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THE FREE ENERGY OF OXYGEN, HYDROGEN, AND THE OXIDES OF HYDROGEN.[1]

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Elementary Oxygen.[2]

The standard state of oxygen will be gaseous oxygen at a pressure of one atmosphere. We might proceed from existing data to calculate the free energy of liquid and solid oxygen, but since the required data are still somewhat uncertain, and since these calculations must be pretty exact to be of value, we shall postpone the calculation of the free energy of oxygen and hydrogen in the liquid and solid state until further data are at hand.

Oxygen unquestionably dissociates, at the high temperatures which are now available, into monatomic molecules, but, as yet, no quantitative

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[1] This is the first of a series of papers in which the free energy of formation of the more important compounds will be calculated and tabulated.

[2] It is perhaps impossible to prepare such tables as these without permitting some errors to creep in, but every precaution which might serve to eliminate such errors has been taken; the experimental data have been most carefully scrutinized in order to determine not only the most probable value in each case, but also the order of magnitude of the possible error. As a rule, however, this estimate of error has been indicated only by the number of significant figures used. As a safeguard against error in computation every calculation has been carried on independently by the two authors.

measurements are at hand for the calculation of the free energy of this important reaction.

$3/2\ O_2 = O_3$.—The heat capacity of ozone has not been accurately determined. We shall, however, make no great error in assuming that the equation which holds for the two triatomic gases,[1] CO_2 and SO_2, is applicable in this case also, namely:

$$O_3;\ C_p = 7.0 + 0.0071T - 0.00000186T^2 \qquad (1)$$

from which we may subtract the heat capacity of 3/2 mols of oxygen from the equation

$$O_2;\ C_p = 6.50 + 0.0010T,$$

whence

$$\Delta\Gamma = -2.75 + 0.0056T - 0.00000186T^2 \qquad (2)$$

and[2]

$$\Delta H = \Delta H_0 - 2.75T + 0.0028T^2 - 0.00000062T^3 \qquad (3)$$

The heat of this reaction has been determined by a number of investigators, who have obtained values for ΔH ranging from 23000 to 36000 cal. These results are fully discussed in Ostwald's "Lehrbuch." We will take 34000 cal. as the most probable value. Hence

$$\Delta H = 34600 - 2.75T + 0.0028T^2 - 0.00000062T^3 \qquad (4)$$

and

$$\Delta F^\circ = 34600 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 + IT \quad (5)$$

The attempts to study the free energy of this reaction have achieved little success. The potential of the ozone electrode has been studied, especially by Luther and Inglis,[3] who obtained nearly reproducible potentials by means of a platinum electrode surrounded by ozone, but they were unable to determine definitely the nature of the electrode reaction, and, in fact, it was later shown by Luther[4] that, with an iridium electrode, values differing from those with the platinum electrode by as much as 0.2 volt could be obtained.

The numerous unsuccessful attempts to detect ozone in oxygen suddenly cooled from a high temperature were shown by Clement[5] to be due to the extremely rapid rate of decomposition of ozone even at comparatively low temperatures. Later Fischer and Braehmer[6] succeeded in obtaining ozone by heating a filament to about 2300° A under liquid oxygen. If we admit the validity of certain assumptions suggested by Fischer and Braehmer, which, however, at best could be only very roughly true,

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[1] Lewis and Randall, THIS JOURNAL, **34**, 1128 (1912).

[2] For a discussion of the fundamental equations and notation see Lewis, *Ibid.*, **35**, 1 (1913).

[3] Luther and Inglis, *Z. physik. Chem.*, **43**, 203 (1903).

[4] Luther, *Z. Elektrochem.*, **11**, 832 (1905).

[5] Clement, *Ann. Physik.*, [4] **14**, 334 (1904).

[6] Fischer and Braehmer, *Ber.*, **39**, 940 (1906).

the oxygen at the temperature of the filament contained one mol per cent. of ozone, whence $K = p_{O_3}/(p_{O_2})^{3/2} = 0.01$; and if R′ is the gas constant in calories per degree, $\Delta F°_{2300} = -R'T \ln K = 21000$ cals. Substituting in (5) gives $I = -22.4$, whence $\Delta F°_{298} = 32400$.

