = {}^1/_2H_2O + {}^1/_2HA + {}^1/_2A' + {}^1/_2Na^{\cdot}.$$

Hence in

$$c_{H^{\cdot}} = \frac{Kc_{HA}}{c_A}$$

inspection shows that $c_A = c_{HA}$, and

$$c_{H^{\cdot}} = K_{acid.}$$

The concentration of $H^{\cdot}$ ion is a weak acid 50% neutralized by a strong base, is equal to the ionization constant of the acid, provided the salt is practically completely ionized. For a weak base 50% neutralized by a strong acid we have similarly

$$c_{OH'} = K_{base}.$$

The equation on pages 141–142 has also been used to determine the concentration of ionized matter in the solution added to a substance obeying the law of mass action, and with very good results. Thus, starting with acetic acid, knowing the concentration of ionized $H^{\cdot}$, and adding sodium acetate, we can find the concentration of ionized CH_3COO' in the salt. In this case the new concentration of ionized $H^{\cdot}$ can be determined from the speed of inversion of sugar (p. 130); and by solving the equation for the amount of CH_3COO' added, we can find the ionization of the salt solution added.

This same process may also be carried out with other systems, mentioned below, so that by it it is possible to determine the concentration of any one kind of ionized matter. *As mentioned above, the ionization has been found to be sensibly the same, by whatever method it may be determined.*

Acids, bases, and salts which are ionized to a considerable extent. Empirical dilution laws.—The application of the law of mass action (the Ostwald dilution law) to the above so-called strong electrolytes does not lead to a constant value for K when the ionization is taken from the conductivity ratio $\frac{\mu_v}{\mu_\infty}$. *As in general the degree of electrolytic dissociation is found to be the same by all of the possible methods, our only conclusion at present is that the law of mass action cannot be applied to the equilibrium of un-ionized and ionized portions in such solutions as these.* Although this is true with regard to very soluble salts, there is a quantitative relation, which we shall develop below, holding for the ionized portions of difficultly soluble substances, when the un-ionized portion is retained constant.

The only known case of a dissociating and very soluble salt to which the law of mass action may be applied, i.e. the only exception to the above conclusion, is cæsium nitrate, when α is determined by the freezing-point method.* And this is not true for α as determined by the other methods. In other words, in this case, the freezing-point results point to a different degree of ionization than any other method. The results for cæsium nitrate as determined by Biltz show that $K = \frac{\alpha^2}{(1-\alpha)V} = 0.34$ for the freezing-point determinations of α, while the value calculated by aid of conductivity shows no trace of constancy.

Biltz attributes the failure of the law of mass action, as applied to strong electrolytes, to a hydration of the substance, i.e. to a chemical reaction between the solute and the solvent, which would remove active solvent from the solution, leaving it really more concentrated than it appears to be. Just why the solution of cæsium nitrate in water should give a constant value for K when α is determined by the freezing-point method, while when α is found from the conductivity it fails to do so, is unknown and thus far nothing but assumption has been possible. It is to be remembered, however, that this value of K, although giving, when solved for α, the ionization according to the freezing-point method, does not give the value determined by other methods, so that too much stress is not to be laid upon it, especially in face of the fact that the law cannot be applied to any other strong electrolyte, determine α by any method that we will. It would certainly seem more

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* Biltz, Zeit. f. phys. Chem., 40, 218, 1902; also "Elements," p. 294.

probable that in this one case some secondary action occurs in the freezing which is absent in all other cases, so that here the freezing-point leads to an incorrect (i.e. abnormal) result. This conclusion, of course, may not be true, but at the present time, in the absence of any indication of such a result for other substances, it is decidedly the most reasonable and logical one. In other words, then, so far as we know to-day, the conductivity leads in all cases to the true value for α, hence it is to be inferred, failing further evidence, that it is also correct here, and we must attribute the case above to some secondary action not yet encountered in studying other substances.

Although the Ostwald dilution law (i.e., the law of mass action) fails utterly to hold for the equilibrium between the ionized and un-ionized portions of a strong electrolyte, certain other empirical dilution laws have been found which allow us to find the respective amounts at any dilution. Thus Rudolphi * found a dilution law which gives a constant value within certain limits for such solutions as do not follow the Ostwald dilution law. This law is $\frac{\alpha^2}{(1-\alpha)\sqrt{V}}=\text{constant}$, where the value of the constant is approximately the same for analogous substances. van't Hoff † altered this to the form $\frac{\alpha^3}{(1-\alpha)^2 V}=\text{constant}$, which holds even better than Rudolphi's. Simplified, this relation is $\frac{c_i^3}{c_s^2}=\text{constant}$, i.e., *the cube of the concentration of ionized matter divided by the square of the un-ionized portion is a constant.*

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* Zeit. f. phys. Chem., 17, 385, 1895.

† Ibid., 18, 300, 1895.

Writing the Ostwald dilution law in this form we obtain *(for binary electrolytes)* $K=\frac{c_i^2}{c_s}$, *while this empirical relation (in either form) remains the same for binary or ternary substances; in other words, is independent of the number of moles of ionized matter formed from one mole of the substance.*

Bancroft [*] proposes a dilution law of the form const. $=\frac{c_i^n}{c_s}$, in which the constant and n are functions of the nature of the electrolyte. Although this relationship is as yet unknown, Bancroft suggests that we may sometime find a relation of the form $n=2-f$ (constant)—where f *(constant)* varies between zero and a value approximating one-half—which will reconcile the Ostwald dilution law, holding only for organic acids and bases, and in which $n=2$, with this form in which n varies in value from 1.36 to 1.5. For KCl at 18° we have the relation $\frac{c_i^{1.36}}{c_s}=2.63$, which holds in a very remarkable way between the volumes 0.3 and 10,000 liters.

Noyes [*] has determined the degree of ionization, $\frac{\mu_v}{\mu_\infty}$, for the chlorides of potassium and sodium at various temperatures and finds a constant value for the ratio $\frac{1-\alpha}{c^{\frac{1}{3}}}$; *that is, the fraction of salt un-ionized is directly proportional to the cube root of the concentration; or the concentration of un-ionized substance, $(1-\alpha)c$, is directly proportional to the 4/3 power of the total concentration, c, of salt.* The

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[*] Zeit. f. phys. Chem., 31, 188, 1899. (In English.)

[†] J. Am. Chem. Soc., 26, 168, 1904.

degrees of ionization of potassium and sodium chlorides were found to be nearly identical (the extreme variation being 2%) at all temperatures and dilutions. In a 0.1 molar solution the dissociation has approximately the following values:

18°	84%	281°	67%
140°	79%	306°	60%
218°	74%	....	....

The values of $K' = \frac{1-\alpha}{c^{\frac{1}{3}}}$ are as follows:

	18°	140°	218°	281°	306°
NaCl...........	0.366	0.448	0.573	0.745	0.877
KCl............	0.321	0.468	0.577	0.713	0.853

Some of the observed facts as to the ionization of strong electrolytes, as summarized by Noyes,* are as follows:

The form of the concentration function is independent of the number of moles of ionized matter into which one mole of salt dissociates. Instead of being proportional for di-ionic, tri-ionic, and tetra-ionic to the square, cube, or fourth power of the concentration of the ionized matter, the un-ionized portion is approximately proportional to the 3/2 power of that concentration, whatever may be the type of salt.

The conductivity and freezing-point depression of a mixture of salts having one kind of ionized matter in common are those calculated under the assumption that the degree of ionization of each salt is that which it would have if present alone at such an equivalent concentration that the concentration of either of the kinds of ionized matter were equal to the sum of the equivalent concentrations of all the positive or negative ionized matter present in the mixture. Suppose that a mixed solution is 0.1 molar with

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* Technology Quarterly, 17, 307, 1904.

respect to sodium chloride and 0.2 molar with respect to sodium sulphate, and that it is 0.18 molar with reference to the positive or negative ionized matter of these salts. The principle then requires that the ionization of either of these salts in the mixture be the same as it is in water alone when its ionic concentration is 0.18 molar. This has been proven conclusively for many mixtures.

The decrease of ionization with increasing concentration is roughly constant in the case of different salts of the same type.

The un-ionized fraction of any definite molal concentration is roughly proportional to the product of the valences of the two kinds of ionized matter in the case of salts of different types.*

From these facts, together with others, Noyes concludes that the form of union represented by the un-ionized portion of a substance differs essentially from ordinary chemical combination, it being so much less intimate that the kinds of ionized matter exhibit their characteristic properties, in so far as these are not dependent upon their existence as separate aggregates. In other words, the law of mass action is inapplicable to the relation between the ionized and un-ionized portions as they exist in strong electrolytes, and hence this is not to be regarded as a *simple chemical equilibrium*, for which, as we know, the law of mass action always appears to hold rigidly.

The heat of ionization.—By aid of van't Hoff's equation (p. 126), it is possible to calculate the heat of ionization of a substance, provided we know its degree of ionization at two different temperatures. This is true not only for those substances that follow the Ostwald

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* Other generalizations of this kind from the standpoint of electrical conductivity will be found in Chapter VII.

dilution law, but, according to Arrhenius,* for all others as well. For binary electrolytes we have, then, $\log_e \frac{K'}{K} = \log_e \frac{\alpha'^2(1-\alpha)}{\alpha^2(1-\alpha')} = \frac{q}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$, where the values of K are for the same dilution and represent the change of ionization, even though the values are not the same as other dilutions, and the values V cancel and need not be considered. *q is then the heat liberated when a mole of substance is formed in solution by the union of the kinds of ionized matter composing it.* It will bc observed here that these values differ from those calculated from the table given on page 95, for these refer to the heat of formation of ionized matter from substance already in solution, while those refer to the compound process of solution and ionization, i.e., the difference in energy between the ionized state and the solid or gaseous state. Some of the results as found by Arrhenius are given below, the unit being the small calorie.

HEATS OF IONIZATION.

Substance.	Temperature.	Calories.
Acetic acid	35°	386
	21°.5	− 28
Propionic acid	35°	557
	21°.5	183
Butyric acid	35°	935
	21°.5	427
Phosphoric acid	35°	2458
	21°.5	2103
Hydrofluoric acid	33°	3549
Potassium chloride	35°	362
" iodide	35°	916
" bromide	35°	425
Sodium chloride	35°	454
" hydrate	35°	1292
" acetate	35°	391
Hydrochlorie acid	35°	1080

The *ionization of substances in solution usually takes place, then, with the evolution of heat.*

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* Zeit. f. phys. Chem., 4, 96, 1889, and 9, 339, 1892.

HEAT NECESSARY TO COMPLETE THE IONIZATION, $(1-\alpha)w$ (1 mole in 200 moles of water).

Substance.	Temperature.	Calories.
Potassium bromide	35°	58
" iodide	35°	132
" chloride	35°	56
Sodium hydrate	35°	180
" chloride	35°	81
Hydrochloric acid	35°	136
Hydrofluoric acid	33°	3304
Phosphoric acid	21°.5	1682

For the temperatures of 35° in the table, $T=273+18$, $T'=273+52$; for 21°.5, $T=273+18$, $T'=273+25$ in the $\log_e \frac{K'}{K}$ formula (p. 126).

From data such as the above it is possible to calculate the heat of neutralization of an acid by a base. The formula for this (p. 92) is

$$q=x-w_3(1-\alpha_3)-w_2(1-\alpha_2+w_1(1-\alpha_1),$$

where the figures 1, 2, and 3 refer respectively to acid, base, and salt, and $w_3(1-\alpha_3)$, the heat *evolved* by the *dissociation* of the salt is subtracted because its *negative* value is equal to the heat of association required in the relation, and x is the heat of formation of 1 mole of water from ionized $H^{\cdot}$ and ionized OH', i.e., 13,700 cal. In the table below the calculated values of q at two temperatures are given, together with the observed values at one of the temperatures.

HEAT OF NEUTRALIZATION OF ACIDS WITH NaOH.
(1 mole of acid + 1 mole of NaOH + 400 moles of H_2O.)

	At 35°.	At 21.5.	
	Calc.	Calc.	Obs.
HCl	12867	13447	13740
HBr	12945	13525	13750
HNO_3	12970	13550	13680
CH_3COOH	13094	13263	13400
C_2H_5COOH	13390	13598	13480
$CHCl_2COOH$	14491	14930	14830
H_3PO_4	14720	14959	14830
HF	16184	16320	16270

It is obvious from the results above *that the value of the heat of neutralization of an acid by a base cannot be considered as indicative of the strength of the acid.* The two latter are relatively weak acids and yet they give rise to the greatest amount of heat.

This formula of van't Hoff's, as was mentioned above, can only be used to calculate the *heat of solution* of substances which are completely ionized (or practically so) or completely un-ionized. And, naturally, until our knowledge of the conditions governing equilibrium in such systems is considerably broadened, we cannot expect to find a formula that will hold.

Solubility or ionic product.—Although, as we have seen, the law of mass action cannot in general be applied to the equilibrium of the ionized and un-ionized portions of a substance in solution (except to organic acid and bases), it can be applied with considerable accuracy to a very large number of saturated solutions. An example of such an equilibrium is a saturated solution of silver chloride, which is found to be practically completely ionized according to the scheme

$$AgCl = Ag^{\cdot} + Cl'.$$

Applying the law of mass action to this we obtain

$$Kc = c_1c_2, \quad \text{or} \quad K = \frac{\alpha^2}{(1-\alpha)V},$$

when c is the concentration of un-ionized AgCl, c_1 that of ionized $Ag^{\cdot}$, and c_2 that of ionized Cl'. Since the solution is saturated, the value of c at any temperature must remain constant, for if the solution were unsaturated, solid would dissolve, or if supersaturated, solid would precipitate. In a saturated solution of silver chloride, at any one temperature, then, we have the relation, since the un-ionized AgCl is small in amount but *constant.*

$$Kc = \text{constant} = c_1c_2;$$

i.e., ***in a saturated solution of a binary electrolyte** (**of this kind**) **the product of the concentrations of the two kinds of ionized matter must remain constant, with unchanged temperature.***

Expressing this in a more general form, we have for the reaction

$$nA \rightleftarrows n_1A_1 + n_2A_2$$

in a saturated solution, the relation

$$c_1^{n_1}c_2^{n_2} = \text{constant} = s,$$

where s has been called by Ostwald *the solubility product of the substance.* This solubility product is of paramount importance in analytical chemistry, *for a precipitate* (*when due to an ionic reaction, and most of them can be shown to be due to this*) *is always and only formed when its solubility product is exceeded.* This, of course, presupposes that no supersaturation phenomenon is possible; if it is, then the so-called *metastable limit* * must first be exceeded.

Just as we found a decrease in the dissociation of a gas or an organic acid, by the addition of one of the products of dissociation from an exterior source, so here the addition of a substance with a kind of ionized matter in common causes the formation and separation in the solid state of the un-ionized substance. In other words, the term s still

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* "Elements," p. 142.

retains its constant value, and consequently the kinds of ionized matter composing the substance unite to form more of the un-ionized portion, which, since the solution is already saturated with it, separates out as solid. This has been found to be true by experiment, *but only true quantitatively for those substances which are difficultly soluble.** The effect may be observed most easily by dissolving the difficultly soluble substance in a solution of the salt with ionized matter in common; but it can also be attained by adding to the saturated water solution of the substance a strong solution of the salt, when a precipitation of the substance, usually in the crystalline state, will be observed. Thus if we add to one portion of a saturated solution of silver acetate a strong solution of sodium acetate containing x moles of ionized CH_3COO', and the same amount of a solution of silver nitrate containing x moles of ionized $Ag^{\cdot}$ to the liter to another equal portion, we observe an equal precipitation of solid silver acetate in the two solutions.

The examples below will serve to show how the solubility product of a substance can be found, and how when once found it can be employed to foresee the solubility of the substance in a solution already containing a common kind of ionized matter.

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* Noyes and Abbott (Zeit. f. phys. Chem., 16, 138, 1895) have found *for those substances which are largely dissociated, and this is general, that the concentration of the un-ionized part of the salt has always the same value when the product of the concentrations of the kinds of ionized matter it produces has the same value, whatever may be the values of the two separate factors of that product.* In other words, if the strong electrolyte AD, ionizing into $A^{\cdot}$ and D', has a concentration of AD in a saturated solution equal to y, when $A^{\cdot}\times D'$ has the value x, it will also have the value of y whenever $A^{\cdot}\times D'$ has the value of x, whether it be produced by $(A^{\cdot}-z)(D'+z)$ or $(A^{\cdot}+z)(D'-z)$, etc.

Silver bromate is soluble at 25° to the extent of 0.0081 moles per liter. Assuming the ionization in this state to be practically complete, and it certainly is nearly so, the concentration of the ionized $Ag^{\cdot}$ and ionized BrO_3' will be the same, and equal each to 0.0081 mole per liter. The solubility product at this temperature, then, will be

$$(0.0081)(0.0081) = s_{\mathrm{AgBrO_3}}.$$

The solubility in a solution of silver nitrate containing 0.1 mole of ionized $Ag^{\cdot}$ (or in potassium bromate containing 0.1 mole of ionized BrO_3') can now be found readily by aid of the relation

$$(0.0081)^2 = (0.0081 + .1 - y)(0.0081 - y),$$

and is equal to $(0.0081 - y)$, for that is the concentration of ionized $Ag^{\cdot}$ and ionized BrO_3' now existing in the solution, and coming from the salt; the amount 0.1 of one being due to the other salt, and y being the $AgBrO_3$ remaining undissolved owing to the presence of this 0.1 mole of $Ag^{\cdot}$ or BrO_3'.

This is true for all binary salts when they can be assumed to be completely ionized, or practically so.

Where the substance dissociates into more than two kinds of ionized matter, and can be assumed to be completely ionized, the relation is quite similar. Suppose the salt to dissociate according to the scheme

$$MA_3 \rightleftarrows M^{\cdots} + 3A'.$$

As solubility product we shall have, if c is the solubility of the completely ionized salt MA_3, $c \times (3c)^3 = s_{\mathrm{MA_3}}$, or $c_{\mathrm{M}^{\cdots}} \times c^3_{\mathrm{A'}} = s_{\mathrm{MA_3}}$, for we must nave three times the number of moles per liter of A' as we have of $M^{\cdots}$ according to the chemical equation, i.e., $c=c_{M^{\cdots}}$ and $3c=c_{A'}$. In case of solution in the presence of 0.1 mole of one of the kinds of ionized matter, we have, then, either

$$(c_{M^{\cdots}}+0.1-y)(c_{A'}-3y)^3=s_{MA_3}$$

or

$$(c_{M^{\cdots}}-x)(c_{A'}+0.1-3x)^3=s_{MA_3},$$

from which it is apparent that the effect of equal addition is not the same for the two kinds of ionized matter, i.e., that x and y, the decreases in the solubility, are not equal.

