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THE FREE ENERGY OF CHEMICAL SUBSTANCES.

INTRODUCTION.

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The problem of chemical affinity is the oldest of chemical problems. But only after the development of the science of thermodynamics could an exact definition or measure of affinity be given. The function commonly employed for such measure is the thermodynamic potential, or free energy, a quantity closely related to the maximum work which is obtainable from a physico-chemical change. Hence a complete free energy table for all common substances will not only serve as a table of chemical affinities, but it will enable the chemist to predict the amount of work that can be furnished under conditions of highest efficiency by each chemical reaction, and will show as well the direction in which the reaction will proceed, and the extent of the yield.

The determination and tabulation of free energy data has therefore become an imperative duty of chemistry. Already a considerable amount of experimental material is at hand. Especially during the past ten years much work in this field has been done in this country and abroad, where the important investigations in the laboratories of Haber in Karlsruhe, Nernst in Berlin, and J. N. Brönsted in Copenhagen, deserve special mention.

Now, therefore, it has become possible to commence a systematic study of free energy, with the hope of furnishing in the near future a table of free energy data as complete as the existing tables of thermochemistry.

The present paper will deal with the general methods used in free energy calculations. It will be followed by papers in which the chemical elements will be taken up in order, and under each element we shall consider the compounds of that element with all the other elements which have been previously discussed.

Notation and Fundamental Units.

In so extensive an investigation as the one which is here planned, involving a very large number of arithmetical computations, it is very desirable that a definit notation and certain conventions be laid down and rigorously adhered to. Such conventions have, as a rule, no theoretical significance, but their practical value will be obvious. Some of these conventions, for example, will be established in order to prevent that confusion of sign which is so likely to be involved in numerical calculations.

In the study of chemical reactions, the gram is not so convenient a unit of quantity as the mol or the equivalent. Of these, the mol is for general purposes the better unit, for one equivalent of a substance may have different meanings, according to the kind of reaction into which the substance enters. Thus one equivalent of permanganic acid has a variable significance according as the power to neutralize a base, or to act as an oxidizing agent in acid or in alkalin solution is being considered. An objection may be raised to the use of the mol, if by this term we mean the number of grams of a substance corresponding to its molecular weight, for in many cases the molecular weight is unknown. A better unit perhaps is the formula weight. But since in nearly all cases, where the molecular weight is known, the formula weight is made identical with the molecular weight, we shall for our present purpose regard these two expressions as synonymous.

When we are discussing a certain chemical reaction, for example, the formation of mercurous chloride from its elements, it is necessary to write an equation in order to determin the amounts of the substances involved, thus:

$$\mathrm{Hg} + \tfrac{1}{2}\mathrm{Cl}_2 = \mathrm{HgCl},$$

or

$$2\mathrm{Hg} + \mathrm{Cl}_2 = 2\mathrm{HgCl}.$$

Moreover, such an equation is not alone sufficient to define the reaction, for we must at a given temperature know also the pressure upon each substance, and its state.[1] Thus in a particular case we might write:

$$\mathrm{Hg(l)(1\ atmos.)} + \tfrac{1}{2}\mathrm{Cl_2(g)(10\ atmos.)} = \mathrm{HgCl(s)(1\ atmos.)},$$

which means that one mol of liquid mercury at one atmosphere and one-half mol of chlorine gas at ten atmospheres are consumed, and one mol of solid mercurous chloride at one atmosphere is produced. In

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[1] Other conditions which may determin the nature of a single substance, such as surface forces when the substance is finely divided, will only be considered in exceptional cases.

general, however, pressure will be assumed to be one atmosphere, unless otherwise specifically indicated, and the distinguishing marks (l), (s), (g), may often be omitted when no ambiguity is possible.

When one or more of the reacting substances is one of the constituents of a solution, it is necessary to specify the nature and composition of the solution. We shall revert to this question presently.

When any quantity, such as the volume, is determined by the initial and final states of the system, that is, by the state of the various substances consumed and produced, it will be convenient to designate the increase in that quantity, accompanying the given reaction, by the symbol Δ. Thus, in the case before us, if v_2 represents the volume of the one mol of mercurous chloride formed, and v_1 the volume of the one mol of mercury and the one-half mol of chlorine consumed, then $v_2 - v_1 = \Delta v$ represents the total increase in volume. Likewise, if Γ represents a sum of heat capacities, then $\Delta\Gamma$ will represent the total increase in heat capacity due to the reaction.

Fundamental Units.—The basic c. g. s. unit of energy is the erg. The joule = 10^7 ergs is also in frequent use. The calorie, namely, the amount of energy required to raise one gram of water one degree, is a unit depending on the temperature of the water. Two different calories are in common use, the 15° calorie, which is the amount of energy required to raise one gram of water from 15° to 16° C, and the mean calorie or the amount of energy required to raise 0.01 gram of water from 0° to 100° C. Fortunately these two units are almost identical. According to the recent calculation of Barnes,[1] the mean calorie is 0.017% higher than the 15° calorie. It is the 15° calorie which we shall use throughout, and call the calorie.

The mechanical equivalent of heat has been determined by numerous experimenters who have for the most part, however, determined the equivalent of the calorie not in units of mechanical energy, but in units of electrical energy; in other words, the relation between the calorie and the volt-coulomb rather than between the calorie and the erg. Since the work of Rowland the only determinations of the former ratio which need be considered are those of Miculescu[2] and of Reynolds and Moorby.[3] Of these, the work of the latter authors deserves the greatest weight. Their value, after a small correction pointed out by A. W. Smith[4] has been applied, is:

$$1 \text{ cal.}_{15^\circ} = 4.1829 \times 10^7 \text{ ergs.}$$

This is in complete agreement with the value 4.183×10^7 obtained by Miculescu.

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[1] *Proc. Roy. Soc.*, (*A*) **82**, 390 (1909).

[2] *J. physique*, [3] **1**, 104 (1892).

[3] *Phil. Trans.*, (*A*) **190**, 301 (1898).

[4] *U. S. Weather Review*, **35**, 458.

Of all the measurements of the mechanical equivalent involving the ratio of volt-coulomb to erg, those of Callendar and Barnes are so complete and reliable that they alone can be given serious weight. Barnes,[1] in his latest recalculation of his results, assumes the electromotive force of the Clark cell at 15° as 1.4330 volts, and of the standard Weston cell at 20° as 1.0187 volts. Since the electromotive force of the latter standard cell is now taken by International agreement,[2] as 1.0183 volts at 20°, the work of Barnes has been recalculated by A. W. Smith.[3] He finds one mean calorie equals 4.1816×10^7 ergs, or

$$1 \text{ cal.}_{15^\circ} = 4.1809 \times 10^7 \text{ ergs.}$$

This calculation, of course, depends upon the assumption that under the new definition of electromotive force, 1 volt-coulomb = 1 joule = 10^7 ergs.

The average between this value and the one obtained by Reynolds and Moorby we shall use as the final value of the mechanical equivalent of heat.

$$\mathbf{1\ cal._{15^\circ} = 4.182 \times 10^7\ ergs.}$$

Another unit of energy which is of frequent service is the cubic-centimeter atmosphere. If one atmosphere equals 1,013,300 dynes per sq. cm.,

$$1 \text{ cc.-atmos.} = 0.10133 \text{ joules,}$$

or

$$1 \text{ cc.-atmos.} = 0.02423 \text{ cal.}$$

Besides these units of energy it is important to decide upon values for several other fundamental constants. If we take the absolute zero as —273.09° ± 0.01° centigrade, and if the volume of a perfect gas[4] at one atmosphere and 0° Centigrade is 22412 ± 2 cc.[5] per mol, then we have for the gas constant:

$$R = 82.07 \pm 0.01 \text{ cc.-atmos. per degree,}$$
$$R = 8.3160 \text{ joules per degree,}$$
$$\mathbf{R = 1.9885\ cal.\ per\ degree.}$$

In order to obtain energy data from measurements of electromotive force, it is necessary to know the electro-chemical equivalent, which is defined as the number of grams of silver deposited per coulomb of electricity in the standard coulometer. The value of this equivalent, which was used as the basis of the new definition of the international volt,[6] is 0.00111800. If we take 107.88 as the atomic weight of silver, we obtain as the Faraday

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[1] *U. S. Weather Review*, **35**, 458.

[2] Circular Bureau of Standards No. 29, Washington, 1910.

[3] *Phys. Rev.*, **34**, 180 (1911).

[4] D. Berthelot, *Z. Elektrochem.*, 10, 621 (1904).

[5] Guye obtains the value 22410, *J. chim. phys.*, 6, 769 (1908).

[6] Circular Bureau of Standards, No. 29, Washington, 1910.

equivalent, that is, the number of coulombs of electricity associated with one gram equivalent of any ion, $\mathbf{F} = 96494$. If $\mathbf{E}$ is the electromotive force of a cell, then the electrical work done by that cell is $96494 \times \mathbf{E}$ volt-coulombs per equivalent, or $23074 \times \mathbf{E}$ calories per equivalent.