It is, however, doubtful whether even the order of magnitude of the equilibrium constant between oxygen and ozone can be safely estimated from the data here employed.

Elementary Hydrogen.

We shall take ordinary gaseous hydrogen at a pressure of one atmosphere as the standard state. The only reaction, involving only elementary hydrogen, which we shall consider here is the very interesting reaction investigated by Langmuir.[1]

$H_2 = 2H$.—Langmuir's measurements of the equilibrium in this reaction between 2500°A and 3300°A depended upon a highly ingenious and novel method of calculation which is apparently correct in principle, but involves certain assumptions which his later work[2] have shown to be in some respects erroneous. In his first paper he calculated the heat of this reaction as —136000 cal., and the degree of dissociation of hydrogen at one atmosphere as 0.04 at 2500°A. Dr. Langmuir has been kind enough to give us the results of a preliminary calculation of his new data, which give the degree of dissociation at 2500°A as about 0.01, and the heat of the reaction as between —54000 and —75000 cal., the most probable value being in the neighborhood of —64000, which is the value obtained theoretically by Bohr[3] from his hypothesis concerning the structure of atoms.

We know little concerning specific heats at these high temperatures, but shall assume, as at lower temperatures,[4] that

$$H_2;\ C_p = 6.5 + 0.0009T$$
$$H;\ C_p = 5.0$$

Hence for the total increase in heat capacity

$$\Delta\Gamma = 3.5 - 0.0009T. \qquad (6)$$

And, assuming ΔH_{2500} to be 64000,

$$\Delta F° = 61000 - 3.5T \ln T + 0.00045T^2 + 20.2T, \qquad (7)$$

where the value of $I = 20.2$ is obtained as follows: At 2500°A, if the pressure of H_2 is one atmosphere, and of H, 0.01 atmosphere, $K = 0.0001$ and $\Delta F°_{2500} = -R'T \ln K = 45800$; and thence $I = 20.2$, and $\Delta F°_{298} = 61100$.

The determination of the dissociation of elementary gases into the

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[1] Langmuir, THIS JOURNAL, 34, 860 (1912).

[2] Langmuir, *Phil. Mag.*, 27, 188 (1914).

[3] Bohr, *Ibid.*, 26, 857 (1913).

[4] Lewis and Randall, THIS JOURNAL, 34, 1128 (1912).

monatomic forms is of the greatest importance. If we could use as the standard state of each element its monatomic gas at standard pressure, this would probably be a most important step towards the theoretical calculation of the thermodynamically undetermined constants of chemical affinity.

Hydrogen Ion.

$^1/_2H_2 + \oplus = H^+$. — Hydrogen ion in water is doubtless largely hydrated. While the hydronium ion OH_3^+ is presumably less stable under similar circumstances than the corresponding ammonium ion NH_4^+, it probably exists in considerable amount, together with higher hydrates of hydrogen ion, in every aqueous acid solution. For the purpose of such thermodynamic calculations as we are about to make, it is justifiable to assume the simplest formula for hydrogen ion, namely, H^+, and the formation of this ion in aqueous solution will be represented by the above equation.

The value of ΔF° for this reaction will be understood to be the increase in free energy when one-half mol of hydrogen, at atmospheric pressure, and one equivalent of positive electricity disappear, and one mol of hydrogen ion appears in aqueous solution at (hypothetical) molal concentration.[1] Now, since it is impossible at present to determine the absolute free energy change in any such "half reaction," it has seemed desirable[2] to regard the normal free energy change of this particular half reaction as zero at all temperatures.

$$^1/_2H_2 + \oplus = H^+;\ \Delta F^\circ = 0 \text{ (all temperatures)} \qquad (8)$$

This is equivalent to the convention that for the normal electrode potential of hydrogen,

$$E^\circ = 0 \text{ (all temperatures)} \qquad (9)$$

Hydrogen and Calomel Electrodes.