In the case the substance is not completely ionized, the solubility product is not so directly related to the solubility of the substance as in the above cases, i.e., to the square in one case and twenty-seven times the fourth power in the other. Consider the case of uric acid, which at 25° is soluble to 0.0001506 mole per liter, and is ionized in that condition to 9.5% into $H^{\cdot}$ and the ionized negative radical which we shall designate as U'. The solubility product here is naturally

$$(0.0001506\times0.095)(0.0001506\times0.095) \\ =s_{HU}=K_{HU}(0.0001506\times0.905).$$

The solubility of uric acid in a molar solution of hydrochloric acid, for which $\alpha=0.78$ (i.e. $H^{\cdot}=0.78$, $Cl'=0.78$), is to be found in the following way:

$$(0.0001506\times0.095+0.78-x)(0.0001506\times0.095-x) \\ =(0.0001506\times0.095)^2,$$

where $(0.0001506\times0.095-x)$ represents the present concentration of $H^{\cdot}$ and U' from the uric acid, and its total solubility in the hydrochloric acid solution is $(0.0001506 \times 0.905) + (0.0001506 \times 0.095 - x)$, i.e., is equal to the sum of that which is un-ionized and that which is ionized.

In general, just as for organic acids, an infinite excess of one of the ions will cause the ionization of the substance to become zero. *It is to be observed here, however, that this excess will only cause the solubility to become zero in the case that the ionization is complete.* In the case of uric acid, an infinite amount of $H^{\cdot}$ or U' at best can only reduce the solubility by 9.5%, the remaining 90.5% being un-ionized and not affected at that temperature by any addition of substance which does not react chemically with it.

That a substance is *always* decreased in solubility by the addition of a substance with ionized matter in common is not true, as the well-known behavior of silver cyanide in potassium cyanide will show. In all such cases, however, the equilibrium which has previously existed is altered in some way, so that the relations are not the same. These cases are usually characterized by the formation of a complex kind of ionized matter the *product* of which is exceeded. The removal of the kinds of ionized matter necessary to form this complex kind disturbs the equilibrium of the difficultly soluble salt; the un-ionized portion then ionizes further, and its loss is replaced by the solid phase. This process continues, dissolving new salt, until equilibrium is attained, i.e., until the solubility product, whatever it may be, is just satisfied, when solution ceases. The ionization of silver potassium cyanide takes place almost completely according to the scheme

$$KAgCN_2 = K^{\cdot} + AgCN_2',$$

but it has been found by Morgan * that in a 0.05 molar solution we have ionized $Ag^{\cdot}$ to the extent of 3.5×10^{-11} and ionized CN' to 2.76×10^{-3} moles per liter.

Knowing the concentration of the ionized metal, for example (which can be determined by methods given in the next chapter), in the complex salt solution and in a water solution of the difficultly soluble salt, we can foresee the behavior of that salt when in a solution of a salt which might dissolve it to form a complex solution of that strength. In general, i.e., *when the concentration of ionized metal in a water solution of salt is greater than that of a water solution of a complex salt, the simple salt will dissolve in the solution which will produce the complex salt in this concentration. If the concentration of ionized metal is smaller, the solid will not dissolve to any greater extent than it does in pure water, for the ionic product of the ionized complex cannot be exceeded.*

By this law it is possible to find the relative solubility of salts of the same metal in water. Thus silver sulphide is the only silver salt which will not dissolve in potassium cyanide solutions; in other words, is the most insoluble salt of silver, and contains less ionized $Ag^{\cdot}$ in a saturated solution than exists even in a solution of silver potassium cyanide, such as that given above.

It is not only for substances in solution that we find this constancy of the product of the concentrations of the kinds of ionized matter, for it also exists in our usual solvent, water, where the ionized portion is so small that the un-ionized portion may be considered as constant, i.e. $1-\alpha$ does not differ appreciably from 1. Expressing the concentrations of ionized $H^{\cdot}$ and ionized OH' in a liter of water by c_1 and c_2, and the

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* Zeit. f. phys. Chem., 17, 513–535, 1895.

un-ionized portion, which is practically 1 liter, i.e. $\frac{1000}{18} = 55.5$ moles, by c, we have

$$c_1c_2 = 55.5K_{H_2O} = s_{H_2O} = \text{constant.}$$

The values of $c_1 = c_2 =$ ionized H˙ (= ionized OH′) in water at various temperatures is as follows:

Temp.	Moles per Liter. $c_1 \times 10^7$.	Temp.	Moles per Liter $c_1 \times 10^7$.
0°	0.30	100°	6.9
18°	0.68	156°	14.9
25°	0.91	218°	21.5
		306°	13.0

The ionic products (we can hardly call them solubility products) then, are as follows:

$$s_{0°} = (0.30 \times 10^{-7})^2, \qquad s_{156°} = (14.9 \times 10^{-7})^2,$$
$$s_{18°} = (0.68 \times 10^{-7})^2, \qquad s_{218°} = (21.5 \times 10^{-7})^2,$$
$$s_{25°} = (0.91 \times 10^{-7})^2 \qquad s_{306°} = (13 \times 10^{-7})^2.$$
$$s_{100°} = (6.9 \times 10^{-7})^2.$$

where the value of s, in each case, is equal to 55.5 times the value of $K = \frac{\alpha^2}{(1-\alpha)V}$, V being 0.018 liter, i.e., the volume occupied by the formula weight, 18 grams, of water.

Knowing the solubility products of two substances with a kind of ionized matter in common, it is possible to find how much of each will dissolve when a mixture of them is exposed to the action of a solvent; and this, of course, may be expanded to three or more substances together.

Assume we have the two completely ionized, difficultly soluble salts MA and MA_1, with the ionized matter $M^{\cdot}$ in common, and that they are dissolved simultaneously in water. Call the amount of MA, which dissolves, x, and the amount of MA_1 y. In the solution, then, we must have $x+y$ moles of ionized $M^{\cdot}$, x of ionized A' and y of ionized A_1'; and, if s is the solubility product of MA and s_1 that of MA_1, the relations must be

$$x(x+y)=s,$$
$$y(x+y)=s_1,$$

so that by solving the simultaneous equations we can find x and y.

An example of this is given by dissolving thallium chloride and sulphocyanate together. The solubilities in water, each for itself, are $TlCl=0.0161$ and $TlSCN=0.0149$. Assuming complete ionization, the solubility products are respectively $(0.0161)^2$ and $(0.0149)^2$, and if x represents the amount of chloride and y that of sulphocyanate dissolving from the mixture, we have $x+y=Tl^{\cdot}$, $x=Cl'$, and $y=SCN'$, and

$$x(x+y)=(0.0161)^2,$$
$$y(x+y)=(0.0149)^2,$$

from which we find $x=0.0118$ and $y=0.0101$, while the values $x=0.0119$ and $y=0.0107$ are found by experiment.

It will be observed that in the above examples, except the last, we have tacitly assumed that the dissociation of the added salt, with a kind of ionized matter in common, is not influenced by the same kind of ionized matter from the difficultly soluble salt. As a rule this is true, for the substances are so insoluble that their effect is infinitesimal; in the last example, this effect has been allowed for, however, and will show the method of treating such cases.

In general, then, we can conclude for difficultly soluble salts (and for ionized complexes) that they are precipitated (formed) when the product of the concentrations of the ionized substances composing them exceeds the solubility (ionic) product. Although this law holds in general for difficultly soluble salts, isolated cases are to be found where the un-ionized portion does not remain rigidly constant, after the addition of a substance giving the same kind of ionized matter in common; and, to a smaller extent, a slight variation is sometimes observed in the solubility product. Since these cases are very few, and are usually observed for the more soluble salts, it would seem probable that they are due to secondary reactions not yet recognized, or to others not properly accounted for.*

Hydrolytic dissociation, or hydrolysis. Hydrolysis is the process taking place in a water solution of a *salt*, which causes the solution to appear alkaline or acid, or results in a neutral equilibrium according to the scheme

$$MA + H_2O = MOH + HA.$$

If the acid formed is insoluble or un-ionized, the base being ionized, the reaction will be alkaline (action of ionized OH′). When the base is insoluble or un-ionized,

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* See foot-note, p. 158.

and the acid ionized, the reaction is acid (action of ionized $H^{\cdot}$). And, finally, if both acid and base are insoluble or un-ionized, the salt is completely transformed into base and acid, and, as there will remain no excess of either OH' or $H^{\cdot}$, the reaction will be neutral. In other words, then, hydrolysis is the name by which we designate the process resulting from the removal of either $H^{\cdot}$ or OH' (or both) from the water by the ionized A' or the ionized $M^{\cdot}$ of the salt, to form un-ionized or insoluble substances; in short, since this removal causes the further ionization of the water, hydrolysis is the chemical process observed to take place between a salt and water.

Examples of this process are most common. For instance, all mercury, copper, zinc, etc., salts are acid, for un-ionized basic substances (for which the ionic products are exceeded) are formed by the reaction with water, leaving free, ionized acid; and potassium cyanide is alkaline, due to the formation of un-ionized hydrocyanic acid, and ionized potassium hydrate.

Since we know the conditions under which insoluble or un-ionized substances will form, i.e. by the exceeding of their solubility products or analogous values, it is possible to find the conditions necessary to produce a hydrolytic dissociation, and to calculate the extent of this when it does take place, i.e., to find the equilibrium which is finally attained in the solution.

We recognize at once that if the product of the concentrations of the ionized $M^{\cdot}$ and the ionized OH' is larger than that which can exist in pure water, un-ionized substance must form. By this formation, however, the equilibrium of $H^{\cdot}$ and OH' will be disturbed, and a further ionization of water must take place, until at length the ionic product is just attained. If the $H^{\cdot}$ and A' at this point do not unite to form un-ionized acid, the further ionization of water will be unlike what it would be in the absence of this excess of ionized $H^{\cdot}$, for, since $c_{H^{\cdot}} \times c_{OH'}$ must at the same time be equal to s_{H_2O}, we can only have $\frac{s_{H_2O}}{c_{H^{\cdot}}}$ moles per liter of ionized OH' present, when $c_{H^{\cdot}}$ is the total concentration of ionized $H^{\cdot}$ at that time.

The process due to the formation of un-ionized or insoluble acid, when no un-ionized base is formed, or forms but slightly, is exactly analogous to the above. In both cases water is decomposed, owing to the removal of one of its two kinds of ionized matter, and the further ionization of water and the formation of the insoluble or un-ionized base or acid continues until the equations representing equilibrium are fulfilled.

For the sake of simplicity we shall first consider separately the cases that the reaction is caused by the formation of base, of acid, or of both.

Case I.—The formation of un-ionized or insoluble base is the direct cause of the hydrolytic dissociation, and the acid formed is largely ionized.

By definition, here, the hydrolysis which may occur according to one of the two typical equations,

$$(a) \quad MA + H_2O = MOH + HA,$$

$$(b) \quad MA_2 + 2H_2O = M(OH)_2 + 2HA,$$

must occur until the product depending upon the valence of the positive ion of the salt,

$$c_{M^{\cdot}} \times c_{OH'},$$

or

$$c_{M^{\cdot\cdot}} \times c_{OH'}^2,$$

is greater than that which can exist in the absence of un-ionized base, for then un-ionized base must form. And the formation of base (and acid) must continue until equilibrium is established *in the solution.* i.e., until the condition for (*a*) or (*b*)

$$\text{final } c_{\mathrm{M}^{\cdot}} \times \text{final } c_{\mathrm{OH}} = K_{\mathrm{MOH}} \times c_{\mathrm{MOH}} \text{ formed}$$

or

$$\text{final } c_{\mathrm{M}^{\cdot\cdot}} \times (\text{final } c_{\mathrm{OH}'})^2 = K_{\mathrm{M(OH)_2}} \times c_{\mathrm{M(OH)_2}} \text{ formed}$$

is fulfilled.

In case the base formed is difficulty soluble, since the criterion of equilibrium holds for the substance in solution, i.e., for a homogeneous equilibrium, the above conditions would naturally simplify to the following

$$\text{final } c_{\mathrm{M}^{\cdot\cdot}} \times \text{final } c_{\mathrm{OH}'} = s_{\mathrm{MOH}},$$

or

$$\text{final } c_{\mathrm{M}^{\cdot\cdot}} \times (\text{final } c_{\mathrm{OH}'})^2 = s_{\mathrm{M(OH)_2}},$$

the excess of un-ionized base formed separating out as a solid, leaving the concentration *in solution* constant.

In addition to the above equilibria in the solution, we must also always have the condition

$$c_{\mathrm{H}^{\cdot}} \times c_{\mathrm{OH}'} = s_{\mathrm{H_2O}},$$

fulfilled. Hence it is evident that the final concentration of OH′ ion can always be readily found by dividing $s_{\mathrm{H_2O}}$ at the temperature in question, by the final concentration of the $\mathrm{H}^{\cdot}$ ion, which is dependent only upon the extent of the hydrolysis, i.e., of the reaction, and the ionization of the acid at the concentration to which it is formed.

If we designate by α the percentage of salt hydrolyzed, i.e., the percentage of salt decomposed by water according to the chemical reaction, by d_S the ionization of the salt left, and by d_A the ionization of the acid, i.e., the fraction of the acid formed which remains ionized, the final concentration of $M^{\cdot}$ or $M^{\cdot\cdot}$ ion, from an original concentration of salt of 1 mole in V liters, will be $\frac{d_S(1-\alpha)}{V}$, and that of the un-ionized base, which causes the reaction will be $\frac{\alpha}{V}$. The total acid formed will be $\frac{\alpha}{V}$ for (a) and $\frac{2\alpha}{V}$ for (b), the concentration of $H^{\cdot}$ ion being respectively $\frac{d_A\alpha}{V}$, $\frac{2d_A\alpha}{V}$.

We have then, substituting these values in the above conditions of equilibrium, when the base is not difficultly soluble,

$$\frac{d_S(1-\alpha)}{V}\left(\frac{s_{H_2O}}{d_A\frac{\alpha}{V}}\right)=K_{MOH}\frac{\alpha}{V},$$

$$\frac{d_S(1-\alpha)}{V}\left(\frac{s_{H_2O}}{2d_A\frac{\alpha}{V}}\right)=K_{M(OH)_2}\frac{\alpha}{V};$$

and when the base is difficultly soluble, i.e., when the solubility product may be substituted for the product of ionization constant and un-ionized base,

$$\frac{d_S(1-\alpha)}{V}\left(\frac{s_{H_2O}}{d_A\frac{\alpha}{V}}\right)=s_{MOH},$$

$$\frac{d_S(1-\alpha)}{V}\left(\frac{s_{H_2O}}{2d_A\frac{\alpha}{V}}\right)^2=s_{M(OH)_2}.$$

By simplification these four conditions become

$$\left.\begin{array}{ll}\frac{\alpha^2}{(1-\alpha)V}\cdot\frac{d_A}{d_S}=\frac{s_{H_2O}}{K_{MOH}}=K_{hyd.} & \text{MOH is soluble.}\\[2ex] \frac{4\alpha^3}{(1-\alpha)V^2}\cdot\frac{d_A{}^2}{d_S}=\frac{s_{H_2O}}{K_{M(OH)}}=K_{hyd.} & \text{M(OH)}_2\text{ is soluble.}\end{array}\right\}$$

$$\left.\begin{array}{ll}\frac{\alpha}{(1-\alpha)}\cdot\frac{d_A}{d_S}=\frac{s_{H_2O}}{s_{MOH}}=K_{hyd.} & \text{MOH is difficultly soluble.}\\[2ex] \frac{4\alpha^2}{(1-\alpha)V}\cdot\frac{d_A{}^2}{d_S}=\frac{s_{H_2O}}{s_{M(OH)_2}}=K_{hyd.} & \text{M(OH)}_2\text{ is difficultly soluble.}\end{array}\right\}$$

In other words, *the constant of a hydrolytic dissociation* ($K_{hyd.}$) *which is caused by the formation of base can be found from the ionic product of water and either the ionization constant or the solubility product of the base which is the cause of the hydrolytic dissociation.* This constant ($K_{hyd.}$) for (*a*) is that for the reaction

$$\text{Salt}+\text{water}=\text{base}+\text{acid},$$

which can also be written, since the water is practically constant,

$$K_{hyd.}=\frac{\text{base}\times\text{acid}}{\text{salt}}.$$

It will be observed that the variation of the hydrolytic dissociation with the dilution depends upon whether the base causing it is difficultly soluble or not. Thus *when 1 mole of salt reacts with 1 mole of water*, (*a*), *if the base is difficultly soluble the extent of the hydrolysis is independent of the dilution of the salt, while when it is soluble the hydrolysis depends upon the dilution V.*

When the hydrolysis is small, i.e., when $1-\alpha$ is practically 1, and d_A and d_S are also equal to 1, it will be seen that, for a *soluble base* the hydrolytic dissociation will vary as $\sqrt{V}$ for (*a*), and $\sqrt[3]{V^2}$ for (*b*); while, when the base is difficultly soluble the hydrolysis will be independent of dilution for (*a*) and will vary as $\sqrt{V}$ for (*b*).

Case II. *The formation of un-ionized, or insoluble, acid is the direct cause of the hydrolytic dissociation, and the base formed is largely ionized.* Here, by definition, hydrolysis, which may occur in one of the forms (*a*) or (*b*) already mentioned, according as the valence of the positive ion of the salt is 1 or 2, must in both cases occur when the product in the solution

$$c_{A^\cdot} \times c_{H^\cdot} ,$$

is greater than that which can exist in the absence of un-ionized acid, for then un-ionized acid must form. And the formation of acid (and base) must continue until the condition

$$\text{final } c_{A^\cdot} \times \text{final } c_{H^\cdot} = K_{HA} \times c_{HA} \text{ formed}$$

is fulfilled. Or until the condition, when the acid is difficultly soluble,

$$\text{final } c_{A'} \times \text{final } c_{H^\cdot} = s_{HA}$$

is fulfilled.