Solutions.—Some of the most important reactions which we shall have to consider involve substances which are not present in a pure state, but in solution. In order to define the reaction, it is necessary to state the composition of every solution. This is best done by stating the mol fraction of each constituent. The mol fraction of a certain substance is defined as the number of mols of that constituent divided by the number of mols of all constituents. Thus, if a solution contains n_1 mols of the substance X_1, n_2 mols of X_2, n_3 mols of X_3, the mol fraction of X_1, which we shall denote by N_1, is given by the formula,

$$N_1 = \frac{n_1}{n_1 + n_2 + n_3}$$

and it is evident that

$$N_1 + N_2 + N_3 = 1.$$

When one of the constituents of a solution is very dilute, its mol fraction is proportional to its concentration (mols per liter of solution) which in turn is proportional to the number of mols per unit amount of solvent. This latter is not, strictly speaking, a concentration; but custom sanctions the use of the term concentration in this case also, and we shall find it convenient to define concentration as mols of solute to 1000 grams of water. One advantage of this definition is that the concentration of a given solution does not change with the temperature, while the true concentration expressed in mols per liter of solution does.

Such quantities as the molal volume and molal heat capacity are easily defined. In a solution there are quantities which play an exactly similar rôle thermodynamically, and which we may call the partial molal volume, partial molal heat capacity, etc.[1] In a solution containing n_1 mols of X_1, n_2 of X_2, the partial molal volume of X_1, which we may designate by $\overline{V}_1$ and define analytically by the equation,

$$\frac{\partial v}{\partial n_1} = \overline{V}_1,$$

where v is the total volume of the mixture. Expressed in words, the partial molal volume of the substance X_1 in a given solution is the increase in volume of a very large amount of this solution when one mol of X_1 is added to it. Unlike the molal volume of a pure substance, the partial molal volume of a substance in solution may be either positive or negative.

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[1] Lewis, "A New System of Thermodynamic Chemistry," *Proc. Am. Acad.*, 43, 273 (1907); *Z. phys. Chem.*, 61, 144 (1907)..

If V is the volume of 1 mol of the solution, that is, the volume of that amount of the solution containing N_1 mols of X_1, N_2 mols of X_2, etc., where N_1, N_2, etc., are the respective mol fractions, then it is evident that

$$V = N_1\overline{V}_1 + N_2\overline{V}_2 + \ldots, \qquad (1)$$

for if to a large quantity of the solution, N_1 mols of X_1 are added, the volume will increase by $N_1\overline{V}_1$, then if N_2 mols of X_2 are added the volume will increase by $N_2\overline{V}_2$, etc., and the total change in volume will be independent of the order in which the constituents are added. The total effect will be merely the addition of one mol of the solution, of volume V.

What has been said of partial molal volumes is true of all partial quantities, such as partial molal heat capacity at constant pressure, $\overline{C}_p$, partial molal internal energy $\overline{E}$, etc.

When in a chemical reaction some of the reacting substances are present in solution, then in order to make the chemical equation show the state of the reacting substance, it is necessary to indicate the nature of the solution and the mol fraction or concentration of each substance. Since water is the most common of solvents, an aqueous solution will be understood unless otherwise specified.

Thus the equation,

$$Hg(l) + \tfrac{1}{2}Cl_2(0.01\ M) = HgCl(s),$$

states that one mol of liquid mercury plus one-half mol of chlorine out of a 0.01 molal aqueous solution are consumed and one mol of solid mercurous chloride is formed. Sometimes it is unnecessary to state the exact concentration of the reacting substance, but only that it is present in dilute aqueous solution, in which case the expression Cl_2 (aq) may be employed, as is customary in thermochemical equations.

The increase of volume, Δv, which occurs when one mol of mercury reacts with one-half mol of chlorine from a solution of given concentration, is evidently expressed by the equation:

$$\Delta v = V_{HgCl} - (V_{Hg} + \tfrac{1}{2}\overline{V}_{Cl}),$$

and in general the partial molal quantities enter in the case of solutions just as the molal quantities in the case of pure substances.

An interesting type of solution is furnished by electrolytes dissolved in water or other dissociating solvent. In this case it is customary to assume the existence of molecular species, namely the ions, which cannot be added independently to the solution; for example, we have no practical means of adding a mol of sodium ion or a mol of chloride ion alone to a solution of sodium chloride in water. We have therefore no means of determining the partial molal volumes, or other partial molal quantities for such substances as sodium ion and chloride ion. It is, however, an easy matter to find from existing density determinations the sum of the partial molal volumes of sodium ion and chloride ion: similarly, the sum for hydrogen ion and chloride ion, or the sum for sodium ion and nitrate ion. In this way it is possible to obtain a series of values such that, if the partial molal volume of any one ion were known, the partial molal volume of every other ion could be found at once. In such a case as this, it will be convenient to assume an arbitrary value for some one ion.

Hydrogen ion, since it is an elementary ion, and one of the ions of water itself, we will choose for this purpose, and call the partial molal volume of hydrogen ion in any dilute aqueous solution at any temperature, equal to zero. Similarly, we shall assume that the partial molal heat capacity, the partial molal internal energy,[1] etc., are all zero for hydrogen ion.

It may be well to illustrate the method of determining a partial molal quantity by calculating the partial molal volume of chloride ion in 0.1 M aqueous solution. Kohlrausch and Hallwachs[2] obtained the densities of hydrochloric acid solutions at 17.15° given in the following table. The first column gives the concentration n in mols per 1000 g. water, the second the densities, the third the volume $v = (1000 + n)/d$ containing 1000 g. of solvent.

n.	$d_4^{17.15}$.	v.
0.00000	0.998775	1001.227
0.01008	0.998964	1001.047
0.02011	0.999153	1000.868
0.05011	0.999709	1000.342
0.09913	1.000596	999.503
0.1973	1.002403	997.800
0.4874	1.007575	992.956

The differences between the volumes in the last column and the volume of 1000 g. of pure water, divided by the concentration, are sometimes taken as the partial molal volumes, but this is only true in case the partial molal volume is constant. The quantity we wish to determin is dv/dn at a given concentration. This quantity may be obtained either by expressing the quantities in the last column analytically as a function of n and differentiating, or by plotting the same values against n and finding the slope of the curve at the desired concentration. Applying this latter procedure in the present case we find at 0.1 M concentration, $dv/dn = \overline{V} = -17.5$ cc., the partial molal volume of hydrochloric acid. Since the partial molal volume of hydrogen ion is taken as zero, we obtain for the partial molal volume of 0.1 M chloride ion this same value —17.5 cc.[3]

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[1] This assumption will be discussed more fully in the section on the laws of energy.

[2] *Ann. Physik*, [3] **53**, 14 (1894). These authors give the concentrations in mols per liter, and the densities referred to water at 17.15°. Their results have been recalculated for the above table.

[3] At a given concentration all the so-called physical properties of dilute aqueous solutions of strong electrolytes, such as volume, thermal properties, optical properties,

The First Law of Energy.

According to the law of the conservation of energy, any system in a given condition contains a definit quantity of energy, and when this system undergoes change, any gain or loss in its content of energy is equal to the loss or gain of the energy contained in surrounding systems. In any physical or chemical process, the increase in energy of a given system is therefore equal to the heat Q absorbed from the surroundings, less the work W done by the system upon the surroundings. If E_1 represents the initial energy content of the system, and E_2 the final energy content, then

$$E_2 - E_1 = \Delta E = Q - W. \qquad (2)$$

The values of Q and W depend upon the way in which the process is carried out, and in general neither is uniquely determined by the initial and final states of the system. Since, however, their difference is so determined, if either Q or W is fixed by the conditions under which the process occurs, the other is also fixed. Thus, if the process is such that no work is done upon the surroundings, as in the case of a chemical reaction taking place in a constant volume calorimeter, then $\Delta E = Q$. In most calorimetric work the pressure, and not the volume, is kept constant. If the increase in volume during the reaction is Δv, then $\Delta E = Q - p\Delta v$, or $(E_2 + pv_2) - (E_1 + pv_1) = Q$, and the heat absorbed during the reaction is again a quantity which obviously depends only upon the initial and final states.

Let us take a more complicated case. Consider a number of substances, each of which is enclosed in a separate chamber[1] provided with a piston maintaining a constant pressure, the pressures on the different pistons, however, not being necessarily the same. Suppose now that a reaction is carried on in such a way that some of the substances are used up and others are formed, each substance being kept always under its particular constant pressure. Then if v_1, v_1', . . ., represent the volumes of the substances which are consumed, under the respective pressures p_1, p_1', . . ., and v_2, v_2', . . ., are the volumes of the substancep roduced at the respective pressures, p_2, p_2', . . ., then if E_1 represents the internal energy of all the substances destroyed and E_2 that of all the substances produced, then

$$E_2 - E_1 = Q - [(p_2v_2 + p_2'v_2' + \ldots) - (p_1v_1 + p_1'v_1' + \ldots)].$$

This may be written:

etc., have been found within the limits of experimental error to be purely additive functions of the constituent ions. In other words, if, for example, the partial volumes of HCl, HBr and KBr are all known in 0.1 *M* concentration, the partial volume of KCl at the same concentration is determined. Therefore the partial molal volume of undissociated hydrochloric acid must be regarded as the sum of the partial molal volumes of hydrogen and chloride ions. It is for this reason that we are justified, for such calculations as these, in assuming the electrolyte to be completely dissociated.