Since we are to take the normal potential of the hydrogen electrode as the arbitrary zero of single potential, and refer all other single potentials to it, it is desirable to know accurately the relation between this standard electrode and others which are in common use. The older work on the hydrogen electrode by Smale, Wilsmore and others[3] has been superseded by work of the last few years. We shall refer especially to the papers of Bjerrum,[4] Lorenz and Böhi,[5] Loomis and Acree,[6] and to an unpublished

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[1] A solution is said to be at (hypothetical) molal concentration with respect to hydrogen ion when the activity of hydrogen ion in this solution is *n* times as great as in a 1/*n* *M* solution of hydrogen ion, where *n* is a large number.

[2] Lewis, THIS JOURNAL, **35**, 25 (1913).

[3] See Wilsmore, *Z. physik. Chem.*, **35**, 291 (1900).

[4] Bjerrum, *Ibid.*, **53**, 430 (1905).

[5] Lorenz and Böhi, *Ibid.*, **66**, 733 (1909).

[6] Loomis and Acree, *Am. Chem. J.*, **46**, 585 (1911).

investigation of Lewis which was interrupted several years ago and has never been completed. However, a number of accurate measurements were made of the hydrogen potential at different temperatures and pressures, and in acid and alkaline solutions, and the results will be given here.

The most important measurements for our purpose are those which have been made in 0.1*M* HCl against a calomel electrode in 0.1*M* KCl or 0.1*M* HCl. In the latter case there is no liquid potential.

The cell H_2, HCl (0.1*M*), KCl (0.1*M*), HgCl, Hg gives, according to Bjerrum, **E** = 0.4270 volt at 25°. At the same temperature Loomis and Acree find **E** = 0.4266. In order to compare these values with those obtained against the 0.1*M* HCl calomel electrode it is necessary to know the e. m. f. of the cell Hg, HgCl, KCl (0.1*M*), HCl (0.1*M*), HgCl, Hg. If we assume, what is undoubtedly very nearly true, that the two single electrode potentials in this combination have the same value,[1] then the whole electromotive force of this cell is the potential between the liquids. This liquid potential calculated by the formula of Lewis and Sargent is —0.0284 volt.[2] Bjerrum[3] has studied the electromotive force of this combination and finds, as Lewis and Rupert also found, that the liquid potential changes with the time. He showed, moreover, that different values were obtained according to the way in which the contact between the two liquids was made. His best value was **E** = —0.0278 volt. The values obtained by Lewis for this combination were, however, near the theoretical value —0.0284 volt, and this is the value we shall adopt for the present.[4]

By adding together the values of **E** obtained for the two cells, we find for the combination H_2, HCl (0.1*M*), HgCl, Hg; **E** = 0.3986 (Bjerrum), and 0.3982 (Loomis and Acree). Lewis found, as a mean of several direct determinations, 0.3987 at 25°.[5] The mean of these values is **E** = 0.3985. In all of these cases the hydrogen was not at atmospheric pressure, but at one atmosphere less the pressure of water vapor at 25°. We must,

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[1] Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).

[2] See Lewis and Rupert, *Ibid.*, 33, 299 (1911). The value obtained by the unmodified formula of Planck, —0.0266, is unquestionably erroneous.

[3] Bjerrum, *Z. Electrochem.*, 17, 61 (1911).

[4] Since this paper was first written the hydrogen electrode potential has been very carefully investigated in this laboratory by Mr. Sebastian. His work is to be published shortly. In the meantime we have rewritten certain sections of this paper in order to include some of his results. His value for the e. m. f. between calomel electrodes in 0.1 *M* KCl and 0.1 *M* HCl is identical with the value chosen above, —0.0284.

[5] Loomis and Acree also measured this cell directly and obtained =0.4001, but they regarded these as preliminary measurements and we need give them no weight. Their discussion of the liquid potentials calculated by the formula of Lewis and Sargent is erroneous in that they have confused certain conductivity values at 18° with values at 25°.

therefore, make a correction of the magnitude $\frac{RT}{2F} \ln \frac{1}{p}$ where p is the actual pressure of the hydrogen in atmospheres and R is the gas constant in joules per degree. At a partial pressure of one atmosphere of hydrogen, therefore, $\mathbf{E} = 0.3985 + 0.0004 = 0.3989$ volt. All these values were presumably obtained in terms of the old value of the standard Weston cell 1.0187 or 1.0186 at 20°. Using the new value 1.0183 lowers the value of **E** to 0.3988.