Since the final $c_{H\cdot}$ is equal to $\frac{s_{H_2O}}{\text{final } c_{OH'}}$, when d_B is ionization of the amount of base formed, α is the percentage of hydrolytic dissociation, and d_S is the ionization of the salt left, we have as before

$$\text{final } c_A = \frac{d_S(1-\alpha)}{V}, \quad \text{final } c_{OH'} = d_B\frac{\alpha}{V}, \quad \left(\text{or } 2d_B\frac{\alpha}{V}\right),$$

$$\text{and} \qquad \text{final } c_{HA} = \frac{\alpha}{V} \quad \text{or} \quad 2\frac{\alpha}{V}.$$

The conditions for (*a*) and (*b*) then, just as before, are respectively

$$\frac{d_S(1-\alpha)}{V}\frac{s_{H_2O}}{d_B\frac{\alpha}{V}} = K_{HA} \times \frac{\alpha}{V},$$

or

$$\frac{d_S(1-\alpha)}{V}\frac{s_{H_2O}}{2d_B\frac{\alpha}{V}} = K_{HA} \times \frac{2\alpha}{V};$$

and when the acid is difficultly soluble and its solubility product is s_{HA},

$$\frac{d_S(1-\alpha)}{V}\frac{s_{H_2O}}{d_B\frac{\alpha}{V}} = s_{HA},$$

or

$$\frac{d_S(1-\alpha)}{V}\frac{s_{H_2O}}{2d_B\frac{\alpha}{V}} = s_{HA}.$$

These, by simplification then become, *for a soluble acid*,

$$(a)\qquad \frac{\alpha^2}{(1-\alpha)V}\cdot\frac{d_B}{d_S}=\frac{s_{H_2O}}{K_{HA}}=K_{hyd.}$$

$$(b)\qquad \frac{4\alpha^2}{(1-\alpha)V}\cdot\frac{d_B}{d_S}=\frac{s_{H_2O}}{K_{HA}}=K_{hyd.};$$

and for a difficultly soluble acid

$$(a)\qquad \frac{\alpha}{1-\alpha}\cdot\frac{d_B}{d_S}=\frac{s_{H_2O}}{s_{HA}}=K_{hyd.}$$

$$(b)\qquad \frac{2\alpha}{1-\alpha}\cdot\frac{d_B}{d_S}=\frac{s_{H_2O}}{s_{HA}}=K_{hyd.};$$

i. e., the extent of the hydrolytic dissociation is independent of the dilution of the salt.

Case III. The formation of both un-ionized acid and un-ionized base causes the hydrolytic dissociation—both are but slightly ionized. This case is to be treated similarly to either I or II above, according as the base or acid has the smaller ionization constant.

Assume K_{HA} is smaller than K_{MOH}. Here the final $c_{OH'}$ is equal to $\frac{K_{MOH}c_{MOH}}{c_{M\cdot}}$, and since both MOH and HA are but slightly ionized, we shall have, practically, $c_{MOH}=c_{HA}=\frac{\alpha}{V}$ and $c_{M\cdot}=c_{A'}=\frac{d_S(1-\alpha)}{V}$. Consequently just as with (*a*) *Case II*, we must have

$$\frac{d_S(1-\alpha)}{V}\;\frac{s_{H_2O}}{\dfrac{K_{MOH}\frac{\alpha}{V}}{\dfrac{d_S(1-\alpha)}{V}}}=K_{HA}\times\frac{\alpha}{V}.$$

which when simplified gives

$$\frac{\alpha^2}{(1-\alpha)^2}\cdot\frac{1}{d_S{}^2}=\frac{s_{H_2O}}{K_{HA}\times K_{MOH}}=K_{\text{hyd.}};$$

the hydrolyiic dissociation of a salt reacting with 1 mole of water to form a slightly ionized acid, and a slightly ionized base is independent of dilution, so long as the salt is completely ionized; and the constant of hydrolysis is equal to the ionic product for water divided by the product of the ionization constants of the acid and base.

This hydrolytic constant for the reaction

$$\text{Salt}+\text{water}=\text{acid}+\text{base},$$

wnere both acid and base are but slightly ionized, must be written then

$$K_{\text{hyd.}}=\frac{\text{acid}\ +\text{base}}{(\text{salt})^2},$$

when the salt is completely ionized.

Knowing the constant for hydrolytic dissociation as given above it is possible to calculate the degree of hydrolysis at any dilution by solving for α. The following examples will serve to show the use which may be made of the above relations.

What is the ionization of water at 25°? A 0.1 molar solution of sodium acetate is 0.008% hydrolyzed, the sodium acetate to be considered as completely ionized, as is also the sodium hydrate formed, and the ionization constant of acetic acid is 0.000018.

Here

$$CH_3COOH=OH'=0.00008+0.1=0.000008,$$

and since

$$0.000018 \times c_{\mathrm{CH_3COOH}} = c_{\mathrm{H^{\cdot}}} \times c_{\mathrm{Ac'}},$$

$$c_{\mathrm{H^{\cdot}}} = \frac{0.000018 \times 0.000008}{0.1} = 1.44 \times 10^{-9}$$

and

$$\sqrt{1.44 \times 10^{-9} \times 0.000008} = \sqrt{c_{\mathrm{H^{\cdot}}} \times c_{\mathrm{OH'}}} = 1.1 \times 10^{-7}.$$

What is the hydrolysis of a 0.1 molar solution of potassium cyanide (assuming $d_S = 1$)? K for HCN $= 13 \times 10^{-10}$ and $s_{\mathrm{H_2O}} = (1.09 \times 10^{-7})^2$ at 25°.

$$K_{\mathrm{hyd.}} = \frac{\alpha^2}{(1-\alpha)V} = \frac{(1.09 \times 10^{-7})^2}{13 \times 10^{-10}},$$

from which, when $d_B = 1$ and $V = 10$, $\alpha = 0.967\%$.

In the table below are given the values of $\frac{\alpha^2}{(1-\alpha)V}$ for various equilibria, in which but 1 mole of water reacts with the substance.

HYDROLYSIS OF HYDROCHLORIDES AT 25°.

Base.	Per Cent Hydrolysis at $V=32$.	$\frac{a^2}{(1-a)V}$	Ionization Constant of Free Base.
Aniline.	2.7	2.25×10^{-5}	5.3×10^{-10}
o-Toluidine.	7.0	1.62×10^{-4}	7.3×10^{-11}
m- "	3.6	4.10×10^{-5}	2.9×10^{-10}
p- "	1.8	1.05×10^{-5}	1.13×10^{-9}
o-Nitroaniline.	98.6	2.1	5.6×10^{-15}
m- "	26.6	3.01×10^{-3}	4.0×10^{-12}
p- "	79.6	9.58×10^{-2}	1.24×10^{-13}
Aminoazobenzene.	18.1	1.25×10^{-3}	9.5×10^{-10}
Urea.	....	0.781	1.5×10^{-14}

An example of Case I, where the salt reacts with two moles of water, is the hydrolysis of aluminum chloride according to the reaction

$$AlCl_3 + 2H_2O = Al(OH)_2Cl + 2HCl,$$

which has been investigated by Kullgren.* We have, then,

$$d_S c(1-\alpha)\left(\frac{s_{H_2O}}{2d_A \alpha c}\right)^2 = K_{Al(OH)_2Cl}\alpha c.$$

or

$$\frac{4\alpha^3}{(1-\alpha)V^2}\cdot\frac{d_A^2}{d_S} = \frac{s^2{}_{H_2O}}{K_{Al(OH)_2Cl}} = K_{hyd.},$$

and from this we can calculate the ionization constant of $Al(OH)_2Cl$, when α is known, or dispense entirely with it, i.e., using the $K_{hyd.}$ so determined for the calculation of other values. It will be observed here that α, instead of being proportional to $\sqrt{V}$ as it is for the reaction with 1 mole of water, is proportional to $\sqrt[3]{V^2}$. The following results will show how well this equilibrium follows the above law, and how it is possible to find the ionization constant by aid of the hydrolytic dissociation, knowing the ionic product for water at that temperature.

HYDROLYSIS OF $AlCl_3$ AT 100° C.

$$AlCl_3 + 3H_2O = Al(OH)_2Cl + 2H^{\cdot} + 2Cl'.$$

V	a	d_A	d_S	$\frac{a^3}{(1-a)V^2}$	$K_{hyd} = \frac{a^3}{(1-a)V^2}\cdot\frac{d_A^2}{d_S}$
96	0.1488	0.966	0.76	420×10^{-9}	516×10^{-9}
384	0.3629	0.977	0.85	509×10^{-9}	571×10^{-9}
1536	0.7142	1	0.91	541×10^{-9}	594×10^{-9}

Average, $K_{hyd.} = 560\times10^{-9}$

The concentrations of base in the three cases are 0.00155 0.000945, and 0.000465, respectively, the acid concen-

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* Om metalsalters hydrolys, p. 108. Dissertation. Stockholm, 1904.

trations being twice these values. The average value of $K_{\text{hyd.}}$ in the last column may be used to determine $K_{Al(OH)_2Cl}$, for $\frac{s^2_{H_2O}}{K_{Al(OH)_2Cl}} = 4\frac{\alpha^3}{(1-\alpha)V^2}\cdot\frac{d_A^2}{d_S}$. We obtain in this way the value $K_{Al(OH)_2Cl} = 2.33 \times 10^{-19}$, where the ionization, presumably, gives $AlCl^{\cdot\cdot}$ and $2OH'$.

Examples of Case II are solutions of barium hydroxy-azobenzene, sodium acetate, sodium carbonate, etc; while Case III is illustrated by solutions of aniline acetate, ammonium borate and ammonium acetate[*].

In certain other cases it has been found that hydrolytic dissociation takes place in stages, i.e., first 1 mole of water reacts, then another, etc. It is quite certain, however, that this does not occur at the dilutions above of $AlCl_3$, for if it did, the formula used would not give a constant value, hence in this one case between these limits of dilution 2 moles of water react with 1 of salt.

$Tl(NO_3)_3$, according to Spencer and Abegg,[†] on the other hand, seems to react directly with 3 moles of water, the $Tl(OH)_3$ having a solubility equal to $10^{-13.58}$ moles per liter, i.e., $s = 10^{-52.896}$, but as yet this is the only case known.

Naturally, any method for determining the concentration of ionized $H^{\cdot}$ or ionized OH', or the undissociated substance formed, will enable us to find the amount of hydrolytic dissociation.

One method,[†] which can be used for salts of weak acids with strong bases, or salts of weak bases with strong acids, has been suggested by Farmer,[§] and this, owing

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[*] "Elements," pp. 360, 361.

[†] Zeit. f. anorg. Chem., 44, 397, 1905.

[‡] See "Elements," pp. 405, 406, for an electrical method.

[§] Trans. Chem. Soc., 79, 863, 1901, and ibid., 85, 1713, 1904.

to the importance of the principle involved, is briefly considered below. The method is based upon the coefficient of distribution of a substance between water and another solvent, benzene (pp. 79–80). Thus, hydroxyazobenzene has a coefficient of distribution between water and benzene equal to 539, i.e., benzene always takes up 539 times as much hydroxyazobenzene as the water, when the two solvents are present in equal volumes. If the two solvents are present in unequal quantity, say 1 liter of water to q liters of benzene, the hydroxyazobenzene in the water will be distributed between them in the ratio $1:539q$.

By shaking a water solution of the barium salt of hydroxyazobenzene with benzene, then, the free hydroxyazobenzene, if it be formed by hydrolysis, will be partially extracted by the benzene. Finding the amount of this present in the benzene solution, multiplying it by $\frac{1}{539q}$, we find what is left in the aqueous solution. This gives us the free base in the aqueous layer, and this when multiplied by the total acid present in the water layer and divided by the salt remaining, gives us $K_{\overline{\text{hyd.}}}$, from which we can calculate α. By this method, for numerous dilutions of the barium salt, the formula $K=\frac{\alpha^2}{(1-\alpha)V}$ was found to give a constant value for K, which at 25° is equal to $24.3+10^{-7}$.*

This method has also been applied to the hydrolysis of the hydrochlorides of weak bases, as aniline, etc. (where the coefficient of distribution of the free base is deter-

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* "Elements," pp. 363–365.

mined), with very satisfactory results. The values in the table on page 175 were found in this manner.

In all such determinations constancy of temperature is of paramount importance, for hydrolytic dissociation, as will have been observed from the foregoing, is largely influenced by the temperature. This is due not only to the increased ionization of water (p. 163) with the temperature, but also to the *decrease* in the ionization constants of acids and bases. Thus for acetic acid $K_{18^\circ}=18.3\times 10^{-6}$, $K_{100^\circ}=11.4\times 10^{-6}$, $K_{156^\circ}=5.6\times 10^{-6}$, and $K_{218^\circ}=1.9\times 10^{-6}$, while for ammonium hydrate $K_{18^\circ}=17.1\times 10^{-6}$, $K_{100^\circ}=14\times 10^{-6}$, and $K_{156^\circ}=6.6\times 10^{-6}$.

Ionic equilibria. — Knowing the solubility or ionic products, and the ionization constants of the constituents, it is often possible to gain an idea of the mechanism of the reaction and the equilibrium that will be produced; or, on the other hand, to calculate some of these factors when the composition of the system at equilibrium is known. Thus it is possible to calculate the ionization constant of an acid (or a base) from its increased solubility in a base (or an acid) with a known ionization constant.* In the same manner, also by aid of the law of mass action, it can be proven that magnesium hydrate is not precipitated by ammonia in the presence of ammonium chloride, *not because of the formation of a double salt of magnesium and ammonium, but simply because the decrease in the amount of ionized* OH' *from* NH_4OH, *by the presence of an excess of ionized* $NH_4^{\cdot}$ *from the* NH_4Cl, *is so great that the solubility product of* $Mg(OH)_2$ *cannot*

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* See "Elements," pp. 365–371; Löwenherz, Zeit. f. phys. Chem., 15, 385, 1898.

be exceeded.[*] And this conclusion has been confirmed by Treadwell,[†] who studied the freezing-points of solutions of $MgCl_2$ and NH_4Cl separately, and then when present together and showed conclusively that no such compound exists in solution.

Findley[‡] has investigated the reversible reaction.

$$\text{solid } PbSO_4 + \text{dissolved } 2NaI \rightleftarrows \text{solid } PbI_2 + \text{dissolved } Na_2SO_4;$$

i.e., expressed in ionic form,

$$\text{solid } PbSO_4 + 2I' \rightleftarrows \text{solid } PbI_2 + SO_4''.$$

Applying the law of mass action to this he found that

$$\frac{c^2_{I'}}{c_{SO_4''}} = \text{constant},$$

where at 25° C. the value of the constant lies between 0.25 and 0.3. The outcome of the investigation may be summed up as follows: *From a mixed solution of sodium iodide and sodium sulphate, by the addition of a soluble lead salt, pure lead iodide (the more soluble) can be precipitated if the ratio of the square of the concentration of ionized iodine to the concentration of the ionized sulphate radical (i.e., SO_4'') is greater than the equilibrium constant. When the ratio becomes equal to this constant, both lead iodide and sulphate are precipitated together, the ratio* $\frac{c^2_{I'}}{c_{SO_4''}}$ *remaining constant. And all this is true for the sulphate (the less soluble) when the ratio is smaller than the constant.*

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[*] "Elements," pp. 375–381; Lovén, Zeit. f. anorg. Chem., 37, 327, 1896; Muhs, Dissertation, Breslau, 1904.

[†] "Elements," pp. 379, 380; Zeit. f. anorg. Chem., 37, 327, 1903.

[‡] "Elements," pp. 381, 382; Zeit. f. phys. Chem., 34, 409, 1900.

It will be observed from these examples that by aid of the law of mass action, even though it fails to hold for strong electrolytes, we can foresee and regulate many, if not most, of the reactions with which we come in contact. Many other examples could be cited here to illustrate the methods of application, but the few above will suffice to bring out the general principles and enable the reader to follow work of this sort.

Naturally, the solubility product, and the other conceptions developed above, are of great importance in analytical chemistry. For an account of these the reader must be referred * elsewhere, however, as it is, only the principles, and not so much the application, that can be included in this small volume.

The color of solutions.—The color of a solution depends apparently upon the condition of the solute in the solvent. If a substance is not at all ionized, or but slightly so, any color it may possess must be attributed to the un-ionized substance. In case the ionization is practically complete the color of the solution will be the result of the mixture of the colors of the kinds of ionized matter present; or if only one kind is colored, that color will be the color of the liquid. When partly dissociated, then, the color of a solution will be the result of the mixture of the colors of the ionized and the un-ionized portions; or if only one of these is colored, that color will be the color of the liquid. The un-ionized portion in cases, however, may also show the color of the ionized portion.†

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* See Ostwald's Scientific Foundations of Analytical Chemistry; or Böttger's Qualitative Analyse.

† Noyes, Technology Quarterly, 17, 306, 1904.

There is always a chance of error here if the color of the solid is assumed to be its color in solution. The color of a crystal, for example, is very often different from that of the substance in the form of powder, and, further, it may be possible that a dissociation takes place in the water of crystallization. In this latter case, of course, the solid would exhibit the same color as the colored ion. The only correct way to find the color of the undissociated portion in solution is to use a solvent in which the substance is not dissociated to any extent, then the color can be directly observed. This is not difficult to carry out, for all solvents have a different ionizing power, and either alcohol, ether, benzene, chloroform, or acetone will be found to serve the purpose.

The ionized matter produced from most acids is colorless, consequently all salts of a metal in very dilute solutions will have the same color, i.e., the color of the ionized metal. In more concentrated solutions this is not true, for many un-ionized substances are colored and, as they are now present to a greater amount, the color of the solution is the result of the mixture of the colors of these and those of the kinds of ionized matter. An example of this is given by solutions of cuprous chloride, where the color of the un-ionized portion is yellow. But the ionized copper is blue, hence the color of a solution of cuprous chloride may be either yellow, green, or blue, according as it is undissociated, or ionized to a lesser or greater degree. All copper solutions when very dilute, however, provided the negatively charged ionized matter is colorless, show the same blue color.

The formation of an ionized complex can be followed very closely when it is produced by a colored and a colorless kind of ionized matter. Thus if a KCN solution is added to a colored copper solution the color instantaneously disappears, due to the formation of the ionized complex $CuCN_4''$. The formation of an ionized complex ion can be proven, of course, in this way, but its nature can only be shown by migration experiments, as will be shown later. (See Chapter VII.)

CHAPTER VII.

ELECTROCHEMISTRY.

THE MIGRATION OF IONIZED MATTER.