[1] Each chamber may of course be provided with such semi-permeable walls as may be useful.

$$(E_2 + \Sigma p_2v_2) - (E_1 + \Sigma p_1v_1) = Q.$$

It is evident that this equation, when the p's are all the same, becomes identical with the simpler equation given above. The quantity $E + \Sigma pv$ is of sufficient importance to be designated by a special symbol. Since in the ordinary case, where the same pressure of one atmosphere prevails throughout the system, the change in this quantity is the heat of reaction as ordinarily measured, we will choose the letter H for this quantity. If there is no danger of confusion, it may simply be called the heat content of a given system. We have, then,

$$H = E + \Sigma pv, \text{ and } \Delta H = H_2 - H_1 = \Delta E + \Delta\Sigma pv = E_2 - E_1 + \Sigma p_2v_2 - \Sigma p_1v_1. \quad (3)$$

Let us now consider a simple thermochemical reaction:

$$Hg(l) + \tfrac{1}{2}Cl_2(g) = HgCl(s) + 31300 \text{ cal.}$$

Such an equation expresses not only the stoichiometry of the reaction, but also the difference between the heat content of mercurous chloride and its elements. For since 31300 cal. is the amount of heat evolved when the reaction takes place at constant pressure (1 atmosphere), this is evidently only a short method of expressing what would be more explicitly stated in the equation:

$$H(Hg) + H(\tfrac{1}{2}Cl_2) = H(HgCl) + 31300 \text{ cal.},$$

where the H's represent the heat content of the separate substances. It is evident, therefore, that the increase, ΔH, in the heat content of the whole system is -31300 cal. In general, we see that ΔH for a given reaction is the negative of the ordinary heat of reaction at constant pressure.

We may, in place of the ordinary thermochemical equations, use the form:

$$Hg(l) + \tfrac{1}{2}Cl_2(g) = HgCl(s); \ \Delta H = -31300 \text{ cal.}$$

Now if we write another similar expression such as

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(g); \ \Delta H = -22000 \text{ cal.},$$

the second equation may be subtracted from the first in the familiar manner, giving

$$Hg(l) + HCl(g) = HgCl(s) + \tfrac{1}{2}H_2(g); \ \Delta H = (-31300) - (-22000) = -9300 \text{ cal.}$$

It is impossible to determin by any calorimetric methods the actual heat content of any substance, and we may therefore select a purely arbitrary value for the heat content of each of the elements in a given state. We shall therefore, at every temperature, assign the value $H = 0$, to every element in what we may call its standard state at atmospheric pressure. This standard state will in most cases be the one in which the element most commonly occurs, or is most stable, at ordinary temperatures. Thus gaseous chlorine, liquid bromine, rhombic sulfur, white phosphorus, all at atmospheric pressure, will be assumed to have zero heat content *at every temperature.* In the case of carbon, we will arbitrarily choose that form as standard which has been used in the study of a number of reversible reactions at high temperatures, namely the so-called gas, or retort, carbon.

According to this convention, when a compound is formed from its elements the heat content of the compound is equal to ΔH for the reaction. Thus, in the case cited above, the value of H for mercurous chloride is —31300.

We must now consider the meaning of similar thermochemical equations when one or more of the substances involved exist in solution. Let us start with a simple case and consider the reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(0.1\,M).$$

This equation means that a half mol each of hydrogen and chlorine gas are consumed, and a mol of hydrochloric acid is produced in a large amount of a $0.1M$ aqueous solution of hydrochloric acid. We may regard this reaction as the sum of the two reactions:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(g),$$

and

$$HCl(g) = HCl(0.1\,M).$$

In the first, one mol of hydrochloric acid gas is formed from its elements, and in the second, it is added to a large volume of $0.1\,M$ solution. If $\overline{H}$ represents the *partial molal heat content* of HCl in the solution, and H the heat content of HCl gas, it is evident that for the second reaction $\Delta H = \overline{H} - H$. For the reaction involving the formation of HCl gas $\Delta H = H$, and adding these together, we find for the original reaction $\Delta H = \overline{H}$. This equation might have been used at the outset as the definition of $\overline{H}$, the partial molal heat content.

In order to illustrate further the meaning of this important partial quantity, we will calculate the value of $\overline{H}$ from the data of Thomsen. The following table gives in the first column the concentration of hydrochloric acid in mols (n) of HCl to 1000 g. of water. The second column gives the amount of heat absorbed (Q) when n mols of HCl gas dissolve in 1000 g. of water. If then the values in the second column are plotted against those in the first, the slope of the curve, $\frac{dQ}{dn}$, is the difference between the partial molal heat of the hydrochloric acid at the chosen concentration and the molal heat of the HCl gas. The latter is —22000 cal. We have then $\overline{H} = \frac{dQ}{dn} - 22000$.

n.	Q.
55.5	—298000
27.75	—315300
18.50	—247200
11.10	—166100
5.55	— 89800
2.775	— 46500
1.110	— 19000
0.555	— 9550
0.185	— 3200

From these data we find for 0.1 *M* solution $\overline{\mathrm{H}}$ = —39300 cal., a value which is nearly constant with further dilution. In general, since the rate of change of $\overline{\mathrm{H}}$ with the concentration is a function of the heat of dilution, $\overline{\mathrm{H}}$ at any very high dilution is constant and is equal to the heat absorbed when one mol of the substance is formed from its elements and dissolved in a large volume of water.

Since we have decided to take the partial heat of hydrogen ion at each concentration equal to zero, $\overline{\mathrm{H}}$ for the chloride ion at the temperature of the measurements and at 0.1 *M* concentration is also equal to —39300 cal.

Change of the Heat of Reaction with the Temperature.—In all the cases where we have considered the value of ΔH, or the heat of reaction, we have assumed a reaction occurring at a constant temperature, and when two or more thermochemical equations are added together, the data must of course all be determined for the same temperature. Most of the older data were obtained at temperatures in the neighborhood of 17° or 18°.

If the heat capacities of all the substances concerned in a reaction are known, it is possible to calculate from the first law of energy the exact way in which the heat of the reaction changes with the temperature. Let us consider a reaction in which the system passes from the state A to the state B, all at atmospheric pressure and at the temperature T. The heat absorbed in this reaction is ΔH. If now the heat capacity at constant pressure of the products of the reaction be represented by Γ_{B}, the heat absorbed in raising these products to the temperature $\mathrm{T} + d\mathrm{T}$ will be $\Gamma_{\mathrm{B}} d\mathrm{T}$. In the two steps we have passed from the factors at temperature T to the products at $\mathrm{T} + d\mathrm{T}$. We might accomplish the same result by heating the factors to the temperature $\mathrm{T} + d\mathrm{T}$ with an absorption of heat $\Gamma_{\mathrm{A}} d\mathrm{T}$, and then allowing the reaction to proceed at the higher temperature where we will call the heat absorbed $\Delta\mathrm{H} + d(\Delta\mathrm{H})$. Since not only the change in internal energy, but also the work done, is the same in either case, we may write:

$$\Delta\mathrm{H} + \Gamma_{\mathrm{B}} d\mathrm{T} = \Delta\mathrm{H} + d(\Delta\mathrm{H}) + \Gamma_{\mathrm{A}} d\mathrm{T}$$

or

$$\frac{d(\Delta\mathrm{H})}{d\mathrm{T}} = \Gamma_{\mathrm{B}} - \Gamma_{\mathrm{A}} = \Delta\Gamma, \qquad (4)$$

where $\Delta\Gamma$ is the increase in heat capacity at constant pressure. This same equation is true in the more general case where the different reacting substances are under different pressures, provided that the pressure on each substance remains constant during the isothermal reaction, and provided that the reaction, at any other temperature, involves the same substances under the same pressures.

For illustration, let us consider the reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(0.1\,M).$$

The heat capacity of one-half mol of hydrogen gas, plus one-half mol of chlorine gas at room temperature is about 7 cal. per degree. The partial molal heat capacity of the hydrochloric acid has, according to the data of Thomsen, a very high negative value, namely, about —40. Therefore, $\Delta\Gamma$ is equal to $-40 - 7 = -47$ cal./deg.

Assuming that the change in the heat capacity in any reaction can be expressed as an algebraic function of the temperature, we may write

$$\Delta\Gamma = \Delta\Gamma_0 + \Delta\Gamma_1 T + \Delta\Gamma_2 T^2 + \cdots \qquad (5)$$

We are then able to integrate equation (4) and find

$$\Delta H = \Delta H_0 + \Delta\Gamma_0 T + \tfrac{1}{2}\Delta\Gamma_1 T^2 + {}^1/_3\Delta\Gamma_2 T^3 + \cdots \qquad (6)$$

In these equations $\Delta\Gamma_0$ is the (calculated) difference in the heat capacities at constant pressure between the products and the factors at the absolute zero, $\Delta\Gamma_1$ involves the temperature coefficients of the heat capacities, and so on. The constant of integration, ΔH_0, represents the (calculated) increase in the heat content at the absolute zero. It must be strongly emphasized, however, that in the use of such quantities as $\Delta\Gamma_0$ we make no pretense of knowing what conditions actually prevail at the absolute zero of temperature, which is from many points of view as far removed from the possibility of direct experimental investigation as an infinit temperature. The mere fact that we have arbitrarily chosen a linear scale of temperature is apt to delude us with the idea that, when we have reached the boiling point of helium, the absolute zero has nearly been attained. The quantities $\Delta\Gamma_0$ and ΔH_0 must be considered only as terms in an empirical equation which is valid over that range of temperature which has been covered by experiments.

The Second Law of Energy.

One of the most general statements of the second law of energy is the following: Every process that occurs spontaneously is capable of doing work; to reverse any such process requires the expenditure of work from outside.