The recent value of Sebastian is 0.3990, and we shall accept this as the final value.

If we make the assumption, as before, that the actual potential of the calomel electrode is the same in $0.1M$ HCl and $0.1M$ KCl, then the same value of **E** holds for the combination[1]

$$H_2, HCl\ (0.1M)\ \|\ KCl\ (0.1M), HgCl, Hg;\ \mathbf{E} = 0.3990. \quad (10)$$

Numerous investigations in this laboratory have fixed the value of the e. m. f. between the decinormal and normal calomel electrode at 25° as —0.0530 volt. This includes the liquid potential between $0.1M$ KCl and $1M$ KCl, which cannot readily be calculated, owing to the change in the transference number of KCl with the concentration, and also to the fact that we have at present no method of applying the laws of dilute solution to a solution of KCl as concentrated as molal. In most exact e. m. f. measurements where the normal electrode has been used, $0.1M$ KCl has been introduced between the normal electrode and the other electrode, so that it is really not important to know the value of the liquid potential in question, since we may regard the whole combination Hg, HgCl, KCl ($1M$), KCl ($0.1M$) as the normal electrode. We shall hereafter call this the normal electrode and designate it by N.E., thus

$$Hg, HgCl, KCl\ (0.1M), N.E.;\ \mathbf{E} = -0.0530 \quad (11)$$

Adding (10) and (11) gives

$$H_2, HCl\ (0.1M)\ \|\ N.E.;\ \mathbf{E} = 0.3460. \quad (12)$$

At the time of writing the preceding sections it was believed that the normal electrode potential of hydrogen could be calculated from the potential in $0.1M$ HCl with the desired accuracy, but the investigation of Lewis,[2] concerning the activity of univalent ions, showed that even in solutions as dilute as $0.1M$ the ion activity is in doubt by several per cent. For this reason, it seemed desirable to determine the hydrogen potential against more dilute solutions. This investigation, to which we have already referred, has been carried on by Mr. Sebastian, who has found for the cell

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[1] The two vertical bars indicate here, and elsewhere, that the value given is exclusive of the liquid potential at the junction indicated.

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

$$H_2, \text{HCl } (0.01M), \text{KCl } (0.01M), \text{KCl } (0.1M), \text{N.E.}; \mathbf{E} = 0.4261. \quad (13)$$

Eliminating the liquid potentials[1]

$$\text{HCl } (0.01M), \text{KCl } (0.01M); \mathbf{E} = 0.0274 \quad (14)$$

and

$$\text{KCl } (0.01M), \text{KCl } (0.1M); \mathbf{E} = 0.0007 \quad (15)$$

we find

$$H_2, \text{HCl } (0.01M) \,||\, \text{N.E.}; \mathbf{E} = 0.3980 \quad (16)$$

According to the calculations of Lewis[2] the corrected degree of dissociation of $0.01M$ HCl would be the same as for $0.01M$ KCl, namely, 0.92 (which is 2% less than Λ/Λ_0 for $0.01M$ KCl).

We are now able to calculate the difference between the hydrogen electrode potential in $0.01M$ HCl and in hypothetical molal H^+. From the formula

$$\mathbf{E} = 0.05915 \log (1/0.0092) = 0.1204$$

we find

$$H_2, \text{HCl } (0.01M) \,||\, H^+ (M), H_2; \mathbf{E} = 0.1204 \quad (17)$$

and combining with (16) gives

$$\text{N.E.} \,||\, H^+ (M), H_2; \mathbf{E} = -0.2776. \quad (18)$$

Since the normal hydrogen electrode is the standard *the potential of the normal calomel electrode is —0.2776 v.*

Effect of Pressure and Temperature on the Hydrogen Electrode Potential.— In order to make sure that the hydrogen electrode actually operates in a reversible manner it is important to test the effect of both temperature and pressure upon the electromotive force. We have given above the equation for the effect of a change of the partial pressure of the hydrogen on its electrode potential. This effect was studied experimentally by Lewis, who raised the hydrogen pressure by allowing the gas which passed through the cell to escape through a column of water of varying height. The results are given in Table I, in which the absolute magnitude of the electromotive force has no significance but only its variation with the pressure.[3] The first line gives the excess pressure in centimeters of water, the second the measured electromotive force, the third the calculated electromotive force, using the first measurement as a basis.[4] The observed and calculated values agree to about 0.00001 v.