Faraday's law. Electrical units.—Before discussing the changes produced in a solution by the passage of the electric current, we must first consider the fundamentals upon which the measurement of such a change depends.

The general guiding principle of electrochemistry is *Faraday's law*, which regulates the relationship between the quantity of electricity flowing and the amount of substance it deposits. This law may be summarized by the two following statements:

1. *The amount of any substance deposited by the current is proportional to the quantity of electricity flowing through the electrolyte.*

2. *The amounts of different substances deposited by the same quantity of electricity are proportional to their chemical equivalent weights.*

In order to make use of this law, however, it is necessary to recall the definitions of the various electrical units employed in describing an electric current.

The resistance offered by a body to the electric current is expressed in ohms, *1 ohm* being the resistance at 0° C. of a column of mercury 106.3 cms. long with a cross-section of 1 square mm. This is equal to 10^9 absolute units.

The unit of electromotive force is the *volt*, i.e., 10^8 absolute units. A Daniell cell has an electromotive force of 1.10 volts.

The *ampere* is the unit of current strength; 1 ampere will separate 0.001118 gram of silver from a solution in 1 second, and is equal to 10^{-1} absolute units.

These three quantities are related, according to Ohm's law, in such a way that in any one circuit we always find

$$\text{current strength} = \frac{\text{electromotive force}}{\text{resistance}}.$$

The actual quantity of current, i.e. amperes per second, is expressed in *coulombs:* 1 gram of ionized $H^{\cdot}$ carries with it 96,540 coulombs.

As the intensity factors of electrical energy, then, we have the voltage, while the capacity factor is expressed in coulombs, i.e.

$$E = \varepsilon\pi,$$

where E is the electrical work, the unit of which is the watt-second, equal to an ampere at 1 volt in 1 second. This is equal to 10^7 absolute units.

The heat equivalent of electrical energy, since the unit of the latter is equal to volt × coulomb or 10^7 absolute units, is

$$\frac{10^7}{42600 \times 980.1} = 0.2394,$$

i.e., 1 watt-second = 0.2394 calories.

To separate 1 gram of hydrogen, then, or the equivalent weight in grams of any other element, we require the work

$$\pi \times 96540 \times \text{watt-seconds} = 96540 \times 0.2394\pi = 23110\pi \text{ cals.}$$

The migration of ionized matter.—The chemical effect of the passage of an electric current through an electrolyte can be divided into two distinct portions, viz., the *conduction* through the electrolyte and the *separation* of substance at the electrodes. It is not necessary that the ionized matter, which serves for the conduction of the current through the liquid, be separated at the electrodes, for *secondary reactions* may take place there, causing other substances to appear as the result of the electrolysis. It is to be remembered here, however, that even in such a case Faraday's law still holds, and the substances separated are chemically equivalent in amount to those which would have been separated in case the secondary action had been avoided.

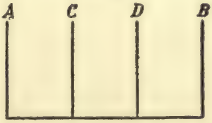
Although the two different effects are observed together in practice, we shall consider them separately, taking up the question of conduction here and putting off that of separation to a later period.

The conduction through the liquid depends upon what we have designated thus far as ionized matter, and varies according to the *mobility* of this, which, in turn, is dependent upon the specific nature of the matter, its concentration, the temperature, and the nature of the solvent.

After the electrolysis of a solution, *excluding, or allowing for, any secondary reaction,* it is found experimentally that the concentrations around the anode and cathode are not always identical, as they were initially. In some few cases they are, it is true, but in these it can be shown (as will be done later) that the mobility, i.e. velocity through the liquid at any voltage, is the same for both the anion, which goes to the anode, as it is for the cathion, which goes to the cathode. In all other cases the mobility, or speed of migration through the liquid, is different for the two kinds of ionized matter of which the substance is composed.

And further than this, the analysis of the anode and cathode liquids after electrolysis, excluding secondary reactions, leads to an expression for the relative mobilities, i.e., the migration ratio of the two kinds of ionized matter. Indeed, when the original solution is colored, this difference in concentration can be observed qualitatively by the eye. The reasons for this change, together with the principle upon which its quantitative calculation is based, will be made clear by the following considerations:

Assume the vessel in the figure below to be divided into three portions, *AC*, *CD*, and *DB*, and filled with a solution containing 30 gram equivalents of HCl. We have, then,



10 gram equivalents in each division. If 96,540 coulombs of electricity are passed through the cell from *A* to *B*, 1 gram equivalent of ionized $H^{\cdot}$ and 1 gram equivalent of ionized Cl' will lose their charges and be separated upon the electrodes *B* and *A*, if secondary action is excluded. These gases we assume to be removed as they are formed. These 96,540 coulombs passing as they do tro ugh the whole solution have a certain effect upon the

equilibrium of the ionized substances. First we will imagine the ionized $H^{\cdot}$ and ionized Cl' to move with the same velocity and then with differing velocities, and find the relation between the change in concentration and the relative mobilities.

It is to be remembered here that two oppositely electrified bodies composing a system will transport a current equal to the sum of the charges carried by the two bodies in the opposite direction, for a negative charge going in one direction is equivalent to an equal and opposite charge going in the contrary direction. In other words, *all* of the current may be transported by the positive material, or a portion may be carried by each in opposite directions, and in all cases the total current is the *sum* of those currents going in the opposite directions.

I. If the velocity for each kind of ionized matter is the same, then, $^1/_2$ gram equivalent of ionized Cl', charged with 48,270 coulombs, will migrate from *BD* through *DC* to *CA*; and $^1/_2$ gram equivalent of ionized $H^{\cdot}$, with the same amount of electricity, will go from *AC* through *CD* to *DB*. Altogether, then, 1 gram equivalent, charged with 96,540 coulombs, will have passed through the section *CD*. Since 1 gram equivalent of ionized $H^{\cdot}$ has been removed as gas by decomposition from *BD*, and $^1/_2$ gram equivalent has migrated to it, we have left $9\frac{1}{2}$ gram equivalents of ionized $H^{\cdot}$ and $9\frac{1}{2}$ gram equivalents of ionized Cl', since but $^1/_2$ gram equivalent of this has migrated from it. Consequently we have in *BD*, $9\frac{1}{2}$ gram equivalents of HCl. In *AC* we have the same number, since 1 gram equivalent of ionized Cl' has disappeared, $^1/_2$ gram equivalent has migrated to it and $^1/_2$ gram equivalent of ionized $H^{\cdot}$ has migrated from it. In the section *DC* the concentration is unaltered, i.e., just as much ionized matter has left it as has been carried to it.

The concentration at the anode is the same as that at the cathode, then, after the electrolysis of a solution composed of two kinds of ionized matter with the same mobility.

II. *Assume* the velocity of the ionized $H^{\cdot}$ to be five times that of ionized Cl'.

In this case, after 1 gram equivalent of H and 1 gram equivalent of Cl have separated in the gaseous state, the whole system will have suffered a change. $^5/_6$ of a gram equivalent of ionized $H^{\cdot}$, charged with $\frac{5}{6}(96,540)$ coulombs, will migrate from *AC* through *DC* to *BD*, and $^1/_6$ of a gram equivalent of ionized Cl', with $\frac{1}{6}(96,540)$ coulombs, will go from *BD* through *CD* to *AC*. Altogether, as before, 1 gram equivalent of ionized matter will go through the section *CD*, carrying with it 96,540 coulombs of electricity.

The original composition of the solution in *CD* is again unchanged. In *BD* we have lost 1 gram equivalent of ionized $H^{\cdot}$ in the form of gas, and gained $^5/_6$ of a gram equivalent by the migration; consequently we have $9\frac{5}{6}$ gram equivalents of ionized $H^{\cdot}$ left. $^1/_6$ of a gram equivalent of ionized Cl' has migrated from it, so that in *DC* we have $9\frac{5}{6}$ gram equivalents of HCl.

In *AC* we have lost $^5/_6$ of a gram equivalent of ionized $H^{\cdot}$ and 1 gram equivalent of ionized Cl' as gas, but have gained $^1/_6$ of a gram equivalent of ionized Cl' by the migration; consequently we have $9\frac{1}{6}$ gram equivalents of HCl left.

From these two examples the following law may be deduced: *The loss on the cathode (BD) is related to that on the anode (AC) as the mobility of the anion matter (Cl') is to that of the cathion matter ($H^{\cdot}$).*

In this way Hittorf determined the relative mobilities or migration ratios of the various kinds of ionized matter.

The practical determination of the relative mobilities is merely a matter of analysis. The apparatus which is used for this purpose is a decomposition-cell, so arranged that no metal can drop from one electrode to the other; or a U tube may serve the purpose so long as the two portions of liquid may be removed and analyzed separately. The apparatus is filled with solution and the current passed through for a certain length of time, the electrodes being of the metal which is contained in the salt or inert, except in cases where certain secondary actions are to be avoided. After a certain time either the anode or cathode portion is withdrawn and analyzed. This analysis will give us the loss of metal on the one electrode, from which that on the other may be calculated.

If n is the fraction of the cathion which has migrated from the anode to the cathode when one gram equivalent has been separated, then $1-n$ is that fraction of the anion which has gone to the anode. These two quantities, n and $1-n$, are called the migration ratios of the cathion and anion. We have then

$$\frac{n}{1-n}=\frac{\text{loss at anode}}{\text{loss at cathode}}=\frac{U_c}{U_a},$$

where U_c is the mobility of the cathion and U_a that of the anion.

An example will make the determination of this clear: Hittorf electrolyzed a solution of $AgNO_3$ until 1.2591 grams of Ag were separated. The volume of liquid at the cathode before the experiment gave 17.46249 grams of AgCl, and after it but 16.6796 grams, i.e., a loss of 0.7828 gram of AgCl or of 0.5893 gram of Ag.

If no Ag had come to the cathode by migration, the solution would have lost 1.2591 grams of Ag; it lost, however, only 0.5893 gram; hence $1.2591-0.5893=0.6698$ gram Ag has come to it by the migration. If just as much of the Ag had come by migration as had been separated, the migration ratio of the ionized Ag would have been 1, i.e., the ionized NO_3' would not have migrated. Only 0.6698 gram of Ag has migrated, however; hence the migration ratio for the ionized $Ag^{\cdot}$ in $AgNO_3$ can be found from the proportion

$$1.2591:0.6698::1:x=0.532;$$

the migration ratio of the ionized NO_3', then, is

$$1-0.532=0.468.$$

These values are not the same for all dilutions, although in general the variation is but slight.

A table containing a large number of results from experiments of this sort is given by Kohlrausch and Holborn, Leitvermögen der Elektrolyte, a few of which will be found below.

HITTORF'S MIGRATION RATIOS FOR IONIZED MATTER.
Solutions 1/10 equivalent normal.

Substance.	$1-n$.	Substance.	$1-n$.
1/2 K_2SO_4	0.60	HN_4Cl	0.508
1/2 $CuSO_4$	0.64	1/2 $BaCl_2$	0.61
1/2 H_2SO_4	0.21	1/2 $CaCl_2$	0.68
1/2 K_2CO_3	0.37	1/2 $MgCl_2$	0.68
1/2 Na_2CO_3	0.48	HCl	0.21
1/2 Li_2CO_3	0.59	KNO_3	0.50
KOH	0.74	$NaNO_3$	0.61
NaOH	0.84	$AgNO_3$	0.526
KCl	0.507	1/2 $Ca(NO_3)_2$	0.61
NaCl	0.63	$KClO_3$	0.46
LiCl	0.70		

Naturally, it is also possible here to use inert electrodes; and in many cases, where a secondary reaction is to be avoided, it is necessary to employ as anode a metal which differs from that contained in the salt.

THE CONDUCTIVITY OF ELECTROLYTES.

The specific, molar,* and equivalent conductivities.—The conductivity of a solution may be determined for the same volume of solution (as for 1 centimeter cube, the *specific conductivity*) independent of the weight of substance dissolved; or for the volume containing 1 formula weight (according to the generally accepted formula); or, finally, for the volume containing 1 *equivalent* formula weight (i.e., the weight equivalent chemically to 1 gram of hydrogen).

The unit of specific conductivity is the conductivity which a centimeter cube possesses when its resistance is 1 ohm. The best conducting aqueous solutions of the strong acids possess this conductivity at about 40° C. We shall designate specific conductivities by κ.

This specific conductivity is the unit which is most employed in physics, but, since the conductivity of a solution depends almost exclusively upon the amount of substance it contains, it is far more convenient to apply chemical conceptions to the physical fact, and express our results in molar or equivalent terms.

The equivalent (molar) conductivity of a substance is the conductivity of the solution which contains 1 equivalent (1 mole) of substance, the electrodes being separated by 1 cm., and large enough to contain between them the

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* From here on we shall employ the word *molar* conductivity in the sense in which *molecular* conductivity was used above (see pages 81–83).

entire solution. This value can be found by dividing κ by the number of equivalents (moles) per cubic centimeter, or by multiplying κ by the number of cubic centimeters in which 1 equivalent (1 mole) is dissolved. When V is the volume containing 1 equivalent (or 1 mole) in liters, then, $\kappa \times 1000 \times V_e = \Lambda$ and $\kappa \times 1000 \times V_m = \mu$, where equivalent conductivity is designated by Λ and molar conductivity by μ.

As to the actual measurement of the specific conductivity, from which the other two values may be calculated, we need only note here that it is similar to the ordinary determination of resistance, except that an alternating current is used in place of the direct, and the galvanometer is replaced by a telephone receiver. Naturally, the alternating current is essential here to prevent actual decomposition, which would produce polarization and cause the concentration of the solution to decrease.

Although it is the specific conductivity that is measured, it is not necessary to possess a set of electrodes exactly 1 cm. in cross-section and separated by exactly 1 cm., nor is it even necessary to know the dimensions of the electrodes, for certain conductivities have been accurately measured with such electrodes, and by determining the value of one of these solutions in any form of electrode vessel it is possible to find a constant factor which will transform results obtained with it into specific conductivities. Thus for a 0.02 molar solution of KCl, Kohlrausch found the values $\kappa_{18^\circ} = 0.002397$, $\Lambda_{18^\circ} = 119.85$, $\kappa_{25^\circ} = 0.002768$, $\Lambda_{25^\circ} = 138.54$.

Ionic conductivities.—Since (by definition, p. 85) the two kinds of ionized matter are the carriers of electricity in solution, the equivalent conductivity at any dilution divided by that at infinite dilution, i.e. when the substance is present only in the ionized form, gives us the definition of the degree of ionization. We have then

$$\alpha=\frac{\Lambda_v}{\Lambda_\infty}.$$

This conductivity at infinite dilution means simply that the equivalent conductivity is not altered by further dilution. This maximum value for the equivalent conductivity Kohlrausch found for a binary electrolyte *to be equal to the sum of two single values, one of which refers to the anion matter and the other to the cathion matter. This law of the independent migration of ionized matter shows that conductivity is an additive property.* The truth of the law is shown by the results in the table below:

MOLAR CONDUCTIVITIES AT INFINITE DILUTION.

	K	Na	Li	NH_4	H	Ag
Cl.	123	103	95	122	353	. . .
NO_3.	118	98	. .	. . .	350	109
OH	228	201	. .	. . .	. . .	. . .
ClO_3	115	. . .	. .	. . .	. . .	103
$C_2H_3O_2$	94	73	. .	. . .	. . .	83

The differences of two corresponding sets of numbers in the vertical rows, and of any two in the horizontal ones, are nearly equal, which can only occur when the result is composed of two single and independent values.

One kind of ionized matter, then, always carries the same amount of electricity with its own velocity, independent of the nature of the ionized matter present with it.

The equivalent conductivity at infinite dilution is consequently

$$\Lambda_\infty=l_c+l_a,$$

where l_c and l_a are the equivalent conductivities of the kinds of ionized matter produced by the substance, the solution being at infinite dilution.

We have then (p. 178)

$$n=\frac{l_c}{l_c+l_a}=\frac{l_c}{\Lambda_\infty} \quad \text{and} \quad 1-n=\frac{l_a}{\Lambda_\infty};$$

in other words, $l_c=n\Lambda_\infty$, $l_a=(1-n)\Lambda_\infty$.

Thus the molar conductivity at infinite dilution μ_∞ (equal here to the equivalent conductivity Λ_∞) of sodium chloride is 110, while $n=0.38$ and $1-n=0.62$; hence

$$l_c=0.38\times 110=41.8(\text{Na}^{\cdot}),$$
$$l_a=0.62\times 110=68.2(\text{Cl}'),$$

i.e., *1 mole of ionized Na˙ possesses a conductivity of 41.8 when between electrodes 1 cm. apart and large enough to contain between them the total volume of solution in which the ionized sodium exists; and* 1 *mole of ionized Cl′ under the same conditions has a conductivity equal to 68.2.*

In all solutions in the same solvent, at the same temperature, these values remain constant, so that it is possible for us to calculate what the conductivity at infinite dilution would be for any substance. This is of great use in experimental work, for it is not always possible to actually reach this limiting value with any degree of accuracy.

A table of such results, then, enables us to find the limiting value of the conductivity at infinite dilution, and not only this, for

$$\Lambda_v=\alpha(l_a+l_c),$$

i.e., *if we know the fraction of a mole of each form of ionized matter present (by any other method) we can find the equivalent conductivity of the solution at any dilution by* *multiplying the sum of the ionic conductivities by the degree of ionization.*

Since most neutral salts are very largely ionized, the value of the equivalent conductivity can be readily determined experimentally. By subtracting the value for the ionized metal from this result it is possible, then, to find the ionic conductivity of the acid radical which is present as negatively charged ionized matter. In the table below are given a few ionic conductivities, from which various values may be calculated.