From this follows the general principle that heat cannot be made to pass from one system to another of higher temperature without the expenditure of work, since heat spontaneously passes from a hot body to a cold. Hence follows the still more special statement that a system passing through a complete cycle of isothermal changes cannot produce work at the expense of the heat of the surroundings, for such work could by friction be converted again into heat in a system of higher temperature, contrary to the principle just stated.

The ideal *reversible* process is one which produces such an amount of work that if this work is again expended in driving back the process (also reversibly) the initial condition of all systems involved can be completely restored. No actual process is ever reversible; but by eliminating friction, electrical resistance, and other factors involving inefficiency, it is often possible to approach the ideal reversible process to any desired degree of approximation.

The maximum work which can be obtained in passing isothermally and reversibly from a state I into a state II is of great importance because it is independent of the particular reversible process employed. If this were not the case, then by proceeding from I to II by one reversible process and returning from II to I by another reversible process, requiring less work, a certain net amount of work would be gained, and this could come only from the heat of the surroundings.

When a system is in equilibrium with respect to certain possible changes, such changes may be made to occur in either direction by infinitesimal changes in the variables (temperature, pressure, etc.) which determin the state of the system. By changing back to the original condition the system will return to its initial state. It is, therefore, evident that any infinitesimal change, occurring in a system which is in equilibrium, is reversible. Thus, in any physico-chemical change, by keeping the system as near as is desired to the equilibrium conditions, it is possible to approach at will the ideal reversible process. The work obtained from any process occurring when the system is kept under conditions of equilibrium is, therefore, the maximum work.

Since this maximum work is independent of the path by which the system passes from the state I to the state II, we may regard it as the difference between two quantities, one of which, A_1, is completely determined by the initial system, and the other, A_2, is determined by the final system. That is, we may write,

$$\text{maximum work} = A_1 - A_2 = -(A_2 - A_1) = -\Delta A. \qquad (7)$$

Another quantity of equal importance is derived from ΔA in a way similar to that in which ΔH is derived from ΔE. Before giving a mathematical expression for this quantity, its significance may be illustrated by a concrete example. Suppose that a voltaic cell, in which zinc acts upon sulfuric acid to form zinc sulfate and hydrogen, operates reversibly under atmospheric pressure, giving the electrical work W. This quantity of work, W, represents in fact the maximum amount of work which can be utilized for any external purpose; for example, by the operation of an electrical motor. It is not true, however, that W is equal to the quantity we have defined as $-\Delta A$, for in addition to the electrical work a certain amount of work has been done against the atmosphere, owing to the increased volume of the products of the reaction. If Δv represents the increase in volume, it is evident that

$$W = -\Delta A - p\Delta v.$$

In a more complicated case, in which the several parts of the system might be at different pressures, each pressure remaining constant, we would have

$$W = -\Delta A - \Delta\Sigma pv.$$

This important quantity, which in general represents the work which is actually available for any desired purpose, is itself dependent only upon the initial and final states of the system. We shall write:[1]

$$F = A + \Sigma pv, \tag{8}$$

$$\Delta F = \Delta A + \Delta\Sigma pv. \tag{9}$$

The quantity F will be known as the free energy,[2] and ΔF as the increase in free energy accompanying the reaction in question.

Let us consider the simple process which occurs when a liquid is converted into its vapor under an external pressure which is exactly equal to the vapor pressure. Since the condition of equilibrium is maintained, this is a reversible process, and the work actually done by the system is the maximum work. Thus we may write:

$$-\Delta A = p\Delta v, \text{ hence, } \Delta F = 0, \text{ or } F_2 = F_1.$$

Similarly, we may show for any process whatever that the condition of equilibrium is given by the equation for an infinitesimal change

$$\Delta F = 0.$$

Since every substance under given conditions possesses a definit free energy per mol, and the increase in free energy in a reaction is the difference between the free energies of the products and of the factors, it is

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[1] See Lewis, *Proc. Am. Acad.*, **43**, 289 (1907); *Z. physik. Chem.*, **61**, 161 (1907).

[2] It was the quantity A and not the quantity F which Helmholtz named the free energy. Unfortunately, however, much confusion has arisen in the literature between these two quantities. Several authors have defined the free energy as A, but what they have used is often F. Thus Nernst (*Theoretische Chemie*, 6th Ed., p. 730) writes on the same page two equations, one connecting ΔA and equilibrium constant, and the other ΔA and electromotive force. Both of these equations are quite erroneous. Similar equations in which ΔF is substituted for ΔA are correct. Even Haber, in his extraordinarily careful work, "The Thermodynamics of Technical Gas Reactions," occasionally confuses these quantities, thus causing a numerical error of 300 cal. on page 177 (English Ed.) and of 700 cal. on page 320.

Owing to this confusion and to the fact that the quantity F is of far greater practical convenience than A, it has seemed justifiable to call F the free energy. Students of Gibbs will observe that the quantities A and F correspond to the functions ψ and ζ. We may, moreover, note that our H is Gibb's χ, and our E his ε.

possible to write reactions analogous to thermochemical reactions, and such equations may be combined by addition and subtraction in the familiar manner. Thus, for example, we shall find later,

$$H_2 + \mathrm{S(rhombic)} = H_2S(g);\ \Delta F = -7830 \text{ cal.}$$

$$\mathrm{S(monoclinic)} = \mathrm{S(rhombic)};\ \Delta F = -18 \text{ cal.}$$

Hence, by addition,

$$H_2 + \mathrm{S(monoclinic)} = H_2S(g);\ \Delta F = -7848 \text{ cal.}$$

It is of course understood that all these reactions are considered at the same temperature (in the present case 25°) and, except when otherwise specified, that all the substances are at atmospheric pressure. When ΔF is negative it shows that the reaction in question tends to occur spontaneously in the direction left to right.

As in the case of the quantity H, one cannot determin experimentally the absolute value of F for any substance. We shall therefore adopt the convention that at every temperature the free energy of an element is zero in its standard state, as previously defined. The above equations therefore give at once the free energy of hydrogen sulfide gas and of monoclinic sulfur, both referred to rhombic sulfur, the standard. Thus, at 25° or 298° A (absolute), we may write for brevity

$$\mathrm{S(monoclinic)};\ F_{298} = 18 \text{ cal.,}$$

$$H_2S(g)\ ;\ F_{298} = -7830 \text{ cal.}$$

When we are dealing with solutions, we must consider the partial molal free energy, which is defined as the total increase in free energy when one mol of the substance in question is produced from its elements, and introduced into a very large amount of the given solution.[1] Thus, for example, if we write,

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(0.1\,M);\ \Delta F_{298} = -34330,$$

then

$$HCl(0.1\,M);\ \overline{F}_{298} = -34330 \text{ cal.}$$

In general, the increase of free energy in a reaction is the sum of the free energies or partial free energies of the products, less the free energies or partial free energies of the factors.

The partial molal volumes, heat capacities, heat contents, etc., approach a constant value as the concentration of the substance in question diminishes, and are therefore nearly independent of the concentration in dilute solutions. Thus, in thermochemical equations, instead of specifying the exact concentration of substances in dilute aqueous solution, it is customary to use the symbol (aq) to indicate that a substance is dissolved in so large a quantity of water that its partial molal heat content is approximately equal to that at infinit dilution. The case is

[1] This partial molal free energy is obviously a potential in the sense used by Gibbs.

quite different with the partial molal free energy, which, instead of approaching a constant value at infinit dilution, approaches the value $-\infty$. In free energy equations the concentrations must therefore be definitly stated, although the highest degree of exactness is not always required, for, as we shall see, an error of 1% in the concentration means an error of only about 6 cal. in the partial molal free energy, at room temperature.

The Change of Free Energy with Pressure; The Relation between Activity and Fugacity and the Free Energy.

Let us consider the change in free energy in the simple process, of which the net result is the disappearance of one mol of a pure substance at pressure p_1, and the appearance of a mol of the same substance at pressure p_2. This may be done reversibly by allowing one mol of the substance to expand or contract under an external pressure which is always kept equal to the pressure of the substance. Then

$$\Delta A = -\int p dv.$$

and

$$\Delta F = -\int p dv + p_2 v_2 - p_1 v_1 = \int v dp. \qquad (10)$$

In the case of a liquid or a solid the volume may often be expressed with sufficient accuracy as a linear function of the pressure $v = v_0 (1 - \beta p)$, where v_0 is the volume of zero pressure, and β the ordinary compressibility. Substituting in equation (10) and integrating gives

$$\Delta F = v_0 (p_2 - p_1) - \tfrac{1}{2}\beta v_0 (p_2^2 - p_1^2). \qquad (11)$$

When the substance is a perfect gas, its molal volume is given by the equation $v = \frac{RT}{p}$, and the integration gives

$$\Delta F = RT \ln \frac{p_2}{p_1}. \qquad (12)$$

It is important to show the relation between the free energy and two other thermodynamic functions, namely, the fugacity and the activity, of which the latter has come into somewhat general use. The fugacity ψ was defined as such a property of a given substance that (1) if ψ is the same for a substance in two phases, the substance will not pass from one phase to the other; (2) if ψ is greater in one phase than in another, the substance will tend to pass from the first phase to the second; (3) the fugacity of a perfect gas is equal to its pressure. These conditions completely define the fugacity of any substance in any condition.[1] It is evident that the fugacity has in general the dimensions of pressure.