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[1] We have assumed here and in the previous calculation the conductance values given by Bray and Hunt (This Journal, 33, 781 (1911)), for HCl, $\Lambda(0.1M) = 390.4$, $\Lambda(0.01M) = 411.6$; for KCl, $\Lambda(0.1M) = 129.0$, $\Lambda(0.01M) = 141.4$. The average transference number of K^+ in KCl between $0.1M$ and $0.01M$ has been taken as 0.494.

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

[3] This cell was of the same type as those previously discussed but with a somewhat different hydrochloric acid concentration.

[4] This series of experiments occupied four hours. In the last experiment the pressure was released too suddenly, driving the liquid in the cell below the electrode.

TABLE I.

Excess pressure, cm. H_2O...	0	37	63	84	100±	84	63	37
E. obs.......	0.40089	0.40134	0.40163	0.40190		0.40189	0.40164	0.40138
E. calc.......	0.40089	0.40134	0.40165	0.40189		0.40189	0.40165	0.40134

Lewis also investigated the effect of temperature upon the cell H_2, HCl (0.1*M*), HgCl in a single series of experiments of a preliminary character. The results, however, appear to be reliable to about 0.0001 v and serve as a basis for further interesting calculations. The measurements were made incidentally over a period of three days and are given in chronological order in Table II. In every case the total pressure of hydrogen and water vapor was 1 atmosphere. The actual pressure of the hydrogen is given in the third line and in the fourth the e. m. f. calculated to 1 atmosphere of hydrogen.

TABLE II.

Temp......	17.85	18.50	25.30	18.30	16.85	46.42	41.85	33.75	27.45
E..........	0.3975	0.3981	0.3991	0.3980	0.3978	0.3999	0.4000	0.3997	0.3991
p_{H_2}.........	746	744	736	744	746	683	699	721	733
E cor.......	0.3978	0.3984	0.3995	0.3983	0.3980	0.4014	0.4011	0.4004	0.3996

It is evident that the electromotive force is very far from being a linear function of the temperature. A discussion of this case affords an illustration of the way in which exact measurements of electromotive force made at different temperatures may be employed in determining thermal quantities. The values of **E** (corrected) given in the table may be summed up in the empirical equation,

$$\mathbf{E} = 0.0964 + 0.001881\mathrm{T} - 0.000002900\mathrm{T}^2,$$

whence,

$$d\mathbf{E}/d\mathrm{T} = 0.001881 - 0.000005800\mathrm{T}.$$

Now we may write the Gibbs-Helmholtz equation in the form

$$\mathbf{E} + \Delta\mathrm{H}/n\mathbf{F}' = \mathrm{T}\, d\mathbf{E}/d\mathrm{T},$$

where, since ΔH is in calories,

$$\mathbf{F}' = \mathbf{F}/4.182.$$

Substituting the above empirical values and writing $n = 2$ we obtain

$$\Delta\mathrm{H}/2\mathbf{F}' = -0.0964 - 0.000002900\mathrm{T}^2$$

$$\Delta\mathrm{H} = -4450 - 0.134\mathrm{T}^2.$$

This gives, at 25°, the value 16350 cal., and at 18°, 15800 as the heat of the reaction, $H_2 + 2HgCl + aq = 2HCl$ (0.1*M*) + 2Hg. From this we may obtain the partial heat of formation of hydrochloric acid in 0.1*M*

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thus preventing another reading at zero excess pressure. The excess pressure of 100 cm. was maintained for only a few minutes in order to approach the equilibrium from the opposite side.

solution by adding twice the heat of formation of HgCl, namely, 2 × 31300 cal., which was obtained by both Nernst[1] and Varet.[2] Thus

$$H_2 + Cl_2 = 2HCl\ (0.1M);\ \Delta H = -78950\ (25°),\ \Delta H = -78400\ (18°)$$

Thomsen obtained the value 78600 at a temperature of about 18°. The value we have calculated is undoubtedly more accurate than any that could be obtained by calorimetric measurements, unless the latter were carried out with extraordinary precision.