IONIC CONDUCTIVITIES AT 18° AND INFINITE DILUTION.*

	l	Temp. Coeff.		l	Temp. Coeff.
$Li^{\cdot}$	33.44	0.0265	$\frac{1}{2}Zn^{\cdot\cdot}$	45.6	0.0251
$Na^{\cdot}$	43.55	0.0244	$\frac{1}{2}Mg^{\cdot\cdot}$	46.0	0.0256
$K^{\cdot}$	64.67	0.0217	$\frac{1}{2}Ba^{\cdot\cdot}$	56.3	0.0238
$Rb^{\cdot}$	67.6	0.0214	$\frac{1}{2}Pb^{\cdot\cdot}$	61.5	0.0243
$Cs^{\cdot}$	68.2	0.0212	$\frac{1}{2}SO_4''$	68.7	0.0227
$NH^{\cdot}_4$	64.4	0.0222	$\frac{1}{2}CO_3''$	70	0.0270
$Tl^{\cdot}$	66	0.0215	BrO_3'	46.2	......
$Ag^{\cdot}$	54.02	0.0229	ClO_4'	64.7	......
F'	46.64	0.0238	IO_4'	47.7	......
Cl'	65.44	0.0216	MnO_4'	53.4	......
Br'	67.63	0.0215	CHO_2'	46.7	......
I'	66.40	0.0213	$C_2H_3O_2'$	35	......
SCN'	56.63	0.0211	C_3H_5O'	31	......
ClO_3'	55.03	0.0215	$C_4H_7O_2'$	27.6	......
IO_3'	33.87	0.0234	$C_5H_9O_2'$	25.7	......
NO_3'	61.78	0.0205	$C_6H_{11}O_2'$	24.3	......
$H^{\cdot}$	318	......			
OH'	174	......			

In addition to the above ionic conductivities, and the relative mobilities, it is also possible to find the absolute mobility, i.e., the velocity with which ionized matter of

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* See Kohlrausch, Berl. Akademieber. 26, 581, 1902, and Sitzungsber. d. Akad. d. Wiss. zu Berlin, 26, 572, 1902.

various kinds moves through a solution under the influence of a current of a given electromotive force. Since 1 equivalent of ionized matter will transport 96,540 coulombs of electricity, and Λ is the amount of current carried in 1 second between electrodes 1 cm. apart when the electromotive force is 1 volt (for current strength $=\frac{\text{voltage}}{\text{resistance}}$, and conductivity $=\frac{1}{\text{resistance}}\Big)$, the term $\frac{\Lambda}{96540}$ must represent the fraction of 1 centimeter traversed by the two kinds of ionized matter in 1 second, i.e., the sum of the distances traversed by each. We have, then,

$$\frac{\Lambda}{96540}=v_a+v_c,$$

and, knowing the relative mobilities, we can find the absolute mobilities of the two. An illustration of this is given by a 0.0001 molar solution of KCl, which at 18° gives $\Lambda=128.9$. We obtain, consequently,

$$\frac{128.9}{96540}=0.001345 \text{ cm. per second,}$$

and since from Hittorf's results $K^{\cdot}=49$ when $Cl'=51$ (p. 179,), the absolute mobility of $K^{\cdot}$ is 0.00066 cm. per second and of Cl' is 0.00069, when the potential gradient is 1 volt and the solution is 0.0001 molar.

Knowing the absolute mobility of the various kinds of ionized matter, then, we can calculate the equivalent conductivity at infinite dilution, or at any other dilution provided we know α, for we have $\Lambda_\infty=(v_a+v_c)96540$, and $\Lambda_v=\alpha(v_a+v_c)96540$, where the v_a and v_c refer to the mobilities in centimeters per second. In the table below are some of the absolute mobilities as given by Kohlrausch.

Absolute Velocity of Ionized Matter at 18° in Cms. per Second.

$K^{\cdot} = 0.00066$
$NH_4^{\cdot} = 0.00066$
$Na^{\cdot} = 0.00045$
$Li^{\cdot} = 0.00036$
$Ag^{\cdot} = 0.00057$
$Cr_2O_7'' = 0.000473$

$H^{\cdot} = 0.00320$
$Cl' = 0.00069$
$NO_3' = 0.00064$
$ClO_3' = 0.00057$
$OH' = 0.00181$
$Cu^{\cdot\cdot} = 0.00031$

Not only can these values be calculated in this way, but they can also be directly observed by experiment. The method, as used by Whetham,* depends upon the speed with which a color-boundary between two equally dense solutions moves during the application of the current. Imagine two solutions which contain a common and colorless kind of ionized matter, but which are colored differently, and designate the salts as *AC* and *BC*. The passage of the current will thus cause ionized *C* to go in one direction and ionized *B* and ionized *A* to go in the other. Provided these solutions are placed in a horizontal tube so that before the current is applied the color-boundary will be quite sharp, the application of the current will cause the boundary to advance with a speed which depends upon the potential gradient, and which can be measured. This speed, however, will be that of the colored ionized matter, for that produces the color. In the table on the opposite page are given the mobilities as found by calculation and by direct experiment, and but a glance is necessary to convince one of the correctness of our conclusions as to electrical conduction in solution:

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* Phil. Trans., 1893A, 337; 1895A, 507.

COMPARISON OF ABSOLUTE IONIC VELOCITIES.

Kind of Ionized Matter.	Whetham, by Experiment.	Kohlrausch, Calculated.
$Cu^{\cdot\cdot}$	0.00026	0.00031
	0.000309	
Cl'	0.00057	0.00069
	0.00059	
	0.00047	
Cr_2O_7''	0.00048	0.000473
	0.00046	

Empirical relations.—There are two empirical relations with regard to electrical conductivity which are often very useful. The first of these is of particular value to the chemist as a means of determining the constitution of chemical substances, while the second applies directly to the electrical behavior of strong (i.e. largely ionized) electrolytes.

Although the Ostwald dilution law,

$$K=\frac{(\mu_v)^2}{\mu_\infty(\mu_\infty-\mu_v)V},$$

holds for all monobasic organic acid, and for dilutions below that at which $\alpha=50\%$ for all polybasic ones. Ostwald found that the difference between the equivalent conductivity, *of the sodium salt of any organic acid*, at the dilution $V=1024$ and that at $V=32$, is approximately equal to $n\times10$ units, where n is the basicity of the acid. Thus formic acid shows a difference of 10.3 units, quininic of 19.8, pyridintetracarboxylic of 41.8, and pyridinpentacarboxylic of 50.1.

The other relation has already been mentioned (p. 153). It enables us to find the equivalent conductivity of a neutral salt at one dilution, provided we know that at another, and the salt is considerably ionized, i.e., when

Λ_v is not very different from Λ_∞. The relation observed is as follows:

$$\Lambda_\infty - \Lambda_v = n_1 \cdot n_2 \cdot c_v,$$

or

$$\Lambda_\infty = n_1 \cdot n_2 \cdot c_v + \Lambda_v,$$

where n_1 and n_2 are the valences of the anion and cathion matter respectively, and c_v is a constant for all electrolytes. When c_v is known for all dilutions, and also the terms Λ_v, n_1, and n_2, we can find the value of Λ_∞, i.e., the equivalent conductivity at infinite dilution. If we designate $(n_1 \cdot n_2 \cdot c_v)$ by d_v, then

$$\Lambda_\infty = \Lambda_v + d_v.$$

Below are given the values of d_v for different dilutions and values of $n_1 \cdot n_2$ at 25°.

Valence, $n_1 \cdot n_2$	d_{64}	d_{128}	d_{256}	d_{512}	d_{1024}
1	11	8	6	4	3
2	21	16	12	8	6
3	30	23	17	12	8
4	42	31	23	16	10
5	53	39	29	21	13
6	60	48	36	25	16

This behavior may be summed up in words as follows: *The decrease of equivalent conductivity is roughly constant for salts of the same type, and the decrease in equivalent conductivity for salts of different types is proportional to the product of the valences of the kinds of ionized matter present.*

The ionization of water.—Water ionizes to a very slight extent into $H^\cdot$ and OH'. The specific conductivity of an especially pure sample, as determined by Kohlrausch, is 0.014×10^{-6} at 0°, 0.040×10^{-6} at 18°, 0.055×10^{-6} at 25°, 0.084×10^{-6} at 34°, and 0.17×10^{-6} at 50°.

From this conductivity, naturally, we can calculate the degree of ionization, provided we know the ionic conductivities of $H^{\cdot}$ and OH' at that temperature. Since 1 mole of ionized $H^{\cdot}$ has a conductivity of 318 at 18°, and 1 mole of OH' 174 units, water, if completely ionized, would give a molar conductivity of 492 units. As the specific conductivity at 18° is 0.04×10^{-6}, that of a liter would be $0.04\times10^{-6}\times10^{3}$; hence

$$\frac{0.04\times10^{-3}}{492}=0.8\times10^{-7},$$

which is the concentration of ionized $H^{\cdot}$ and of ionized OH' in 1 liter of water, or, in other words, there are 17 grams of ionized OH' and 1 gram of ionized $H^{\cdot}$ in 12,000,000 liters of water.

It is to be remembered here that 492 is the value which would be given if 1 mole of ionized $H^{\cdot}$ and 1 mole of ionized OH' were present together, between electrodes 1 cm. apart and large enough to contain between them the 18 grams of water, or any other volume containing 1 mole each of $H^{\cdot}$ and OH'. The calculation of the ionization is usually made for 1 liter, since that is the volume to which we make up solutions.

The solubility of difficultly soluble salts.—When a saturated solution of any so-called insoluble salt is so dilute that we may assume complete ionization, $(\Lambda_\infty=\Lambda_v)$, we have

$$\kappa_{\text{solution}}-\kappa_{H_2O}=\kappa$$

and $$\Lambda_v=\Lambda_\infty=\kappa\times1000V,$$

i.e., $$c=\frac{1}{V}=\frac{\kappa\times10^3}{\Lambda_\infty}\text{ moles per liter.}$$

This method is exceedingly satisfactory, so long as the specific conductivity of the saturated solution differs sufficiently from that of water, and we can safely assume the degree of ionization to be 1 or determine it. The calculation of Λ_∞ must naturally be made by aid of the results on page 196, for by experiment it would be impossible for us to find the term Λ_∞ without knowing the solubility of the salt. In case the conductivities of the constituents of the salt for which we are to determine Λ_∞ are not included in the table we can naturally calculate them from the values at infinite dilutions of salts for which Λ_∞ can be found by experiment. In general, then, we would have

$$\Lambda_\infty(MX)=\Lambda_\infty(MX_1)+\Lambda_\infty(M_1X)-\Lambda_\infty(M_1X_1).$$

Thus for $BaSO_4$, we have

$$\Lambda_\infty(\tfrac{1}{2}BaSO_4)=\Lambda_\infty(\tfrac{1}{2}BaCl_2)+\Lambda_\infty(\tfrac{1}{2}K_2SO_4)-\Lambda_\infty(KCl),$$

i.e., $\Lambda_\infty(\tfrac{1}{2}BaSO_4)=115+128-115=121.$

The influence of temperature upon conductivity is primarily the result of temperature upon the speed of migration (for the ionization does not change very greatly with the temperature, see page 152) and is shown in the table on page 196. In general the variation in the equivalent conductivity of largely ionized salts is about 2½% per degree, and this, naturally, must always be considered when calculating ionization or solubility, as was done above.

For the calculation of the conductivity of a mixture of substances the reader must be referred elsewhere,* for the relations are too complex to be discussed here.

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* "Elements," pp. 419–422.

ELECTROMOTIVE FORCE.

The chemical or thermodynamical theory of the cell.—We shall not consider here either the methods for determining the electromotive force nor the standard cells upon which such measurements are based, but shall devote ourselves exclusively to the consideration of those factors which condition the rise and magnitude of an electromotive force in a system.

Since in general it is the chemical energy of a process which is transformed into electrical energy, and since the heat developed by a chemical reaction under certain conditions is proportional to the chemical energy involved, it is possible to derive a formula from which the electrical energy can be calculated when the heat developed by the reaction is known. Such a formula, however, proves to be satisfactory only in isolated cases, and the variation has been shown to be due to the loss or gain of heat during the process, i.e., either less or more than the heat developed by the chemical reaction itself is transformed into electrical energy.*

Imagine a reversible cell in which the amount of heat q is liberated or absorbed during the passage of 1 gram equivalent of ionized matter through the solution. Assume this cell to be in a constant temperature bath so

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* To obtain electrical energy from a chemical reaction it is usually necessary to so separate the process that it may take place in two portions, at points which are spatially separated. Thus zinc dissolves in acid, giving off hydrogen gas and evolving heat. When the zinc is connected by a wire to a plate of platinum, however, and both are placed in acid, the zinc dissolves, but the hydrogen is evolved from the platinum plate and a current of electricity flows through the wire; the process has been separated into two spatially separated portions, and a current is the result.

that its temperature cannot vary—i.e., if heat is absorbed it is replaced, if liberated it is removed—thus preventing q from causing any change in the temperature of the cell.

It is quite evident, if the chemical energy is being transformed completely into electrical energy, and no heat is either evolved or absorbed as the reaction progresses, that the chemical energy (expressed as heat) transformed is equivalent to the electrical energy produced, i. e.,

$$E_c = E_e.$$

If the reaction evolves or absorbs heat, however, it will be necessary, if the temperature is to be kept constant, to remove or supply heat to the system, and it is clear that this will involve either a decrease or increase in the electrical energy produced. In short, in addition to E_c, we must know the effect of this absorbed or liberated heat upon the electrical energy, if the total amount produced by the cell is thus to be calculated. This can be found by aid of the following ideal cyclic process. Heat the cell from the temperature T to $T+\Delta T$. The electromotive force will then go from π to $\pi+\Delta\pi$. The cell is now allowed to run until the amount of current ε_0 has been developed. In order that the cell may be retained at this constant temperature, the heat $q+\Delta q$ must be absorbed, and the electrical work done by the cell will be $\varepsilon_0(\pi+\Delta\pi)$.

Next cool the cell again to T, where the electromotive force is π and send the amount of curent ε_0 through it in the opposite direction, thus doing the electrical work $\varepsilon_0\pi$. Heat equal to q must be removed at this point to keep the temperature constant, and, provided the cell is reversible, it will again be in its original condition.

The total work involved in the circle of operations is $\varepsilon_0(\pi+\Delta\pi)-\varepsilon_0\pi$, i.e., $\varepsilon_0\Delta\pi$, and the amount of heat Δq

has been transformed into work, hence by the 2d law of thermodynamics (p. 50) we have

$$\frac{\Delta q}{q}=\frac{\varepsilon_0\Delta\pi}{q}=\frac{\Delta T}{T}:$$

i.e.,

$$q=\varepsilon_0 T\frac{\Delta\pi}{\Delta T},$$

and the correct, general, relation between the chemical and electrical energies becomes

$$E_e=\pi\varepsilon_0=E_c+\varepsilon_0 T\frac{\Delta\pi}{\Delta T},$$

or

$$\pi=\frac{E_c}{\varepsilon_0}+T\frac{\Delta\pi}{\Delta T}.$$

The electrical energy producable from chemical energy is equal to the heat of the chemical reaction, expressed in electrical units, plus the absolute temperature times the temperature-coefficient of the electrical energy, which may be either positive or negative.

The actual E.M.F., π, is only equal to that calculated from the chemical energy (as heat) of the process when the E.M.F. is independent of the temperature. Otherwise π is smaller or larger than $\frac{E_c}{\varepsilon_0}$, according as $T\frac{\Delta\pi}{\Delta T}$ is negative or positive in value.

An illustration of the application of this formula is furnished by the Grove gas-cell. Here $\pi=1.062$ volts and E_c, the heat evolved by the chemical reaction, is 34,200 calories, hence $1.062=\frac{34200}{23110}+T\frac{\Delta\pi}{\Delta T}$, i.e., $\frac{T\Delta\pi}{\Delta T}=-0.418$ volts, in place of -0.416 as found by actual experiment. The value 23,110 here is the quantity 96,540 coulombs expressed in calories, i.e., is $96,540 \times 0.2394 \times \pi = 23,110\pi$. In other words, $23,110\pi$ is the work in calories necessary to separate 1 gram equivalent of any substance at π volts.

The osmotic theory of the cell.—Considering a cell from the standpoint of our conclusions respecting the nature of electrolytes, it is possible to see more clearly into the cause of the rise of a difference in potential between two solutions, or a metal and a solution.

Assume we have two solutions in contact, and that they contain the same kind of *monovalent* ionized matter in differing concentration. The difference of potential existing on their boundary can now be calculated by aid of the following process of reasoning: If U_a and U_c are the mobilities of the respective kinds of ionized matter, then, by the passage of 96,540 coulombs of electricity, the following changes must take place: Assuming that the current enters on the concentrated side and passes through both solutions, $\frac{U_c}{U_c+U_a}$ gram equivalents (moles in this case) of positively charged ionized matter will go from the concentrated side to the dilute, and, during the same time, $\frac{U_a}{U_c+U_a}$ gram equivalents of negatively charged ionized matter will go from the dilute solution to the other. Let p be the osmotic pressure of the two kinds of ionized matter in the concentrated solution and p' that of those in the dilute solution, the maximum osmotic work to be done by the process, then, will be (p. 106)

$$\frac{U_c}{U_c+U_a} RT \log_e \frac{p}{p'} - \frac{U_a}{U_c+U_a} RT \log_e \frac{p}{p'} = \frac{U_c-U_a}{U_c+U_a} RT \log_e \frac{p}{p'},$$

and this must be equal to $\pi\varepsilon_0$ for the process going in this way, i.e., to the electrical work done at the contact surface of the two solutions. Since R in calories, when divided by 23,110, gives the value in electrical units, we can find in this way the difference of potential of two solutions, and experiment has shown the calculated values to agree with those observed.

This same method of reasoning may be applied to the cell

Concentrated amalgam of the metal M.	Water solution of a salt of the metal M.	Dilute amalgam of the metal M.

In this case the passage of 90,540 coulombs causes 1 gram equivalent of the metal M to go from the concentrated side to the dilute, and, if there are n equivalents to the mole (i.e., the metal is n valent), the maximum work per equivalent will be

$$\frac{1}{n}RT\log_e\frac{c_1}{c_2},$$

where c_1 and c_2 are the concentrations of the metal M in the two amalgams. Again, here, the value of π in volts can be found by dividing the expression by 23,110.

And in the same way we can calculate a formula for a cell with electrodes of the same soluble metal in two different concentrations of a solution of a salt or salts of that metal. Consider, for example, the cell

$$\mathrm{Cu}\left|\begin{matrix}\text{dilute}\\ \mathrm{CuSO_4}\end{matrix}\right|\overset{\longrightarrow}{\begin{matrix}\text{concentrated}\\ \mathrm{CuSO_4}\end{matrix}}\left|\,\mathrm{Cu}.\right.$$

By passing a current through this cell in the direction of the arrow the following changes will take place:

1. For each 96,540 coulombs of electricity 1 gram equivalent of copper will dissolve from the electrode in the dilute solution, i.e., will be transformed from the metallic to the ionic state;

2. At the boundary of the two solutions the process described above will take place; and

3. One gram equivalent of ionized $Cu^{\cdot\cdot}$ will be deposited from the concentrated solution upon the electrode.

As the result of processes (1) and (3) 1 gram equivalent of ionized $Cu^{\cdot\cdot}$ will go from the concentrated to the dilute solution. The maximum work of this process, then, for each 96,540 coulombs, will be

$$\frac{RT}{n}\log_e\frac{p_1}{p_2},$$

where n is the valence of the metal and p_1 and p_2 are the osmotic pressures exerted by the ionized $Cu^{\cdot\cdot}$ in the two solutions.