The activity ξ is a similar function which has the dimensions of concentration and is related to the fugacity by the equation,

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[1] The proof that these simple conditions do completely define ψ need not be given here. See Lewis (*Proc. Am. Acad.*, **37**, 49 (1901); *Z. physik. Chem.*, **38**, 205 (1901)).

$$\psi = \xi \mathrm{RT}. \qquad (13)$$

The activity may, like the fugacity, be independently defined by the conditions (1) and (2) and the condition that the activity of a perfect gas is equal to its concentration.[1]

If one mol of a perfect gas passes at constant temperature from pressure p_1 to pressure p_2, we may write:

$$\Delta \mathrm{F} = \mathrm{RT} \ln \frac{p_2}{p_1} = \mathrm{RT} \ln \frac{\psi_2}{\psi_1} = \mathrm{RT} \ln \frac{\xi_2}{\xi_1}.$$

If, now, a substance, whose vapor is a perfect gas, exists in any two states, whether as pure liquid or solid, or in a solution, and the vapor pressures of the substance above those two states are p_1 and p_2, then the substance may be carried reversibly from the first state to the second by evaporating at p_1, changing the pressure of the vapor from p_1 to p_2, and finally introducing into the second state. In the first and third processes the change in free energy is zero, and therefore the total change in free energy of the whole process is

$$\Delta \mathrm{F} = \mathrm{RT} \ln \frac{p_2}{p_1} = \mathrm{RT} \ln \frac{\psi_2}{\psi_1} = \mathrm{RT} \ln \frac{\xi_2}{\xi_1}. \qquad (14)$$

Now ψ_1 is not only the fugacity of the vapor at pressure p_1, but also, by definition, of the substance in equilibrium with the vapor at this pressure, and the same is true of ψ_2. Similarly, ξ_1 and ξ_2 are the activities in the two states in question. Thus, whenever we know the fugacity or activity of a substance in any two phases, we may calculate the change in free energy by equation (14). This proof is, of course, not rigorous, since it assumes the existence of a perfect gas, but can readily be made so by the methods employed in the papers already referred to.

The definition of the activity and the fugacity in terms of the concentration and pressure of a perfect gas has some great theoretical advantages which will be pointed out more fully in a later paper. For practical purposes it is not always the most convenient, for it is sometimes difficult to determin the numerical value of these functions. Moreover, it is usually unnecessary to know this numerical value, but only the ratio between the activities or fugacities of a substance in two different states at the same temperature. We might, therefore, at a given temperature, choose for any substance a convenient standard and refer the activity in any other state to this. Thus, if ξ° is the activity in the state chosen as standard and ξ the activity in any other state, we may write,

$$a = \frac{\xi}{\xi^\circ}, \qquad (15)$$

and call a the relative activity. Similarly, we might define f the relative

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[1] See Lewis, *Proc. Am. Acad.*, **43**, 259 (1907); *Z. physik. Chem.*, **61**, 129 (1907).

fugacity, but this is unnecessary, since it is evident that a and f are both quantities of zero dimensions and identical with each other.

Perhaps the simplest convention for our purpose is to choose the standard states such that if F is the free energy of the substance in any state,

$$F = RT \ln a, \text{ or } \overline{F} = RT \ln a, \qquad (16)$$

then

$$\Delta F = F_2 - F_1 = RT \ln \frac{a_2}{a_1}, \qquad (17)$$

which is identical with equation (14). By this definition a becomes unity for every chemical element in its standard state at every temperature.

The statement that the activity of a perfect gas is proportional to its concentration is equivalent to the statement that the activity of a substance in an ideal dilute solution is proportional to its concentration.[1]

Free Energy and Equilibrium Constant.

The condition of equilibrium in any chemical reaction

$$dD + eE + \cdots = gG + hH + \cdots$$

is given by the equation

$$\Delta F = 0,$$

or, if F_D, F_E, ··· represent the molal (or partial molal) free energies of the substances involved,

$$(gF_G + hF_H + \cdots) - (dF_D + eF_E + \cdots) = 0, \qquad (18)$$

or by (16),

$$(gRT \ln a_G + hRT \ln a_H + \cdots) - (dRT \ln a_D + eRT \ln a_E + \cdots) = RT \ln \frac{a_G^g\, a_H^h \cdots}{a_D^d\, a_E^e \cdots} = 0. \qquad (19)$$

Now, if the substances G, H, ···, etc., are all present as gases, or in dilute solution, so that the activities may, with sufficient accuracy, be regarded as proportional to the concentrations, we may replace each activity by the corresponding concentration, multiplied by a constant. Since, however, it is customary in dealing with gases to use pressures rather than concentrations, and since the pressure, in the cases considered, is proportional to the concentration, we will replace the activity of each gas by its

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[1] See Lewis (*loc. cit.*, and THIS JOURNAL, 30, 668 (1908)). In the latter paper the perfect solution is defined as one in which the given substance has an activity proportional to the mol fraction. It is only in dilute solutions that this is equivalent to the condition that the activity is proportional to the concentration. In the case of solutions which are perfect, but concentrated, it is therefore preferable to use mol fractions rather than concentrations. Thus, in the paper cited, the mass law for such solutions is given in the exact form, $K = \frac{N_B^b \cdots}{N_A^a \cdots}$ where K is a constant for the reaction

$$aA + \cdots = bB + \cdots$$

pressure multiplied by a constant, and the activity of each substance in dilute solution by the concentration multiplied by a constant.

If, then, we are dealing with a reaction,

$$dD + \cdots + eE + \cdots + fF + \cdots = gG + \cdots + hH + \cdots + iI + \cdots,$$

where $D\cdots$, $G\cdots$ are gases, $E\cdots$, $H\cdots$ are in dilute solution, and $F\cdots$, $I\cdots$ are pure liquids or solids (of which the activities are constant at a given temperature) then the condition of equilibrium (19) may be rewritten in the form

$$RT \ln \frac{p_G^g \cdots c_H^h \cdots}{Kp_D^d \cdots c_E^e \cdots} = 0, \quad \text{or} \quad K = \frac{p_G^g \cdots c_H^h \cdots}{p_D^d \cdots c_E^e \cdots}, \tag{20}$$

where K collects the various constants mentioned above. The constant K will be called the equilibrium constant, and has been so chosen that the products of the reaction appear in the numerator and the factors in the denominator. This convention will be adhered to throughout the work.

Equation (20) can be used in the case of all reactions except those involving concentrated solutions, or gases under high pressure. In deriving it we have made no assumption regarding the units of pressure and concentration. We shall find it convenient to choose one atmosphere as the unit of pressure, and in the case of aqueous solutions one mol per 1000 grams of water as the unit of concentration. If all substances involved in the reaction are at unit pressure and those which are in solution are at unit concentration, the substances will be said to be under *normal* conditions.

We may now obtain a relation between the change in free energy of a reaction in which all the substances are under normal conditions, and the equilibrium constant of the reaction. This normal free energy change we will denote by $\Delta F°$. Let us consider the chemical reaction which we have discussed above, and let p_D, c_E, etc., represent a set of pressures and concentrations which satisfy the equilibrium conditions, and let p'_D, c'_E, etc., represent any other set of conditions. We may allow the reaction under the latter conditions to proceed in a roundabout way by changing the factors from p'_D to p_D, c'_E to c_E, etc., then allowing the reaction to proceed under equilibrium conditions, and finally changing the products from p_G to p'_G, c_H to c'_H, etc. The change in free energy in the second stage, which occurs under equilibrium conditions, is zero, and the total change in free energy may therefore be written as the sum of terms involving the change in free energy in carrying d mols of D from p'_D to p_D, etc. Thus:

$$\Delta F = dRT \ln \frac{p_D}{p'_D} + \cdots + eRT \ln \frac{c_E}{c'_E} + \cdots + gRT \ln \frac{p'_G}{p_G} + \cdots + \\ hRT \ln \frac{c'_H}{c_H} + \cdots = RT \ln \frac{p'^g_G \cdots c'^h_H \cdots}{p'^d_D \cdots c'^e_E \cdots} - RT \ln K. \tag{21}$$

Under normal conditions p'_D, etc., are all unity and we therefore have for the change of free energy under normal conditions

$$\Delta F^\circ = -RT \ln K. \qquad (22)$$

It must be borne in mind that equations (20) to (22) are only approximate equations and approach exactness as the solutions and the gases considered approach infinit dilution.

Free Energy and Electromotive Force.

On account of the importance in free energy calculations of those chemical reactions which occur in a voltaic cell during the passage of a current, it is very desirable that suitable conventions be adopted for the sign of an electromotive force or of a single potential difference.

It is not sufficient to state that a cell composed of cadmium amalgam, saturated cadmium sulfate solution, mercurous sulfate, and mercury, gives an electromotive force of 1.0183 volts at 20°; for a person unacquainted with the cadmium cell would not know whether this cell would do work through the consumption of cadmium and the deposition of mercury, or *vice versa*. We may, however, in this, as in other cases, eliminate any ambiguity by writing the chemical equation,

$$\begin{aligned}&\mathrm{Cd}(12.5\%\ \text{amalg.}) + \mathrm{Hg_2SO_4(s)} + 8/3\mathrm{H_2O}\\ &\qquad(\text{saturated with } \mathrm{CdSO_4}\ 8/3\mathrm{H_2O}) = \mathrm{CdSO_4}\ 8/3\mathrm{H_2O(s)} + 2\mathrm{Hg(l)}.\end{aligned}$$

And now if we say that at 20° the e. m. f. is + 1.0183 volts, the positive sign will indicate that the cell is capable of doing work when the reaction runs from left to right. So also we write for the reaction

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} = \mathrm{HCl}(0.1\,M);\ \mathbf{E} = +1.4881$$

at 25°, meaning that work is done by a cell in which hydrogen and chlorine combine to form hydrochloric acid in 0.1 M solution.