By differentiating the above equation, we find for the change in heat capacity in the reaction $H_2 + 2HgCl = 2HCl\ (0.1M) + 2Hg$

$$\Delta\Gamma = d(\Delta H)/dT = -0.268T$$

and this formula should be valid in the temperature range of our experiment. At 25° $\Delta\Gamma$ becomes —80 cal. per degree. This extraordinarily large value of $\Delta\Gamma$ is in good agreement with the value actually obtained from Thomsen's specific heat measurements, which show a very large negative partial molecular heat capacity for hydrochloric acid in aqueous solution.

The accuracy of the measurements upon which these calculations have been based could doubtless be increased tenfold without much difficulty; and this would furnish a method of determining not only heats of reaction to an extraordinary degree of precision, but also partial heat capacities in aqueous solution with a greater accuracy than has been attained by most methods.

The temperature coefficient of the cell

$$H_2,\ HCl\ (0.1M),\ HgCl,\ Hg;\ d\mathbf{E}/dT = 0.001881 - 0.0000580T \quad (19)$$

will apply also to the cell H_2, HCl (0.1M) || KCl (0.1M), HgCl, Hg, if our assumption is correct that the calomel electrode in 0.1M KCl has the same potential as in 0.1M HCl, that is

$$Hg,\ HgCl,\ KCl\ (0.1M)\ ||\ HCl\ (0.1M),\ HgCl,\ Hg;\ d\mathbf{E}/dT = 0. \quad (20)$$

The temperature coefficient of the e. m. f. between decinormal and normal calomel electrodes should be determined more accurately. At present we can obtain only an approximate result as follows: The e. m. f. at 25° we have shown to be —0.0530 v, and at 18°, Sauer[3] has found for the same combination —0.0514. Hence, for the temperature coefficient we find —0.00023. If, instead of using Sauer's result, we take 0.0530 at 25°, and assume the e. m. f. of the combination to be proportional to the absolute temperature, then we find —0.00018 for the coefficient. For want of better information we shall average these two values and assume the temperature coefficient to be independent of the temperature. Hence

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[1] Nernst, *Z. physik. Chem.*, **2**, 23 (1888).

[2] Varet, *Ann. chim. phys.*, [7] **8**, 102 (1896).

[3] Sauer, *Z. physik. Chem.*, **47**, 174 (1904).

$$\text{Hg, HgCl, KCl } (0.1M), \text{ N.E.}; \; d\mathbf{E}/dT = -0.00021 \qquad (21)$$

Combining (19), (20) and (21) gives

$$H_2, \text{ HCl } (0.1M) \,\|\, \text{N.E.}; \; d\mathbf{E}/dT = 0.00167 - 0.00000580T. \qquad (22)$$

From equations (12) and (18) we find

$$H_2, \text{ HCl } (0.1M) \,\|\, H^+ (M), H_2; \; \mathbf{E} = 0.0684. \qquad (23)$$

We may assume without serious error that the electromotive force of this cell is proportional to the absolute temperature. Therefore,

$$H_2, \text{ HCl } (0.1M) \,\|\, H^+ (M), H_2; \; d\mathbf{E}/dT = 0.00023. \qquad (24)$$

Combining (22) and (24) gives

$$\text{N.E.} \,\|\, H^+ (M), H_2; \; d\mathbf{E}/dT = -0.00144 + 0.00000580T. \qquad (25)$$

This is the temperature coefficient of the potential of the normal calomel electrode, since the potential of the normal hydrogen electrode is zero at all temperatures. It is very desirable that this important temperature coefficient be further investigated.

Hydroxide Ion.

The determination of the free energy of formation of hydroxide ion is involved with the determination of the free energy of formation of water and the free energy of ionization of water. We shall consider the latter process first.