By the second process (contrast with direction of current in the case above) we have as the work

$$\frac{RT}{n}\cdot\frac{U_a-U_c}{U_a+U_c}\log_e\frac{p_1}{p_2}.$$

Neglecting the difference of potential between the liquids, which is usually very small, we have

$$\pi=\frac{RT}{n\varepsilon_0}\log_e\frac{p_1}{p_2},$$

or, including that,

$$\pi=\frac{RT}{n\varepsilon_0}\frac{2U_a}{U_c+U_a}\log_e\frac{p_1}{p_2},$$

i.e. the sum of the two, where, when the value 2 calories is substituted for R, and 23,100 for ε_0, π is given in volts.

By separating the amount of work $\frac{RT}{n\varepsilon_0}\log_e\frac{p_1}{p_2}$ into two portions, so that each will represent the maximum work at an electrode, we can write, neglecting the difference of potential at the boundary of the two solutions,

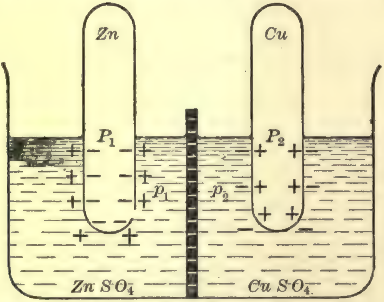
$$\frac{RT}{n\varepsilon_0}\log_e\frac{P}{p_2}-\frac{RT}{n\varepsilon_0}\log_e\frac{P}{p_1},$$

where P is a constant for any one metal at one temperature in the same solvent, and is called the *electrolytic solution pressure.*

Here, again, it is not so much a question of what electrolytic solution pressure *is*, as it is of what we mean by the word electrolytic solution pressure. It will be seen that this conception leads to a constant value for any one metal, and a value for other metals which can be found in terms of the first by finding the electromotive force when the solutions contain the same quantity of ionized metal, for this is then equal to $\frac{RT}{n\varepsilon_0}\log_e\frac{P_1}{P_2}$. We speak of positive electrolytic solution pressure when the metal dissolves, negative when the ionized metal deposits upon it.

If a metal has a tendency to dissolve in a solution, i.e. to form ionized metal, the solution must be positive against it, for the metal loses positive electricity. Unless there is some means of neutralizing this difference of potential, it is quite evident that solution must soon cease, and that all the positively charged ionized matter present (and remaining as such) must be immediately attracted back again to the metal. Naturally, if the negative charge on the plate becomes neutralized by a positive charge from without the system, solution will continue until the electrolytic solution pressure is compensated by the osmotic pressure of the ionized metal in the solution, or until the metal is all dissolved. This is the case, for example, with zinc, where the electrolytic solution pressure is positive and has a very high value.

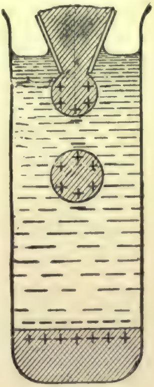
The other extreme, i.e. where ionized metal from the solution is usually precipitated, i.e. is transformed to the un-ionized metallic state, is illustrated by copper in its solutions. Here ionized metal is precipitated upon the electrode, which thus acquires a positive charge. Naturally, here also, the amount deposited is exceedingly small, for it also produces a difference of potential; and when the positive charge is neutralized by a negative one from without the system, the process of precipitation continues.



By combining the electrodes of two such systems, i.e. the zinc and copper by a wire, the solutions by a siphon, the process in each may continue, for the charges upon the electrodes can neutralize and consequently give rise to a current which flows until the zinc is all dissolved or the ionized copper all precipitated, with a loss of its charge, as metal. Further, in such a case, by applying a positive current to the copper electrode, it is possible, if the impressed electromotive force be greater than that of the cell, to reverse the process, i.e., to dissolve copper and precipitate zinc. The action of such a cell, when in operation, then, is to transform metallic zinc into the ionized metal, and ionized copper into un-ionized metal.

The condition of the zinc and copper electrodes before they are connected is shown in the figure on page 210. To obtain an E.M.F. from them it is only necessary to connect the solutions by a siphon and the electrodes through a wire.

From the formula on page 208 it will be seen that it is the ratio $\frac{P}{p}$ which is of importance. The osmotic pressure p, then, has much to do with the size of this ratio. This fact is observed best by the addition of potassium cyanide to the copper solution in which there is a copper electrode. Here experiment (loss of color, for example) shows the formation of the ionized complex $CuCN_4''$ from the ionized $Cu^{\cdot\cdot}$, and at the same time it is observed that the copper electrode dissolves, i.e. becomes negative in value (all ionized $Cu^{\cdot\cdot}$ is removed as it is formed), so that P appears positive in value. Indeed, the addition of potassium cyanide to the copper side of such a combination of a copper and zinc system, for this reason, reverses the polarity of the cell, and the copper becomes the negative pole.



The actual presence of such a layer of ionized matter around the oppositely charged metal (*the Helmholtz double layer*, as it is called), as we have concluded must necessarily be present, has been shown by Palmaer * with an arrangment which in principle is like that shown in the accompanying figure.

Drops of mercury are allowed to fall into a weak solution containing ionized mercurous mercury; metallic

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* Wied. Ann., 28, 257, 1899.

mercury being in the bottom of the tube containing the solution. If now the double-layer theory is true, the drops of Hg as they form should have the electricity of the ionized $\ddot{Hg}_2$ deposited upon them, and these positively charged drops should then attract the negatively charged ionized matter, forming on each a double layer. When such a drop reaches the mercury at the bottom it will unite with that, forming ionized $\ddot{Hg}_2$ once more and releasing the ionized radical, and the concentration of mercury salt should be greater at the bottom than at the top; and Palmaer's experiments showed this difference in concentration to actually exist.

Experiment has shown that the metals Na, K . . . , etc., up to Zn, Cd, Co, Ni, and Fe are always negative against their solutions, i.e., $P > p$.

The noble metals, on the contrary, are positive against their solutions, although in some few cases it is possible to get a solution in which $P > p$. In general, though, for the noble metals $P < p$.

A negative element has exactly the same action except that, in general, as far as is known, $P > p$. Here, although $P > p$, the electrode is positive against the solution, for the negatively charged ionized matter formed from the electrode leaves positive electricity behind.

In general, the electrolytic solution pressure depends upon the temperature, the nature of the solvent, and the concentration of the substance in the electrode (see p. 206).

Naturally, from this experimental conception of electrolytic solution pressure it is possible to derive the formula for the E.M.F. given by any combination. When 1 mole of ionized metal is formed from an electrode against the osmotic pressure p, the osmotic work is

$$\int_p^P RT\frac{dp}{p} = RT\int_p^P \frac{dp}{p},$$

from which, by integration, we obtain

$$RT \log_e \frac{P}{p}.$$

The corresponding electrical work, however, is $\pi\varepsilon_0$, where π is the difference of potential and ε_0 is the quantity of electricity carried by 1 gram equivalent of ionized matter. We have then

$$\pi\varepsilon_0 = RT \log_e \frac{P}{p},$$

i.e.

$$\pi = \frac{RT}{\varepsilon_0} \log_e \frac{P}{p},$$

from which when $P = p$, $\pi = 0$. Expressing this in electrical units we find, in general, where n is the valence of the metal,

$$\pi = \frac{0.0002}{n} T \log \frac{P}{p} \text{ volts},$$

so that at 17°

$$\pi = \frac{0.0575}{n} \log \frac{P}{p} \text{ volts}.$$

For a substance forming negatively charged ionized matter we have, correspondingly,

$$\pi = -\frac{0.0002}{n} T \log \frac{P}{p} = \frac{0.0002}{n} T \log \frac{p}{P} \text{ volts}.$$

Combining two electrodes, knowing that ionized matter is formed at one and disappears at the other, we have

$$\pi=(\pi_1-\pi_2)=\frac{0.0002}{n_1}\log\frac{P_1}{p_1}-\frac{0.0002}{n_2}T\log\frac{P_2}{p_2}\text{ volts.}$$

Differences of potential. Calculation of the electrolytic solution pressure.—In order to measure the electrolytic solution pressure, i.e. P in the equation

$$\pi=\frac{0.0002}{n}T\log\frac{P}{p},$$

when p, the osmotic pressure of the ionized metal, is known, it is necessary first to determine π, the difference of potential between the metal and its solution. To do this, naturally, it is necessary to combine the electrode with another, which gives a known difference of potential, and thus, knowing π and π_1 (see above), we can readily find π_2. It has been found that when mercury drops into an electrolyte the difference of potential soon becomes zero. Any cell of which this arrangement is one electrode, then, gives as its electromotive force the difference of potential existing between the metal and solution at the other electrode. As this dropping electrode is cumbersome and inconvenient for general use, it is usual to employ the so-called normal (or tenth-normal) electrode for the purpose, its value being determined once for all against the dropping electrode. The electrode in common use is made up of metallic mercury in a molar (or 0.1 molar) solution of potassium chloride which is saturated with calomel. The value of the normal electrode * is -0.56 volt at 18°, i.e., the solution (to which the sign always refers) is negative by 0.56 volt against the metal. The value of the electrode when 0.1 molar salt is used is -0.613 at 18°, for mercury has a negative electrolytic solution pressure, and the weak solution of KCl dissolves a greater amount of calomel, i.e., contains a greater amount of ionized mercury.

Since p, the osmotic pressure of the ionized metal in atmospheres, is equal to the product of the concentration in moles per liter and $22.4\frac{T}{273}$, we can readily calculate P in the equation

$$\pi=\frac{RT}{n\varepsilon_0}\log_e\frac{P}{p},$$

if we know π, the difference of potential between the metal and its solution at the absolute temperature T. At 17° C., thus, we have

$$\log P=\frac{\pi n}{0.0002T}+\log p,$$

from which the value of P in atmospheres can be found. The values of P for the various metals, obtained in this way, are given in the table on the following page. It is to be remembered here that these values are merely symbolical, for the gas laws may not be applied to such an extent. The relation between these numbers, however, are those that would be found if the E.M.F.' were measured under the condition that the osmotic pressures of the ionized metals were the same.

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* For details as to this, see "Elements," pp. 442–445.

ELECTROLYTIC SOLUTION PRESSURES OF THE METALS.

Zinc	9.9×10^{18}	atmospheres
Cadmium	2.7×10^{6}	“
Thallium	7.7×10^{2}	“
Iron	1.2×10^{4}	“
Cobalt	1.9×10^{0}	“
Nickel	1.3×10^{0}	“
Lead	1.1×10^{-3}	“
Hydrogen	9.9×10^{-4}	“
Copper	4.8×10^{-20}	“
Mercury	1.1×10^{-16}	“
Silver	2.3×10^{-17}	“
Palladium	1.5×10^{-36}	“

When the metals acting as electrodes are inert, as in the so-called *oxidation and reduction cells*, the significance of the conception of electrolytic solution pressure naturally disappears. An example of such a cell is given by the arrangement

$$\text{plat. Pt—}FeCl_3\text{ sol. . . . }SnCl_2\text{ sol.—plat. Pt.}$$

Here it is simply a question of the electric charge upon the ionized matter, and the action may be expressed by the equation

$$2Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} = 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}.$$

The heat of ionization.—Knowing the difference of potential existing between a metal and a solution, and its rate of change with a variation in the temperature, it is possible from the formula on page 192 to find the heat of ionization of the metal. We found there that

$$E_e = E_c + \varepsilon_0 T \frac{\Delta\pi}{\Delta T},$$

or

$$\pi = \frac{E_c}{\varepsilon_0} + T \frac{\Delta\pi}{\Delta T}.$$

The term E_c, here, is the heat produced when 1 gram equivalent of the metal goes from the metallic to the ionic state, and its value is given by the formula

$$E_c=\left(\pi-T\frac{\Delta\pi}{\Delta T}\right)\varepsilon_0.$$

But (page 174),

$$\varepsilon_0\pi=96540\times0.2394\times\pi \text{ volts}=23110\pi \text{ cals.};$$

hence the heat of ionization E_c, for 1 gram equivalent, can be found from the relation

$$E_c=\left(\pi-T\frac{\Delta\pi}{\Delta T}\right)23110 \text{ cals.}$$

For copper in copper acetate (molar) at 17°, $\pi=0.6$, and $\frac{\Delta\pi}{\Delta T}=0.000774$, while $\frac{\Delta\pi}{\Delta T}$ for copper in copper sulphate is 0.000757, i.e. an average value of $\frac{\Delta\pi}{\Delta T}$ of 0.000766 volt, hence E_c, the heat of ionization of copper, is 8736 cals. per gram equivalent, or 17,472 cals. per mole. It was in this way that the value for H was determined for use in the table given on page 101.

Concentration cells.—If the electrodes of a cell are amalgams containing different concentrations of the same metal, and the solutions are identical with respect to the ionized metal, our general formula for the electromotive force (p. 214),

$$\pi=\frac{0.0002}{n_1}T\log\frac{P_1}{p_1}-\frac{0.0002}{n_2}T\log\frac{P_2}{p_2} \text{ volts},$$

becomes, since $n_1 = n_2$, and $p_1 = p_2$,

$$\pi = \frac{0.0002}{n} T \log \frac{P_1}{P_2},$$

where P_1 and P_2 are the electrolytic solution pressures of the two amalgams with respect to the dissolved metal. We have, then, a concentration cell in which the electrodes have different concentrations. Since the electrolytic solution pressure due to the dissolved metal is proportional to the amount of this dissolved in the mercury, the formula acquires the simpler form $\pi = \frac{0.0002}{n} T \log \frac{c_1}{c_2}$ volts. This equation has been tested experimentally for zinc and copper amalgams and found to express very accurately the relations observed.

Zinc in amalgams, as well as most other metals, exists in monatomic form, i.e., the formula weight (by freezing-point definition, for example) is found to be identical with the combining weight. If it were diatomic, i.e. the formula weight contained two combining weights, the above formula would have assumed a different form. For the movement of the same weight of ionized matter (see page 201) the osmotic work would *then* have been $\frac{1}{2} RT \log_e \frac{c_1}{c_2}$, and, since the electrical work would have been unchanged, i.e. $2 \times 96540\pi$, we should have had

$$\pi = \frac{1}{2} \frac{0.00002}{n} T \log \frac{c_1}{c_2} \text{ volts},$$

i.e., the electromotive force would have been one-half what it has been found to be.

Another example of a concentration cell due to a different concentration in the electrodes is given by cells of the type of the Grove gas-battery in an altered form. The electrodes, here, are of platinized platinum, in which the gas is absorbed under different pressures, and are placed partly in a liquid and partly in the gas at a corresponding partial pressure. Such an electrode is to be considered as a perfectly reversible gas electrode,* i.e., one from which the material absorbed as a gas is given up in the ionized state, for the metal acts simply as a conductor, as has been shown experimentally by the use of different metals, the same result being always obtained. In this way reversible gaseous electrodes of all kinds can be made. Oxygen as an electrode, however, gives off ionized OH′, since ionized O″ is not known to exist, and forms O and H_2O when the ionized OH′ gives up its charge to it.

If we have two electrodes of H, under different pressures, in contact with a liquid containing ionized $H^{\cdot}$, we shall obtain a certain E.M.F. This may be calculated in two ways, as we did in the case of amalgams. In the second way, however, the process is slightly different, since one mole of H gas forms two moles of ionized $H^{\cdot}$ (p. 88). The osmotic work is equal to $RT \log_e \frac{P_1}{P_2}$, as before. The electrical work, however, which corresponds to this is $2\varepsilon_0\pi$, for $H_2 = 2H^{\cdot}$; hence

$$\pi = \frac{RT}{2\varepsilon_0} \log_e \frac{P_1}{P_2};$$

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* The electrolytic solution pressure here of the gas electrode is proportional to the nth root of the gaseous pressure, where n is the number of combining weights in one formula weight of gas.

i.e., we have 2 in the denominator, notwithstanding the fact that the gas is monovalent.

When the electrodes of the cell are of the same metal, but the concentration of ionized metal in solution differs on the two sides, we have the typical form of a concentration cell. An example of this arrangement is

$$\mathrm{Ag(AgNO_3\ conc.)—(AgNO_3\ dilute)Ag},$$

for which, since $P_1=P_2$, we have the formula

$$\pi=0.0002T\log\frac{p_1}{p_2},$$

p_1 being the osmotic pressure of ionized $Ag^{\cdot}$ on the concentrated side, and p_2 that on the dilute. But, since osmotic pressure is proportional to the concentration, we may also use the formula

$$\pi=0.0002T\log\frac{c_1}{c_2}.$$

Conductivity experiments show that the concentration of ionized $Ag^{\cdot}$ in a 0.01 molar solution is 8.71 times as great as that in one that is 0.001 molar (not 10 times), hence the E.M.F. at 18° of the cell

$$\mathrm{Ag(AgNO_3\ 0.01\ molar)—(AgNO_3\ 0.001\ molar)Ag}$$

is $\pi=0.0002\times 291\times\log 8.71=0.054$ volt, while direct measurement shows 0.055 volt.

Since at 17° we have $\pi=\dfrac{0.058}{n}\log\dfrac{c_1}{c_2}$ volts, a concentration ratio of ionized matter equal to 10 would give

0.0575 volt for a monovalent metal, 0.02875 for a divalent one, etc.