Instead of writing the chemical reaction in such a case, we may express the same facts in another way, which shows better the actual construction of the cell in question. The form $\mathrm{H_2(g)},\ \mathrm{HCl}(0.1\,M),\ \mathrm{Cl_2(g)};\ \mathbf{E} = +1.4881$ expresses the same facts. In such an expression *the positive e. m. f. indicates the tendency of the positive current to run through the given cell from left to right.*

The total e. m. f. is the sum of a number of single potentials which are present whenever there is a junction between an electrode and an electrolyte, or between two electrolytes. Thus in the cell

$$\mathrm{Hg,\ HgCl,\ KCl}(M),\ \mathrm{KCl}(0.1M),\ \mathrm{HCl}\ 0.1M,\ \mathrm{Cl_2};\ \mathbf{E} = 1.1130,$$

we have besides the two electrode potentials the potential between (M)KCl and (0.1 M)KCl, and between (0.1 M)KCl and (0.1 M)HCl. It is often possible to measure or calculate such single liquid potentials, and it is sometimes convenient to indicate the electromotive force of the cell due to the electrode potentials alone (exclusive of the liquid potentials) in which case we write

$$\mathrm{Hg, HgCl, KCl}(M), \| \mathrm{HCl}(0.1\,M), \mathrm{Cl_2};\ \mathbf{E} = 1.1423,$$

where the vertical bars indicate that the liquid potential or potentials between the KCl(M) and the HCl(0.1 M) are not included in the e. m. f.

The single potential of each junction is indicated in the same way as the e. m. f. of a whole cell. Thus when we write

$$\mathrm{Zn, Zn^{++}}(0.1\,M);\ \mathbf{E} = \text{a positive quantity},$$

we mean there is a potential difference tending to send positive electricity across the junction from left to right. Similarly, the expression

$$\mathrm{KCl}\ (0.1\,M),\ \mathrm{HCl}\ (0.1\,M);\ \mathbf{E} = -0.0286\ (18^\circ\,\mathrm{C})$$

indicates that in this case negative electricity tends to pass through the junction from left to right, or positive from right to left.

Thus in place of the above form

$$\mathrm{H_2, HCl}\ (0.1\,M),\ \mathrm{Cl_2};\ \mathbf{E} = +1.4881,$$

we may write:

$$\mathrm{H_2, HCl}\ (0.1\,M);\ \mathbf{E} = x,$$

and

$$\mathrm{HCl}\ (0.1\,M),\ \mathrm{Cl_2},\ \mathbf{E} = y,$$

where $x + y = 1.4881$. If the 0.1 M solution of hydrochloric acid is assumed to have a certain degree of ionization, say 76%,[1] the same results can be expressed by the form

$$\mathrm{H_2, H^+}\ (0.076\,M);\ \mathbf{E} = x,$$
$$\mathrm{Cl^-}\ (0.076\,M)\ \mathrm{Cl_2};\ \mathbf{E} = y,$$

where x and y have the same value as before.[2]

Corresponding to such single potentials, we may write the equations of the "half-reactions" in the form

$$(a)\ \tfrac{1}{2}\mathrm{H_2} + \oplus = \mathrm{H^+}\ (0.076\,M);\ \mathbf{E} = x.$$
$$(b)\ \tfrac{1}{2}\mathrm{Cl_2} = \mathrm{Cl^-}\ (0.076\,M) + \oplus\ ;\ \mathbf{E} = y,$$

where the symbol $\oplus$ represents one equivalent of positive electricity. Each of these half-reactions is so written as to correspond to the above form; that is, the positive current passes the junction $\mathrm{H_2}$, $\mathrm{H^+}$ from left to right when the reaction (a) runs from left to right. In the other case, the positive current passes through the junction $\mathrm{Cl^-}$, $\mathrm{Cl_2}$ from left to right when the reaction (b) runs from left to right. Adding these reactions together, we obtain the reaction for the whole cell.

Having established these arbitrary but important conventions, let us consider the application of thermodynamics to the voltaic cell. A working cell, for example a lead storage battery, gives a potential on discharge,

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[1] See Lewis, This Journal, 34, 1631 (1912).

[2] It must, however, be remarked that while this latter form is the more convenient for many purposes, it is by no means as explicitly a statement of things which are actually measured as the first form.

which is lower the larger the current. On the other hand, on charging such a cell the potential required is higher when the current is larger. In both cases, as the current is diminished, the e. m. f. approaches the same limiting value, which is the reversible e. m. f. of the cell. The reaction in the cell is therefore strictly reversible only for an infinitesimal current, but in many cases (in which the electrodes are said to be practically unpolarizable) the e. m. f. is approximately constant for small currents, and in such cases a measurement of the electromotive force furnishes a very convenient and exact determination of the free energy of the cell reaction.

If the e. m. f. of a reversible cell is $\mathbf{E}$, and the reaction of the cell involves the passage of n Faraday equivalents, then the electrical work done by the cell is $n\mathbf{FE}$. If the reaction is accompanied by a change of volume, there is also work done against the external pressures, and we may write for the total reversible work

$$-\Delta \mathrm{A} = n\mathbf{FE} + \Delta\Sigma pv,$$

whence by equation (9)

$$\Delta \mathrm{F} = -n\mathbf{FE}. \tag{23}$$

Let us consider the reaction

$$l\mathrm{L} + m\mathrm{M} + \cdots = r\mathrm{R} + s\mathrm{S} + \cdots,$$

and write the free energy of each substance in terms of its activity,

$$l\mathrm{F}_{\mathrm{L}} = l\mathrm{RT} \ln a_{\mathrm{L}} = \mathrm{RT} \ln a_{\mathrm{L}}^{l}, \text{ etc.}$$

Hence we may write from equation (16)

$$\mathbf{E} = -\frac{\mathrm{RT}}{n\mathbf{F}} \ln \frac{a_{\mathrm{R}}^{r}\, a_{\mathrm{S}}^{s} \cdots}{a_{\mathrm{L}}^{l}\, a_{\mathrm{M}}^{m} \cdots}. \tag{24}$$

Now if all the substances concerned in the reaction are present in sufficiently dilute solution (or as gases at sufficiently low pressures), each activity may be replaced by the concentration (or pressure) multiplied by a constant. If all these constant terms are collected in a single term $\mathbf{E}^{\circ}$, we may then write

$$\mathbf{E} = \mathbf{E}^{\circ} - \frac{\mathrm{RT}}{n\mathbf{F}} \ln \frac{c_{\mathrm{R}}^{r}\, c_{\mathrm{S}}^{s} \cdots}{c_{\mathrm{L}}^{l}\, c_{\mathrm{M}}^{m} \cdots}. \tag{25}$$

When all the concentrations (or pressures) are unity, the last term vanishes and therefore $\mathbf{E}^{\circ}$ represents the e. m. f. of the cell under normal conditions, and may be called the *normal* e. m. f.

We may apply the same reasoning to the half-reaction occurring at one electrode. Let us consider the half-reaction,

$$l\mathrm{L} + m\mathrm{M} + \cdots + n\,\oplus = r\mathrm{R} + s\mathrm{S} + \cdots,$$

then precisely as before[1]

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[1] It is perhaps best to adhere to this standard form, and always write the reaction so that the symbol $\oplus$, with a positive sign, occurs on the left side of the equation. If,

$$\mathbf{E} \doteq \mathbf{E}^\circ - \frac{RT}{n\mathbf{F}} \ln \frac{c_R^r\, c_S^s \cdots}{c_L^l\, c_M^m \cdots}.$$

Since the activity of any pure solids or liquids is constant (at constant pressure), they do not enter into the logarithmic term.

As illustrations we may consider the following reactions:

(*a*) $Ag + (\underset{\smile}{+}) = Ag^+$,

(*b*) $2Cl^- + 2\,(\underset{\smile}{+}) = Cl_2$,

(*c*) $Fe^{++} + (\underset{\smile}{+}) = Fe^{+++}$,

(*d*) $Fe(CN)_6^{----} + (\underset{\smile}{+}) = Fe(CN)_6^{---}$,

(*e*) $Br_2 + 6H_2O + 10\,(\underset{\smile}{+}) = 2BrO_3^- + 12H^+$

The corresponding formulas[1] (representing for convenience concentration by ( ), pressure by [ ] are:

$$(a)\quad \mathbf{E} = \mathbf{E}^\circ - \frac{RT}{\mathbf{F}} \ln (Ag^+),$$

$$(b)\quad \mathbf{E} = \mathbf{E}^\circ - \frac{RT}{2\mathbf{F}} \ln \frac{[Cl_2]}{(Cl^-)^2}$$

or, if we consider the Cl_2 solution,

$$(b)\quad \mathbf{E} = \mathbf{E}^{\circ\prime} - \frac{RT}{2\mathbf{F}} \ln \frac{(Cl)_2}{(Cl^-)^2},$$

$$(c)\quad \mathbf{E} = \mathbf{E}^\circ - \frac{RT}{\mathbf{F}} \ln \frac{(Fe^{+++})}{(Fe^{++})},$$

$$(d)\quad \mathbf{E} = \mathbf{E}^\circ - \frac{RT}{\mathbf{F}} \ln \frac{(Fe(CN)_6^{---})}{(Fe(CN)_6^{----})},$$

$$(e)\quad \mathbf{E} = \mathbf{E}^\circ - \frac{RT}{10\mathbf{F}} \ln \frac{(BrO_3^-)^2(H^+)^{12}}{(Br_2)}$$

Now all these formulas involving concentrations are only correct when the activity of each substance concerned is proportional to its concen-

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however, it is desired to use the symbol $(\underset{\smile}{+})$ with either positive or negative sign on the left side, the above formula remains true, but n will then be numerically positive or negative, respectively.