$H_2O\ (l) = H^+ + OH^-$ —The difference between the potential of hydrogen in acid and alkaline solutions gives the most accurate means of determining the ionization constant of water. Accurate measurements of such cells have been made by Lorenz and Böhi[1] and by Lewis.[2] Lewis measured the cell: H_2, KOH (0.1M), KCl (0.1M), HgCl, Hg, and found **E** = 1.0836 at 25°, and **E** = 1.0799 at 18°. Corrected to the new value of the International Volt these values become **E** = 1.0833 at 25° and **E** = 1.0796 at 18°. The liquid potential KOH (0.1M), KCl (0.1M), calculated by the formula of Lewis and Sargent,[3] is 0.0165 at 25° and 0.0161 at 18°. Hence we find

$$H_2, \text{ KOH } (0.1M) \,\|\, (\text{KCl } (0.1M), \text{ HgCl, Hg}; \quad \mathbf{E} = 1.0998\ (25^\circ),\ 1.0957\ (18^\circ). \qquad (26)$$

We have previously found

$$H_2, \text{ HCl } (0.1M) \,\|\, \text{KCl } (0.1M), \text{ HgCl, Hg}; \quad \mathbf{E} = 0.3990\ (25^\circ);\ 0.3978\ (18^\circ) \qquad (27)$$

the value at 18° being obtained from the temperature coefficient given. Hence

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[1] Lorenz and Böhi, *Z. physik. Chem.*, **66**, 733 (1909).

[2] This is the same unpublished investigation which has been previously referred to.

[3] We have used at 25° for KCl, as before, Λ (0.1M) = 129.0, Λ (0.01M) = 141.4; for KOH some preliminary measurements give Λ (0.1M) = 245, Λ (0.01M) = 256; at 18° for KCl Λ (0.1M) = 112.0, for KOH Λ (0.1M) = 213 (Kohlrausch).

H_2, KOH (0.1*M*) || HCl (0.1*M*), H_2;
E = 0.7008 (25°); 0.6979 (18°), (28)

Lorenz and Böhi measured directly at several temperatures the cell
H_2, KOH (0.1*M*), KCl (0.1*M*), HCl (0.1*M*), H_2;
E = 0.6560 (25°); 0.6531 (18°). (29)

Excluding liquid potentials (—0.0284 and —0.0165 at 25°, and —0.0286 and —0.0161 at 18°) we find for (28) **E** = 0.7009 (25°), 0.6978 (18°). The agreement between these values and those obtained by Lewis is surprisingly good.[1] The former should, perhaps, be reduced one- or two-tenths of a millivolt, owing to the change in the International Volt. We may take the mean as 0.7008 at 25°, and 0.6978 at 18°.

The recent measurements of Sebastian give at 25°

H_2, KOH (0.1*M*), KCl (0.1*M*), N.E.; **E** = 1.0303 (30)
H_2, KOH (0.01*M*), KCl (0.01*M*), KCl (0.1*M*), N.E.; **E** = 0.9761. (31)

The liquid potentials are —0.0165 in the first cell, and —0.0152 and 0.0007 (Equation 15) in the second cell. Hence

H_2, KOH (0.1*M*) || N.E.; **E** = 1.0468 (32)
H_2, KOH (0.01*M*) || N.E.; **E** = 0.9906. (33)

Combining these equations respectively with (12) and (16)

H_2, KOH (0.1*M*) || HCl (0.1*M*), H_2; **E** = 0.7008 (34)
H_2, KOH (0.01*M*) || HCl (0.01*M*), H_2; **E** = 0.5926. (35)

The value at 0.1*M* is identical with the result obtained above from the work of Lorenz and Böhi, and of Lewis. It is to be noted that, if there is any error in the value of the liquid potential between KOH and KCl, it affects equally the results of the several observers.