Determination of ionization from electromotive-force measurements.—Applying the formula we have used for concentration cell, where it is the concentration of ionized matter in solution that varies, it is very simple to determine the concentration of ionized matter on one side, provided that of the same kind on the other side is known. Naturally, here, we can only apply this to the ionized matter coming from the electrode, but indirectly from the effect that other kinds of ionized matter have upon this (pp. 141, 158, 159) we can find the concentration of the other kinds. An example of the direct method here, and of course the other is identical so far as the electrical part is concerned, for it simply necessitates after that the application of the law of mass action, is given by Goodwin's determination of the concentration of ionized $Ag^{\cdot}$ and Cl' in a saturated solution of AgCl, i.e., the solubility of AgCl on the justified assumption that the ionization of AgCl is practically complete. The E.M.F. at 25° of the cell

$$Ag(AgNO_3\,{}^m/_{10})\text{—}KNO_3\text{—}(AgCl\text{ in }KCl\,{}^m/_{10})Ag$$

is 0.45 volt. Since α for $AgNO_3\,{}^m/_{10}$ is 0.82, and for $KCl\ {}^m/_{10}$ is 0.85, we have

$$\log\frac{0.082}{c_2}=\frac{0.45}{0.0002\times 298},\quad \text{i.e. } c_2=1.94\times 10^{-9},$$

where c_2 is the concentration of ionized $Ag^{\cdot}$ in a saturated solution of AgCl in ${}^m/_{10}$ KCl. Since the concentration of ionized Cl' in the KCl is 0.085 molar, the solubility product of AgCl is

$$1.94\times 10^{-9}\times 0.085=1.64\times 10^{-10},$$

and its solubility is $\sqrt{1.64\times 10^{-10}} = 1.28\times 10^{-5}$ moles per liter in pure water, i.e., where the amount of ionized $Ag^{\cdot}$ is equal to that of ionized Cl'.

In case we had had a solution of a known concentration of a silver salt in place of the AgCl in KCl we could have determined the fraction of ionized $Ag^{\cdot}$ in it. Or, in the case as it is, we might dissolve the AgCl in some other chloride, and determine, from the known solubility of AgCl in pure water (by conductivity, for example) and the law of mass action, the concentration of ionized Cl' in that salt.

One thing to be noted concerning this method is *that the smaller the concentration of ionized* $Ag^{\cdot}$ (page 203) *on the left side, the greater the E.M.F., and, consequently, the more accurate the determination.*

Another illustration of the use of this formula in this way is Ostwald's determination of the ionization of water. The E.M.F. of the cell (H in plat. Pt) acid—base (H in plat. Pt) at 17° is 0.081, using molar acid and base. Since α for the molar acid is 0.8 (i.e. $H^{\cdot} = 0.8$ mole per liter), we have

$$\log\frac{0.8}{c_2} = \frac{0.81}{0.0575};\quad \text{i.e., } c_2 = 0.8\times 10^{-14}.$$

In other words, the concentration of ionized $H^{\cdot}$ from water in the presence of molar base containing 0.8 mole of ionized OH' is 0.8×10^{-14}. Hence the ionic product for water is

$0.8\times 0.8\times 10^{-14}$, and since $\sqrt{0.8\times 0.8\times 10^{-14}} = 0.8\times 10^{-7}$,

1 liter of water contains 0.8×10^{-7} moles each of ionized $H^{\cdot}$ and ionized OH', which is the same value

as that found by Kohlrausch from the conductivity of pure water.

The processes taking place in the cells in common use.—We shall now consider, by aid of the things we have found above, the processes which take place in cells.

The Clark cell is made up according to the scheme

$$Hg - Hg_2SO_4 - ZnSO_4 - Zn.$$

The Hg_2SO_4 although difficultly soluble goes into solution to a slight extent, so that we have a small amount of ionized $Hg_2^{\cdot\cdot}$ present in the solution. The zinc, owing to its high electrolytic solution pressure, goes into solution and consequently forces positively charged ionized matter ($Hg_2^{\cdot\cdot}$) to give up its charge. The zinc is thus negative from the loss of ionized zinc, while the mercury is positive owing to the deposition upon the electrode of ionized mercury. The rapid polarization of the cell when short-circuited is due entirely to the removal of the ionized $Hg_2^{\cdot\cdot}$, but the value is restored as soon as the solution again becomes saturated with the mercury salt, i.e., so soon as the original concentration of ionized $Hg_2^{\cdot\cdot}$ is restored.

The Leclanché cell consists of a solution of ammonium chloride, in which we have two electrodes, Zn and $C + MnO_2$. The action of the MnO_2 is to prevent polarization, the processes taking place without it and with it being as follows:

In the cases without MnO_2 the Zn with its high solution pressure goes into solution, driving before it the other positively charged matter, i.e., the ionized $NH_4^{\cdot}$. This ionized matter decomposes on losing its change, forming NH_3 and H gases. The bubbles of H collecting upon the electrode are absorbed and so given off to the air, but as this process is slow, the ionized matter is prevented from giving up its charge and consequently the E.M.F. decreases. It is to get rid of this action of the H gas that the MnO_2 is used. In contact with water we have, to a small extent, a solution of MnO_2, which ionizes according to the scheme

$$MnO_2 + 2H_2O = Mn^{::} + 4OH'.$$

This tetravalent ionized $Mn^{::}$ has the tendency to go into the divalent state by giving up two equivalents of electricity, i.e., to form ionized $Mn^{\cdot\cdot}$. In consequence of this the ionized $Mn^{::}$ with the ionized $NH_4^{\cdot}$ is driven to the electrode by the ionized $Zn^{\cdot\cdot}$, and, since it gives up two equivalents of electricity more readily than any other kind of ionized matter gives up its entire charge, the electricity is given up by it without any substance which might cause polarization being deposited. We have, then, $MnCl_2$ (i.e., ionized $Mn^{\cdot\cdot}$) formed in the solution, and the process continues so long as there is solid Zn and MnO_2 present.

The Bichromate cell is arranged according to the scheme

$$Zn - H_2SO_4 — K_2Cr_2O_7 - C.$$

The action of the two substances in solution forms chromic acid ($H_2Cr_2O_7$). This ionizes into

$$2H^{\cdot} + Cr_2O_7''$$

to a considerable extent, and to a smaller degree as follows:

$$H_2Cr_2O_7 + 5H_2O = 2Cr^{\because\because} + 12OH'.$$

This hexavalent ionized $\mathrm{Cr}^{:::}$ has the tendency to give up three equivalents of electricity and to go into the trivalent state (i.e., into ionized $\mathrm{Cr}^{\cdots}$). Accordingly the ionized $\mathrm{Zn}^{\cdot\cdot}$, which is forced from the electrode, drives before it the ionized $\mathrm{Cr}^{:::}$, which gives up three of its equivalents and becomes $\mathrm{Cr}^{\cdots}$, remaining as such in the solution as ionized matter in equilibrium with ionized $\mathrm{SO_4}''$ (i.e., as $\mathrm{Cr_2(SO_4)_3}$). Finally, then, we have a solution of $\mathrm{Cr_2(SO_4)_3}$ left in the jar. This change in the number of electrical equivalents by a change of valence always takes place more readily than the change from the ionic to the elemental state, and is of great value as a means of preventing polarization.

Accumulators.—The action of the lead accumulator or storage-cell also depends upon a change of valence Any reversible cell can be recharged, after it is used up, by the passage of a current through it in the direction opposite to that in which it goes of itself. The lead cell, however, is generally used for the purpose owing to its high E.M.F. Before charging it consists of two lead plates, one of which is coated with litharge (PbO), in a 20% solution of sulphuric acid. If the current is passed through these plates (the PbO being positive), the PbO is transformed into $\mathrm{PbO_2}$, lead superoxide (or supersulphate), while spongy lead is deposited upon the other electrode. The flow of current is now stopped, and the cell is charged.

The $\mathrm{PbO_2}$ is soluble to a small degree, and ionizes as follows:

$$\mathrm{PbO_2 + 2H_2O = Pb^{::} + 4OH'}.$$

This tetravalent, ionized $\mathrm{Pb}^{::}$ has the tendency to give up two of its electrical equivalents and to go into the divalent form. Since this is true, the Pb electrode must have the higher solution pressure, and the ionized matter formed from it will drive the ionized $Pb^{::}$ to the electrode, where it will lose two charges of electricity and become divalent. This will continue as long as PbO_2 is present, i.e., until it is all transformed into the divalent state, $PbSO_4$. Other theories, by Liebenow and others, have also been advanced to explain this cell, but the reader must be referred elsewhere for them (see Dolezalek and von Ende, The Theory of the Lead Accumulator *).

Dolezalek has been able to calculate the value of such a cell from the concentration of acid and the vapor pressure of the solution, and finds an excellent agreement between theory and experiment. This proves the process, according to him, to be a primary one such as the theory of Le Blanc and that of Liebenow would make it.

ELECTROLYSIS AND POLARIZATION.

Decomposition values.—We must now consider those processes which are just the reverse of those we have been considering. In place of studying what takes place at the electrodes when a current of electricity is produced, we shall consider the changes at the electrodes, and in the solution, when the current is applied to inert electrodes, as those of gold, platinum, carbon, etc. It is observed that, when a current is passed through a solution for a certain time, using such electrodes, and then shut off, an electromotive force in the opposite direction arises; this is called the *electromotive force of polarization.*

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* A glance at this book will show the value in electrochemistry of the general physical chemical relations we have considered, and will convince the reader of the especial importance of the law of mass action.

Experiment has shown that every solution requires a definite minimum impressed electromotive force to produce continuous decomposition. Some of the values observed for this are given in the tables below.

DECOMPOSITION VALUES FOR THE ACIDS.

Sulphuric	= 1.67 v.	Dextrotartaric	= 1.62 v.
Nitric	= 1.69 v.	Pyrotartaric	= 1.57 v.
Phosphoric	= 1.70 v.	Trichloracetic	= 1.51 v.
Monochloracetic	= 1.72 v.	Hydrochloric	= 1.31 v.
Dichloracetic	= 1.66 v.	Oxalic	= 0.95 v.
Malonic	= 1.72 v.	Hydrobromic	= 0.94 v.
Perchloric	= 1.65 v.	Hydriodic	= 0.52 v.

DECOMPOSITION VALUES FOR THE BASES.

Sodium hydroxide	= 1.69 v. $m/4$
Potassium hydroxide	= 1.67 v. $m/2$
Ammonium hydroxide	= 1.74 v. $m/8$
Methylamine $m/4$	= 1.75
" $m/2$	= 1.68
" $m/8$	= 1.74

DECOMPOSITION VALUES FOR SALTS.

$ZnSO_4$	= 2.35 v.	$Ag(NO)_3$	= 0.70 v.
$Cd(NO_3)_2$	= 1.98 v.	$CdSO_4$	= 2.03 v.
$ZnBr_2$	= 1.80 v.	$CdCl_2$	= 1.88 v.
$NiSO_4$	= 2.09 v.	$CoSO_4$	= 1.94 v.
$NiCl_2$	= 1.85 v.	$CoCl_2$	= 1.78 v.
$Pb(NO_3)_2$	= 1.52 v.		

It will be observed that for acids and bases there is a certain maximum value, which is reached by many and exceeded by none, and is equal to 1.70 volts. Further, in all cases where the decomposition point is approximately 1.7 volts it is noticed that the products of decomposition are hydrogen and oxygen, and that those with lower values which usually give off other products also attain this value when so dilute that these gases are evolved. Thus we find the following values for hydrochloric acid solution, which, when strong, decompose into hydrogen and chlorine: 2 molar = 1.26, $^1/_2$ molar = 1.34, $^1/_6$ molar = 1.41, $^1/_{16}$ molar = 1.62, $^1/_{32}$ = 1.69. At the dilution of $^1/_{32}$ molar hydrogen and oxygen are evolved.

Le Blanc found by experiment that when a solution ($CdSO_4$) is decomposing steadily the potential difference existing between the cathode (which was originally of platinum) and the solution is the same as that observed when a stick of the metal which is deposited is in contact with a solution. Thus a molar solution of $CdSO_4$ is decomposed steadily at 2.03 volts, and when decomposing the potential difference between the cathode and the solution is $+0.16$ volts, which is the same as that given by massive cadmium in molar $CdSO_4$.

The process up to the decomposition-point, then, can be readily followed. Originally the electrolytic solution pressure of the inert electrode is zero. The small amount of current which passes through the solution, however, will suffice to deposit metal upon the electrode, and thus increase the electrolytic solution pressure from zero to a definite, small value. This increase in P naturally prevents the passage of the current at the original voltage. An increase in the voltage, then, will cause the passage of current and the deposition of more metal, and that will again raise the electrolytic solution pressure and prevent the passage of more electricity at this voltage. This process will continue, each increase of the impressed voltage depositing more metal and raising the electrolytic solution pressure. And only at that voltage which is slightly greater than the counter electromotive force exerted by the deposited metal in that solution will the decomposition be steady and continuous.

At the same time that this action is taking place at the cathode a similar one proceeds at the anode, where the negatively charged ionized matter is separated in its un-ionized state.

For water two decomposition values are observed. The one with electrodes of platinized platinum has the value 1.07 volts, i.e., is practically the same as the electromotive force given by a gas-cell with such electrodes; the other, observed when polished inert electrodes are employed, being 1.68 volts. It will be seen here that in the first case we have a reversible process, while in the second it is irreversible. It has been *assumed* that water is ionized to a very slight extent in $H^{\cdot}$ and O'', as well as into $H^{\cdot}$ and OH', and that the first, reversible action is due to the ionized O'', the value 1.68 volts being given when ionized OH' is separated according to the scheme $2OH' = H_2O + \frac{1}{2}O_2$.

It is quite usual, indeed, to designate the value 1.07 as being due to O'', and that of 1.68 to OH'. Although we shall use this designation (see table, page 231) *we shall only mean that O'' denotes reversibility and OH' irreversibility at the electrode.*

Hildburgh * has employed a reversible electrode with an irreversible one in a device for rectifying an alternating current. He used a large piece of platinized platinum for one electrode, the other being a small point of polished platinum, while the electrolyte is a solution of sulphuric acid which covers one-half of the large electrode. Before being stoppered the bottle, containing

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* Jour. Am. Chem. Soc., 22, 300, 1900.

the sulphuric acid solution and the electrodes, is filled with hydrogen gas at a certain pressure and sealed. When the point is the cathode, i.e. the large platinized electrode is the anode, it is observed that we get a continuous decomposition of water at about 1.1 volts, hydrogen being evolved from the point and oxygen absorbed in the platinum black. When the point is the anode, however, we get bubbles of oxygen first at 1.68 volts, the hydrogen being absorbed in the platinum black. In this way, by taking enough cells in series, one can rectify an alternating current, i.e., transform it into a series of impulses all in the one direction.

Primary and secondary decomposition of water.—The electromotive force of decomposition of a substance giving off hydrogen and oxygen is dependent upon the concentration of the ionized $H^{\cdot}$ and ionized OH', but independent of the nature of the electrolyte. The decomposition value is thus the same for acids and for bases, so long as only hydrogen and oxygen are separated. Since by the law of mass action the product of the concentration of the ionized $H^{\cdot}$ and the ionized OH' must always be the same in any water solution, it follows that for all electrolytes, since the electromotive force of the cell is the sum of the differences of potential at the two electrodes, the minimum value must be the same for all substances giving off oxygen and hydrogen. With the exception, then, of the solutions of metallic salts which are decomposed by hydrogen, and the chlorides, bromides, and iodides which are decomposed by oxygen, the ionized products of water are the only factors in the decomposition of solutions, and not those of the dissolved salt. *Excluding these solutions, then, we may say that all solutions when electrolyzed show primary decomposition* *of water.* The current is conducted through the solution by all the kinds of ionized matter which are present. At the electrodes, however, that process takes place which involves the expenditure of the smallest amount of work and that is the separation of hydrogen and oxygen. Thus we see in all cases that there must be an accumulation of the various kinds of ionized matter around the electrode, but that only that kind is separated which does so most easily. Naturally, if the amount of current conducted through the liquid is so great that hydrogen and oxygen cannot be separated with the least work (owing to the small concentration of ionized $H^{\cdot}$ and ionized OH') some other material may be separated instead, which will then decompose the water. But for small currents it is undoubtedly true that the decomposition of water is primary, and not secondary.

In the table below are given the values necessary for the separation of the various kinds of ionized matter, on the assumption that that for ionized $H^{\cdot}$ is zero. The values are for molar solutions.

$Ag^{\cdot} = -0.78$
$Cu^{\cdot\cdot} = -0.34$
$H^{\cdot} = +0.0$
$Pb^{\cdot\cdot} = +0.17$
$Cd^{\cdot\cdot} = +0.38$
$Zn^{\cdot\cdot} = +0.74$

$I' = 0.52$
$Br' = 0.94$
$O'' = 1.08$ (in acid)
$Cl' = 1.31$
$OH' = 1.68$ (in acid)
$OH' = 0.88$ (in base)
$SO_4'' = 1.9$
$HSO_4' = 2.6$

The values of O'' and OH' are true in the presence of a molar solution of ionized $H^{\cdot}$. If we have $H^{\cdot}$ and OH' in a base, the above value of $H^{\cdot}$ becomes 0.8 and the value of OH' and O'' is decreased by 0.8.

CHAPTER VIII.

PROBLEMS.*

GASES.

1. An open vessel is heated to 819° C. What portion of the air which the vessel contained at 0° remains in it? *Ans.* 0.25.

2. An open vessel is heated until one-half of the gas contained at 15° is driven out. What is the temperature of the vessel? *Ans.* 303° C.

3. A volume of gas, measured at 15°, is 50 c.c. At what temperature would its volume become 44 c.c.? *Ans.* −19°.6 C.

4. A volume of gas at 766 mm. pressure is 137 c.c. What would it be at 757 mm.? *Ans.* 138.7 c.c.

5. What volume does 1 mole of gas occupy at 50°, the pressure being 760 mm.? At 100°, p being 900 mm.? *Ans.* $v_{50°}=26.5$, at $v_{100°}=25.8$ liters.

6. A volume of air in a bell jar over water measures 975 c.c. The water in the jar is 68 mm. above the water in the trough, and the barometer stands at 756 mm. What would the volume be if exposed to standard pressure, the specific gravity of Hg being 13.6? *Ans.* 963.4.

7. At 14° C. and 742 mm. pressure a volume of gas measures 18 c.c. What will be its volume at 0° and 760 mm. pressure? *Ans.* 16.72.

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* For further problems, see "Elements," pp. 477–517.

8. A volume of H at a temperature of 15° measures 2.7 liters with the barometer at 752 mm. What would have been its volume had the temperature been 9° and the pressure 762 mm.? *Ans.* 2.6 liters.

9. An inclosed volume of air changes its pressure from 1 to 0.89 atmospheres when its volume is increased by 450 c.c.. What was the original volume? *Ans.* 3641 c.c.