[1] It is to be noted that, when two reactions can be added to give a third, the free energy change of the third reaction is the sum of the free energy changes of the other two, but the electromotive forces are not in general simply additive (see Luther, *Z. physik. Chem.*, **30**, 661 (1899)). Thus consider the three reactions:

(*a*) $Cu + (\underset{\smile}{+}) = Cu^+$,

(*b*) $Cu^+ + (\underset{\smile}{+}) = Cu^{++}$,

(*c*) $Cu + 2\,(\underset{\smile}{+}) = Cu^{++}$,

then we have

$$\Delta F_a = \mathbf{F}\mathbf{E}_a,\ \Delta F_b = \mathbf{F}\mathbf{E}_b, \text{ and } \Delta F_c = 2\mathbf{F}\mathbf{E}_c.$$

$$\text{Hence } \mathbf{E}_c = \frac{\mathbf{E}_b + \mathbf{E}_a}{2}$$

tration, but it is precisely in the case of electrolytes that the validity of this assumption is most doubtful, even in pretty dilute solutions.

This whole question is discussed in another paper[1] in which it is shown that if the degree of dissociation, and hence the concentration of ions and unionized salts, are calculated in the ordinary way from the conductivities, it is in general the unionized salt which is greatly abnormal, but that in the case of the ions also the activity is not exactly proportional to the concentration, even up to concentrations as low as tenth molal. For salts of higher type than uni-univalent, and especially for ternary salts, where there is the possibility of intermediate ions, the existing data do not at present enable us even to approach a satisfactory solution of this problem. In the case of the uni-univalent salts, it is shown that the degree of dissociation calculated from conductivity measurements is certainly incorrect, and that probably the actual degree of dissociation is lower than the one obtained in that way. In order to avoid confusion, the degree of dissociation and the concentration calculated from the new assumptions will be called provisionally the *corrected degree of dissociation* and the *corrected concentration.* If these values be chosen, the activity of the univalent ions is in most dilute solutions strictly proportional to the corrected concentration and the same is approximately true of the unionized salt. Whether or not all the views presented in that paper are correct, the fact that these corrected concentrations are proportional to the activities enables us, without error, to introduce them into equation (25).

No satisfactory method has been found for determining the absolute magnitude of any single electrode potential. It is therefore necessary in this case also to assume arbitrarily the value of some one potential; that is, we must arbitrarily assume the free energy of some one half-reaction. As in other cases, we shall choose the reaction

$$\tfrac{1}{2}H_2 + \ominus = H^+,$$

for which we may write the formula

$$\mathbf{E} = \mathbf{E}^\circ - \frac{RT}{\mathbf{F}} \ln \frac{c_{H^+}}{p_{H_2}^{1/2}},$$

or, if we understand that the hydrogen gas is at one atmosphere,

$$\mathbf{E} = \mathbf{E}^\circ - \frac{RT}{\mathbf{F}} \ln c_{H^+}.$$

Unless the concentration of the hydrogen ion is exactly proportional to the activity, the value of $\mathbf{E}^\circ$ calculated from this equation will not be a constant, but in any case it will approach a constant value as the concentration approaches zero. We will now adopt the convention that this

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[1] Lewis, THIS JOURNAL, 34, 1631 (1912).

value of $\mathbf{E}^\circ$ is equal to zero, at any temperature. This definition suffices to fix all single potentials.

The partial free energy of an ion is closely related to a single potential thus we have for hydrogen ion,

$$\overline{\mathrm{F}} = \overline{\mathrm{F}}^\circ + \mathrm{RT} \ln c_{\mathrm{H}^+},$$

and evidently, if $\mathbf{E}^\circ$ is zero, F° must also be zero; that is, the partial molal free energy of hydrogen ion under normal conditions is zero. A word of explanation must, however, be added here; $\overline{\mathrm{F}}^\circ$ is not, strictly speaking, the partial molal free energy of hydrogen ion at molal concentration, if the activity is not proportional to the concentration, as it seldom is in solutions as concentrated as molal. Rather, $\overline{\mathrm{F}}^\circ$ is the free energy in a hypothetical molal solution in which the activity is n times as great as in a solution of concentration $\left(\frac{1}{n}M\right)$, where n is a large number. So also $\mathbf{E}^\circ$ is the potential of hydrogen against such a hypothetical molal solution of hydrogen ion. The numerical relationship between this standard of potential and others which are in common use will be discussed in a later paper.[1]

The Free Energy of Concentrated Solutions.

The determination of the partial molal free energy of a substance in concentrated solution is in general a matter of some difficulty. In some cases the vapor pressure of the substance from the solution can be determined, or the distribution of that substance between the solution and some other liquid phase, in which latter the substance obeys the laws of the perfect solution. In such cases the free energy can be readily determined. In other cases it is possible by electromotive force measurements to determin such a partial free energy. Thus the electromotive force of a cell with zinc and chlorine electrodes and an electrolyte containing zinc chloride at any given concentration gives at once the partial molal free energy of the zinc chloride in that solution. Likewise, the free energy of hydrochloric acid in a concentrated solution may be obtained by means of hydrogen and chlorine electrodes. Or, in the latter case, we may use

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[1] The committee of the Bunsen Gesellschaft has adopted two symbols ε_c and ε_h for electrode potentials measured against the two standards, the normal calomel electrode and the normal hydrogen electrode. The potentials as given in the following papers, based upon the standard above defined, are approximately equal to ε_h except for sign. (The committee of the Bunsen Gesellschaft makes the potential of sodium negative, that of chlorine positive. I have adopted the opposit sign in conformity with the older and more common usage). Exactly what the committee means by the normal hydrogen electrode, they have not stated. The potential of hydrogen against a normal solution of hydrochloric or of sulphuric acid is a perfectly definit thing, but the potential of hydrogen against a solution normal in hydrogen ion must depend upon some assumption regarding the degree of dissociation, and different views will lead to values differing by 5 or 10 millivolts.

a hydrogen electrode on one side and an electrode of mercurous chloride and mercury on the other, in which case the electromotive force measures the difference between the free energy of mercurous chloride and the partial free energy of hydrochloric acid.

In case such devices fail, we may have recourse to a very valuable theorem due to Duhem. This theorem states that if a binary mixture composed of the substances X_1 and X_2, of which the mol fractions are N_1 and N_2, is changed in composition by the addition of one or the other of the constituents at constant temperature and pressure, there is a simple relation between the change in the partial molal free energy $\overline{F}_1$ and the change in the partial molal free energy $\overline{F}_2$; namely,

$$N_1 d\overline{F}_1 + N_2 d\overline{F}_2 = 0. \tag{26}$$

If we substitute the relative activities for the free energies according to equation (16), we have

$$N_1 d \ln a_1 + N_2 d \ln a_2 = 0. \tag{27}$$

If the vapors of the two constituents are nearly perfect gases, the vapor pressures may be substituted for the activities to give, the approximate equation

$$N_1 d\ ln\ p_1 + N_2 d\ ln\ p_2 = 0. \tag{28}$$

All these equations may be readily extended to systems of more than two constituents.[1]

If therefore the partial free energy of one component of a binary mixture be known as a function of the composition, then the ratio of the activities, or the difference in partial free energies, of the other component between two different concentrations can be obtained by the integration of the Duhem equation between these limits.

This principle will be of great value in the determination of the partial free energy of substances in concentrated aqueous solution, where it is possible by a variety of means to determin the partial free energy of the water as a function of the concentration. A further elaboration of these various methods of studying concentrated solutions will be postponed until a later paper.

Influence of Temperature on the Free Energy Change.

The increase in free energy, ΔF, which accompanies a given reaction at a certain temperature is not in general the same as the increase in free energy accompanying the same reaction at another temperature. Indeed, the change in ΔF with the temperature has no definit meaning until we state precisely the conditions of the initial and final substances at each temperature. When, therefore, we speak of the rate of change of ΔF with the temperature, $\frac{d(\Delta F)}{dT}$, we shall understand that for all the

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[1] For a simple proof of these relations see Lewis, THIS JOURNAL, 28, 569 (1906); also *Proc. Am. Acad.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907).

temperatures considered the reacting substances are at constant pressure (or pressures), and that the composition of every solution is the same.

Let us consider a reversible cycle in which (1) a reaction occurs at a temperature $T + dT$, (2) the products of the reaction are cooled to the temperature T, (3) the reaction is allowed to proceed in the reverse direction, and (4) the factors are heated to the temperature $T + dT$, thus bringing the system to its original state.