10. What volume is occupied by 44 grams of oxygen at 70 cm. Hg pressure and 35° C.? *Ans.* 37.7 liters.

11. $\frac{1}{2}$ mole of H, $\frac{1}{2}$ mole of O, and $\frac{1}{3}$ mole of N are mixed in a volume of 10 liters at 0° C. What are the partial pressure of H, O, and N?

Ans. $p_H = 1156.96$, $p_O = 1156.96$, and $p_N = 771.65$ grams per sq. cm.

12. What would these pressures (11) be in atmospheres at 10° C.?

Ans. $p_H = 1.164$, $p_O = 1.164$, and $p_N = 0.774$.

13. 1 liter of N weighs 1.2579 grams at 0° and 760 mm. Calculate the specific gas constant, r.

Ans. 3007 grams per sq. cm.

14. The specific gas constant, r, for N was found above (13). What is it for H? The combining weight of N is 14.04, and of H is 1.008. *Ans.* 39,080 grams per sq. cm.

15. How much will 100 liters of chlorine (Cl_2) at 74 cm. Hg pressure and 30° C. weigh? *Ans.* 278.7 grams.

16. A solid gives off a gas which is dissociated to 41%, into two products. What is the work done, in calories, gram-centimeters, and liter-atmospheres, when 1 mole of solid goes into the gaseous state, the temperature of dissociation being 55° C.?

Ans. 925 cals., 39,410,000 gr.-cm., 37.96 L. A.

17. How much work will be done by 1 kg. of CO_2 when heated 200°? *Ans.* 373.1 L. A., 9090 cals.

18. H is at the partial pressure of 2.136 atmospheres in a space of 10 liters. How many moles per liter are there, the temperature being 0°? *Ans.* $c = 0.0954$.

19. Starting with 1 mole of A in 22.4 liters (at 0°, 760 mm. of Hg), assume the dissociation according to the scheme $A = 2B + 3D$ (where A, B, and D represent moles) to be 23%. What will be final volume where pressure and temperature remain unchanged? *Ans.* 43 liters.

20. What are the final concentrations of A, B, and D in the above?

Ans. $A = 0.0179$, $B = 0.0107$, and $D = 0.01604$ mole per liter.

21. The formula weights of the above are $M_A = 170$, $M_B = 25$, and $M_D = 40$. How many grams per liter are there of each at equilibrium?

Ans. $A = 3.04$, $B = 0.268$, and $D = 0.642$.

22. Assume 17 grams of A ($M = 170$) in 2.24 liters (0°, 760 mm. Hg). Find concentrations, partial pressures, and grams per liter of A, B, and D where the dissociation of A is 20% ($M_B = 25$, $M_D = 40$), and the volume and temperature remain constant. What is the total pressure of the system?

Ans. $A = 0.036$, $B = 0.018$, $D = 0.027$ mole per liter.
$A = 0.8$, $B = 0.4$, $D = 0.6$ atmosphere.
$A = 6.06$, $B = 0.447$, $D = 1.07$ gr. per liter.
Total pressure = 1.80 atmospheres.

23. When heated, PCl_5 dissociates into PCl_3 and Cl_2. The formula weight of PCl_5 is 208.28. At 182° the density is 73.5, and at 230° it is 62. Find the degree of dissociation at 182° and 230°.

Ans. $\alpha_{182°} = 41.7\%$, $\alpha_{230°} = 68\%$.

24. The density of a gas is 2.786 referred to N (molecular weight = 28). What is its molecular weight? *Ans.* 78.

25. The specific heat under constant pressure for helium is 1.25; the formula weight is 4. How many combining weights are there in the formula weight? *Ans.* 1.

26. What is the specific heat at constant volume, i.e., c_v? 1 gram of the gas at 0° and 760 mm. occupies 509 c.c., and $c_p = 0.21$. *Ans.* 0.164.

27. The specific heat at constant volume of a substance is 0.075; its formula weight is 40. How many combining weights are there to one formula weight? *Ans.* 1.

28. The specific heat, c_v, of CO_2 is 0.2094. What is the ratio of that for constant pressure to that at constant volume? *Ans.* $\frac{c_p}{c_v} = 1.22$.

29. c_p for H_2 is 3.409. What is c_p for N_2 at the same temperature? *Ans.* 0.2435, Exp. 0.2438.

30. c_p for argon (monatomic, $M = 40$) is 0.075. What is c_p for gaseous mercury, which is of the same type, at the same temperature? *Ans.* 0.015; Exp. 0.0151.

SOLUTIONS.

31. What is the osmotic pressure of a 1% solution of glucose ($M = 180$) at 0° C.? *Ans.* 94.6 cm. H; obs. = 94 cm.

32. The osmotic pressure of a solution of cane-sugar at 0° is 49.3 cm. of Hg. What percentage of sugar ($M = 342$) is contained in it? *Ans.* 0.99%; obs. = 1.0%.

33. The osmotic pressure of a sugar solution at 32°C. is 54.4 mm. What is it at 14°.2? *Ans.* 51.2 mm.

34. The osmotic pressure of solution containing 10 grams of sugar to a certain volume is 200 mm. What is that for the same volume containing 13.5 grams? *Ans.* 270 mm.

35. 10.442 grams aniline in 100 grams of ether give a vapor pressure of 210.8 mm. Ether alone ($M = 74$) gives 229.6. Find the formula weight of aniline in ether.

Ans. 87.

36. Find osmotic pressure at 0° of aniline in (35) in atmospheres and gram per square centimeter. (*d* for ether is 0.737.) *Ans.* 19.82 atmos., or 20,460 gr. per sq. cm.

37. The osmotic pressure of a substance in water solution is 100 cm. at 0° C. Find the vapor pressure of the solution: that of water at 0° is 4.57 mm.

Ans. 4.56 mm.

38. What is the work, in gr.-cms. and calories, necessary to separate 200 grams of a substance ($M = 60$) from the solvent at 20° C.? 10 grams of substance to the liter of solvent. *Ans.* 1953 cals.; 83,200,000 gr.-cm.

39. The increase in the boiling-point of 54.65 grams of CS_2 caused by the addition of 1.4475 grams of P is 0°.486. What is the formula weight of P in CS_2? *Ans.* 129.2.

What is the formula, the combining weight being 31?

40. Calculate the increase in boiling-point of ether when to 100 grams we add a mole of a substance. The boiling-point of ether is 34°.47, the latent heat of evaporation is 88.39. *Ans.* 21°.5.

41. The molecular increase of the boiling-point of H_2O, as caused by the addition of 1 mole of substance to 100 grams, is 5°.2. Find heat of evaporation of H_2O.

Ans. 535.1 cals.

42. In (39) find the osmotic pressure at 46° of P in the CS_2 solution. (Density of CS_2 is 1.2224.)

Ans. 6.84 atmos.

43. Find the vapor pressure in (39) of P in CS_2 solution at 0°; the vapor pressure of CS_2 at 0° is 127.91 mm.

Ans. 125.9 mm.

44. 10 grams of a substance in 100 grams of a solvent increase the boiling-point by 0°.87. The formula weight of the substance is 60. Find the molecular increase of the boiling-point. *Ans.* 5.22.

45. 0.284 gram of the oxime $(CH_3)_2CNOH$ causes a decrease of 0°.155 in the freezing-point of 100 grams of glacial acetic acid. k for acetic acid is 38.8. Find the formula weight of the oxime in acetic acid. *Ans.* 71.

46. The ionization of a molar solution is 80%, two kinds of ionized matter being formed. What will the depression of the freezing-point be, water ($k=18.9$) being the solvent? *Ans.* 3°.4.

47. The molecular depression of an aqueous solution containing an ionized substance is 22°. Find the degree of ionization of the substance in that volume.

Ans. $\alpha=16.3\%$.

48. In (45) find the osmotic pressure of the oxime in glacial acetic acid at 17°. (Sp. gr. of acetic acid = 1.056.)

Ans. 1 atmos.

49. What is the relation between the osmotic pressures of 0.01 mole of substance in 1000 grams of water and in 1000 grams of ether (sp. gr. = 0.7370), assuming the same formula weight of the solute in each?

Ans. $P_e=0.7370P_w$.

50. In (45) find the vapor pressure of the solution at 40° C., the vapor pressure of glacial acetic acid at 40° being 34.77 mm. *Ans.* 34.69 mm.

51. A 0.1 molar solution of acetic acid in water freezes 0°.1927 lower than H_2O. Find the degree of ionization of the acetic acid into $H^{\cdot}$ and CH_3COO'. *Ans.* $\alpha=2\%$.

52. A 0.15 molar solution of succinic acid freezes 0°.2864 lower than H_2O. Find the ionzation of the acid. *Ans.* $\alpha=1\%$.

53. α for KCl is 0.748 for a molar solution; 0.780 for 0.5 molar; 0.853 for a 0.1 molar; and 0.883 for a 0.05 molar. Calculate the ionization of 0.5 molar $BaCl_2$ into $Ba^{\cdot\cdot}$ and $2Cl'$. *Ans.* 56%.

54. From (53) calculate the ionization of 0.05 molar $MgSO_4$ into $Mg^{\cdot\cdot}$ and SO_4''. *Ans.* 53%.

55. What is the heat of formation of a very dilute solution of magnesium chloride? (See text). *Ans.* 187500 cals.

CHEMICAL MECHANICS.

56. In the volume of 1 liter there are 0.14 mole of hydrogen and 0.081 mole of iodine. At the temperature of 440° C. $K=\frac{p_1p_2}{p^2}=0.02$. Find the amount of hydriodic acid formed. *Ans.* 0.14855 mole.

57. The initial pressure of I is 38.2 cm., the fraction uniting with H is 0.8. What was the original pressure of H, $t=440°$? ($K=0.02$.) *Ans.* 40.35 cm.

58. At 440° in 50 liters we have a mixture of 2.74 moles of HI, 0.5 mole of H, and 0.3011 mole of I. ($K=0.02$.) In which direction and to what extent will the reaction go?

59. At 440° ($K=0.02$) 5.30 c.c. of H are mixed with 7.94 c.c. of I. How much HI will be formed?

Ans. 9.475 c.c.; observed, 9.52 c.c.

60. At 279° and 737.2 mm. pressure α for the reaction $2NO_2=2NO+O_2$ is 0.13. Find K_p and K_c both for the reaction as written, and also for 1 mole of NO_2, i.e., $NO_2=NO+O$.

Ans. $K_p=0.00132$ for $2NO_2$; 0.0364 for NO_2 $K_c=0.0000292$ for $2NO_2$; 0.0054 for NO_2.

61. 6.63 moles of amylene with 1 mole of acid shows that 0.838 mole is formed in the total volume of 894

liters. How much will be formed when we start with 4.48 moles of amylene and 1 of acid in the volume of 683 liters? *Ans.* 0.8111 mole.

62. The ratio of distribution of acetic acid between water and benzene is as $\frac{0.245}{0.043}$ and $\frac{0.314}{0.071}$ at two dilutions. What is the formula weight of acetic acid in benzene? In water it is 60. *Ans.* 2.02×60.

63. For the reaction—solid $NH_4HS = H_2S + NH_3$—$K = 62,400$ (for pressures in mm.) at 25°.1 C. In a vacuum at 25°.1 we introduce NH_3 and H_2S until we have a partial pressure of the former of 300 mm., and of the later of 594 mm. Then the reaction is allowed to take place. How much does each gas lose in pressure? (Here the pressure of gaseous NH_4HS is so small as to be negligible.) *Ans.* 157.2 mm.

64. At 18°.4 1 mole of $BaSO_4$ dissolves in 50,055 liters; at 37°.7 in 31,282 liters. On the justified assumption that the $BaSO_4$ is completely ionized, calculate the heat of ionization per mole. *Ans.* −8836 calc.

EQUILIBRIUM IN ELECTROLYTES.

65. To 1 liter of a molar solution of a monobasic acid ($K = 0.000018$), a binary salt, with ionized matter in common, having an ionization in that dilution equal to 100%, is added. How much (in moles) in the dry state must be dissolved in the acid solution to decrease the concentration of ionized $H^{\cdot}$ to 0.1 of its pevious value? *Ans.* 0.04211 mole.

66. A small amount of base is mixed with an excess of a solution containing an equal number of formula

weights of acetic and lactic acids. In what proportion will the corresponding salts be formed?

Ans. Lactate: acetate: :0.0117:0.00424.

67. PbI_2 is soluble to 0.00158 mole per liter at 25°.2, and ionizes completely (practically) into $Pb^{\cdot\cdot}$ and $2I'$. What is its solubility in presence of a 0.1 molar solution of ionized I' from another salt?

Ans. 1.58×10^6 moles per liter.

68. The solubility product of the substance AC_2 is 0.00621. What is the concentration of ionized $A^{\cdot\cdot}$ and C' when the ionization is complete into $A^{\cdot\cdot}$ and $2C'$?

Ans. 0.1157 mole per liter of $A^{\cdot\cdot}$, and 0.2314 of C'.

69. MA (solubility is 0.02 and is ionized completely) is hydrolytically dissociated in solution. s for HA is $13+10^{-10}$, and $s_{H_2O}O$ (25°) is $(1.09+10^{-7})^2$. Find the amount of ionized $M^{\cdot}$ from another salt which must be present to prevent hydrolytic dissociation.

Ans. 0.02162 mole per liter.

70. At the dilution of 32 liters a binary substance is 0.9% hydrolyzed. What is the percentage of hydrolysis at the same temperature when the dilution is 100 liters? *Ans.* 1.584%.

71. The constant of hydrolytic dissociation at 100° for NH_4Cl is $337+10^{-10}\left(\text{i.e., } K=\frac{\alpha^2}{(1-\alpha)V}\frac{d_A}{d_S}\right)$. What is the ionization constant of NH_4OH? (s_{H_2O} at 100° is $(8.5+10^{-7})^2$.) *Ans.* $214+10^{-7}$.

72. AgCl, AgBr, and AgI are dissolved together. What are the concentrations of ionized $Ag^{\cdot}$, Br', Cl', and I'? The solubilities are $1.25+10^{-5}$, $86+10^{-8}$, and 0.97×10^{-8} respectively.

73. Bromisocinnamic acid at 25° is soluble to 0.0176 mole per liter, and is ionized to 1.76% into $H^{\cdot}$ and a

negatively charged radical. What is the solubility product of the acid? *Ans.* $9.6+10^{-8}$.

What amount of the acid must always remain in solution at this temperature, even in the presence of an infinite amount of ionized $H^{\cdot}$ from another acid?

Ans. 0.0173 mole per liter.

What is the solubility of the acid in the presence of a 0.001 molar solution of ionized $H^{\cdot}$ from another acid?

Ans. Solubility $=0.0173+0.0000883$ mole per liter.

74. Find the heat of neutralization of 1 mole of acetic acid (in 200 moles (3600 gr.) of H_2O) with 1 mole of sodium hydrate (in 200 moles of H_2O) at 35°. (α for acetic acid is 0.009, its heat of ionization is 386 cals.; α for NaOH is 0.861, its heat is 1292 cals., and α for sodium acetete is 0.742, its heat being 391 cals. The heat of ionization of water at 35° is 12,632 cals.)

Ans. 13,093 cals.

ELECTROCHEMISTRY.

75. An aqueous solution of $CuSO_4$ is electrolyzed until 0.2955 gram of Cu is deposited, using inert electrodes. The solution at the cathode before the passage of the current gave 2.2762 grams of Cu, and after the passage 2.0650 grams. Find the mobility of ioinzed $Cu^{\cdot\cdot}$ and of ionized SO_4''.

Ans. $U_{Cu^{\cdot\cdot}}=0.285$, $U_{SO_4^{\cdot\cdot}}=0.715$.

76. A 0.02 molar solution of KCl ($\kappa=0.002397$) gives in a certain cell a resistance of 150 ohms. What is the factor that will transform conductivity results determined in this cell into specific conductivities? *Ans.* 0.36.

77. The equivalent conductivity of a solution of Na_2SO_4 in 256 liters at 25° is 141.9 What is it at infinite dilution? *Ans.* 153.9

78. The conductivity of a solution of AgCl saturated at 18° is 2.4×10^{-6}; that of the water used is 1.16×10^{-6}. Find the solubility of AgCl on the justified assumption that it is completely ionized. ($\Lambda_{\infty KCl} = 131.2$, $\Lambda_{\infty AgNO_3} = 116.5$, and $\Lambda_{\infty KNO_3} = 126.1$.)

Ans. 1.02×10^{-5} moles per liter.

79. Find the heat of amalgamation of cadmium at 0°. (π for a cell made up of a 1% cadmium amalgam and mercury in a solution of $CdSO_4$ is 0.06836 volt at 0° and 0.0735 at 24°.45.) *Ans.* $q = 510$ cal. per mole of Cd.

80. Zn in a molar solution of $ZnSO_4$ gives a difference of potential of 0.51 volt and $\frac{\Delta\pi}{\Delta T} = -0.00076$. What is the heat of ionization of Zn at 17°? *Ans.* 33,740 cals.

81. A cell with electrodes of the same monovalent metal gives an E.M.F. at 17° of 0.35 volt. The concentration of ionized metal at the positive electrode is 0.02 mole per liter. What is its concentration at the other electrode? (The two solutions are connected with a siphon to prevent diffusion.)

Ans. 1.637×10^{-8} moles per liter.

82. What would be the E.M.F. of the above concentration cell with electrodes of a divalent metal, the concentration of ionized metal being 0.02 and 1.847×10^{-8} moles per liter? *Ans.* 0.175 volt.

83. In a hydrogen-gas cell (platinized platinum electrodes, one-half in solution, one-half in gas) we have acetic acid on one side and propionic on the other, the concentration being identical, i.e., molar. What is the E.M.F. of the cell at 17°? Which is the positive electrode?

Ans. Acetic acid positive, $\pi = 0.00369$ volt.

84. Find the E.M.F. of the cell at 25°: H gas – KOH

$n/10$ ($\alpha = 0.85$) – HCl $n/1$ ($\alpha = 0.7$, H gas. $s_{H_3O} = (1.09 \times 10^{-7})^2$.
Ans. 0.757 volts.

85. What is the relation of the electrolytic solution pressure of Zn to that of Cu? (The E.M.F. of Cu in $CuSO_4$ against Zn in $ZnSO_4$ is 1.06 volts at 17° when the concentration of ionized $Zn^{\cdot\cdot}$ is equal to that of ionized $Cu^{\cdot\cdot}$.)
Ans. $\frac{P_{Zu}}{P_{Cu}} = 10^{36 \cdot 5}$.

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