The pressure on each phase is kept constant during these operations, and thus the total work done against the external pressures is zero. It is therefore evident that the total work done by the system, which we may call dW, is given by the equation:

$$dW = -(\Delta F + d\Delta F) + \Delta F = -d(\Delta F),$$

where the increase in free energy of the reaction is $\Delta F + d(\Delta F)$ at $T + dT$, and ΔF at T.

The second law of thermodynamics gives us a well known equation for the work obtainable from such a reversible cycle, namely,

$$dW = \frac{QdT}{T},$$

where Q is the heat absorbed at the higher temperature. In the present case we have

$$Q = \Delta H - \Delta F,$$

for ΔH is the heat which would be absorbed by the reaction under ordinary calorimetric conditions and $-\Delta F$ is the additional heat absorbed when the reaction occurs reversibly, that is, in such a way as to do the maximum amount of outside work. Combining these equations, we have finally

$$T\frac{d(\Delta F)}{dT} = \Delta F - \Delta H. \qquad (29)$$

This is the desired equation. If the reaction is the formation of a substance from its elements in their standard state, the equation takes the form

$$T\frac{dF}{dT} = F - H.$$

In order to integrate equation (29) we may separate the variables by means of the obvious identity,

$$\frac{d\left(\frac{\Delta F}{T}\right)}{dT} = \frac{1}{T}\frac{d(\Delta F)}{dT} - \frac{\Delta F}{T^2}, \quad \text{or} \quad \Delta F - T\frac{d(\Delta F)}{dT} = T^2\frac{d\left(\frac{\Delta F}{T}\right)}{dT}$$

whence, by (29),

$$\frac{d\left(\frac{\Delta F}{T}\right)}{dT} = \frac{-\Delta H}{T^2}$$

We have already seen by (6) that ΔH may be expressed as a function of T,

$$\Delta H = \Delta H_0 + \Delta\Gamma_0 T + \tfrac{1}{2}\Delta\Gamma_1 T^2 + \tfrac{1}{3}\Delta\Gamma_2 T^3 + \cdots. \qquad (30)$$

Substituting in (30) and integrating gives

$$\frac{\Delta F}{T} = \frac{\Delta H_0}{T} - \Delta\Gamma_0 \ln T - \tfrac{1}{2}\Delta\Gamma_1 T - \tfrac{1}{6}\Delta\Gamma_2 T^2 + I, \qquad (31)$$

or

$$\Delta F = \Delta H_0 - \Delta\Gamma_0 T \ln T - \tfrac{1}{2}\Delta\Gamma_1 T^2 - \tfrac{1}{6}\Delta\Gamma_2 T^3 + IT, \qquad (32)$$

where I is the constant of integration. In this expression for the free energy change, all the quantities with the exception of I are capable of direct calorimetric determination, and in a very large number of cases are at present known with a fair degree of accuracy. If therefore ΔF can be determined at one temperature, I becomes known, and the change in free energy at any other temperature can be immediately determined.

It is of great interest to inquire whether the integration constant I itself can be calculated in advance of any measurements of free energy from the known physical and chemical properties of the substances involved in a reaction.

Le Chatelier[1] was the first to integrate the free energy equation and investigate the relation between the values of I, obtained for various physicochemical processes. The only regularity of consequence which he could discover was one which is known as the law of Deprez and Trouton, according to which the value of I, for the process of evaporation, is approximately the same for a large number of liquids. It is unfortunate that, owing to the inaccessibility of the journal in which Le Chatelier's paper was published, this part of his great memoir has been until recently entirely overlooked.

In 1899 the free energy equation was again integrated by Lewis,[2] who attempted to find a relationship between the constant of integration and the change in heat capacity in a reaction. A number of cases were found in which the constant I appeared to be approximately equal to zero. Thus equation 43*a* of that paper, namely in our notation,

$$\Delta F = RT \ln \frac{c_2}{c_1} + \Delta H, \qquad (33)$$

gave the change in free energy in the transfer of a substance in concentrated solutions from one concentration to another, or from one solvent to another. This equation was in agreement with the results of Cady[3] on the electromotive force of amalgam concentration cells. It was shown

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[1] Le Chatelier, *Ann. mines*, **13,** 157 (1888).

[2] "Development and Application of a General Equation for Free Energy and Physicochemical Equilibrium" (*Proc. Am. Acad.*, **35,** 3 (1899); *Z. physik. Chem.*, **32,** 364 (1900)).

[3] *J. phys. Chem.*, **2,** 551 (1898).

by the author to apply also to cells in which thallium sulfate was transferred from water to methyl, and to ethyl alcohol, and has since been corroborated in special cases by other investigators.[1]

In 1902 Richards,[2] in a paper dealing with his theory of the compressible atom, discussed and amplified the results obtained by Lewis. In order to show more explicitly the conditions under which the above equation might be expected to hold, he wrote it in the form

$$\Delta F = RT \ln \frac{c_2}{c_1} + \Delta H + f(\Delta \Gamma),$$

where $f(\Delta\Gamma)$ was some unknown function of the change in heat capacity. He was thus led to the statement: "If the heat capacity of a system does not change during the reaction, and concentration effects are eliminated, the changes in free energy and total energy are equal." In other words, in all cases where the term involving concentrations vanishes, $\Delta F = \Delta H$ when $\Delta\Gamma = 0$. This means that $I = 0$ when $\Delta\Gamma = 0$. In this paper Richards brought forward also a new and striking relationship between $\frac{d(\Delta F)}{dt}$ and $\frac{d(\Delta H)}{dt}$ (the latter being equivalent to $\Delta\Gamma$). In a number of reactions occurring in voltaic cells, these two quantities were almost invariably opposit in sign and roughly proportional to one another numerically. Furthermore, he pointed out the probability that each of these quantities becomes numerically less as the absolute zero of temperature is approached.

In 1904 van't Hoff[3] discussed further the results obtained by Lewis and by Richards. He investigated also the probable form of the free energy curve in the neighborhood of the absolute zero, and obtained one generalization which seems to hold true in a very large number of cases, namely, that when two forms (solid or liquid) of a substance are known, the one which is stable at higher temperatures is the one with the larger specific heat.

In 1905 two very important publications on this subject appeared. One of these by Haber[4] dealt with the whole subject of gas reactions. In the introductory chapters he considered at length the nature of the thermodynamically undetermined constant I, and concluded in the case of gas reactions involving no change in the number of molecules (in which therefore $\Delta\Gamma$ is ordinarily small) that I is zero. A paper of Nernst,[5] which appeared at the same time as Haber's book, contained a searching

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[1] Bancroft, *J. phys. Chem.*, 10, 319 (1906); Richards, Wilson and Thomas, *Carnegie Inst. Pub.*, 118.

[2] *Z. physik. Chem.*, 42, 129 (1902).

[3] Boltzmann Festschrift, p. 233 (1904).

[4] "Thermodynamics of Technical Gas Reactions."

[5] *Göttingen Nachr.*, 1906, 1.

investigation of the problems in question. He concluded that the value of $\Delta \Gamma$ at the absolute zero is equal to zero for all reactions involving only pure liquids and solid substances, that the molal heat capacity of any gas at the absolute zero is a function only of the number of atoms in the molecule. He concluded, furthermore, that the constant I is zero for a reaction involving only liquids and solids, in agreement with the results of the preceding investigators, and finally that for gaseous reactions I can be regarded as the algebraic sum of a number of constants, each characteristic of a single substance, and capable of being calculated by a method suggested vaguely by Le Chatelier, involving a consideration of the vapor pressure curve of the substance in question. It is evident that the question of calculating I from other data than those obtained from direct free energy measurements is one of great theoretical and practical importance, and it will be one of the chief purposes of this series of articles to investigate the laws which determin the value of this interesting quantity.[1] It seems preferable, however, first to collect all the data concerning free energy at present available, rather than to form at the outset any theory which might prejudice these calculations. This is the plan which will be followed in the succeeding papers.

In conclusion, I wish to express my thanks to Dr. Merle Randall for valuable assistance in the preparation of this paper.

THE CONSTITUTION OF ALUMINATES.

By Edward G. Mahin, D. C. Ingraham and O. J. Stewart.

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The solubility of aluminium hydroxide in alkalin bases and the existence of several minerals containing aluminium oxide and other metallic oxides in apparently constant proportions, have led to the hypothesis that aluminium hydroxide is amphoteric in character, forming salts with acids as well as with bases. Upon this assumption "aluminic acid" may be supposed to be mono-, di- or tri-basic, forming salts, perhaps hydrated, of $H^+,H_2AlO_3^-$, $H_2^{++}.HAlO^{--}_3$ or H_3^{+++},AlO_3^{---}. The corresponding salts might be written $M, AlO_2.H_2O$, M_2HAlO_3 or M_3AlO_3. Spinel, a mineral typical of the natural aluminates, is represented by the formula $Mg(AlO_2)_2$. The reprecipitation of aluminium hydroxide from a solution of a hypothetical aluminate by the addition of an aluminium salt of a strong acid would be accomplished by such a reaction as

$$AlCl_3 + 3MAlO_2 + 6H_2O \longrightarrow 3MCl + 4Al(OH)_3.$$

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[1] It must, however, be pointed out that the experimental data concerning specific heats may often be equally well expressed by widely different empirical equations, the use of which leads to very different values of I. For this reason, when the equation for the specific heat of a substance has once been chosen, it must be employed without modification in all other calculations involving that substance.