From (35) we are now in a position to calculate the ionization constant of water for **E** = 0.5926 = 0.05915 log (a_1/a_2), where a_1/a_2 is the ratio of the activity or of the corrected concentration of H^+ in 0.01*M* HCl and in 0.01*M* KOH. Hence $a_1/a_2 = 1.043 \times 10^{10}$. Now we will take as before the corrected concentration of H^+ in 0.01*M* HCl as 0.0092 and take the same value for the corrected concentration of OH^- in 0.01*M* KOH. The ionization constant of water $(H^+)(OH^-)$ we may call K_w, hence

$$\frac{K_w}{0.0092} = \frac{0.0092}{1.043 \times 10^{10}}$$

whence $K_w = 0.81 \times 10^{-14}$ at 25°.

This result is probably correct within 2%, the chief source of error entering in the estimation of the corrected degree of ionization of 0.01*M* KOH

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[1] It is perhaps worth while to point out that the values of Lorenz and Böhi and of Lewis were entirely independent; the latter although unpublished were presented at the Baltimore meeting of the American Chemical Society in 1908. Those of Lorenz and Böhi were published in 1909.

and HCl. The final value obtained by Heydweiller[1] from the conductivity of the purest water obtainable was 1.04×10^{-14}. All other methods which have been used for determining this important quantity have been subject to errors of at least 15 or 20%, owing to methods of calculation alone.

For the ionization of water we have from the measurements of Thomsen at 18°, $\Delta H = 13730$ and $\Delta\Gamma$ is about —44, whence $\Delta H_0 = 26540$ and

$$H_2O(l) \rightleftharpoons H^+ + OH^-;\ \Delta F^\circ_{298} = -R'T \ln K_w = 19235,^{2} \qquad (36)$$

$$\Delta F^\circ = 26540 + 44T \ln T - 275.19T. \qquad (37)$$

This equation gives $K_w = 0.466 \times 10^{-14}$ at 18°, and 0.093×10^{-14} at 0°.

$^1/_2O_2 + {}^1/_2H_2 + \ominus = OH^-$.—In order to obtain the free energy of this reaction it is necessary to know the free energy of formation of liquid water from its elements. In making this series of calculations we have attempted to avoid reference forward, but in this case we shall assume the equation (53) which will be obtained in a later section of this paper, namely,

$$H_2 + {}^1/_2O_2 = H_2O(l);\ \Delta F^\circ_{298} = -56620.$$

Now combining this equation with (8) and (36) gives

$$^1/_2O_2 + {}^1/_2H_2 + \ominus = OH^-,\ \Delta F^\circ_{298} = -37385. \qquad (38)$$

$^1/_4O_2 + {}^1/_2H_2O + \ominus = OH^-$.—The free energy of this reaction gives us the normal potential of the oxygen electrode. From (37) and (38)

$$\Delta F^\circ_{298} = -9075;\ \mathbf{E}^\circ_{298} = -0.3933 \text{ v.}^{3} \qquad (39)$$

Water.

$H_2 + {}^1/_2O_2 = H_2O$ (gas).—The existing data on the heat of formation of liquid water have been summarized by Lewis[4] and shown to be very concordant. The mean value is 68470 at 0°. The heat of vaporization of water at 100° has recently been the subject of careful research. Richards and Matthews[5] obtained the value 538.1 cals. per gram of water. A. W. Smith[6] has reviewed his earlier work upon this subject with extraordinary care and finds the value 540.7 cals. We will adopt the value 540.0 or 9730 cals. per mol. Taking 8.4 and 18.0 as the average molal heat ca-

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[1] Heydweiller, *Ann. Physik*, **28**, 503 (1909).

[2] The absolute temperature corresponding to 25° is not 298 but approximately 298.1. Wherever the experimental data are sufficiently accurate to warrant the distinction ΔF_{298} will mean the free energy change at 25° = 298.1A.

[3] It may be well to recall here the convention regarding the sign of **E**. The general equation is $\Delta F = -n\mathbf{E}F'$ where n is the number of equivalents of positive electricity appearing on the left side of the chemical equation. In the present case, therefore, $n = -1$.

[4] Lewis, THIS JOURNAL, **28**, 1390 (1906).

[5] Richards and Matthews, *Proc. Amer. Acad.*, **46**, 511 (1911).

[6] A. W. Smith, *Phys. Rev.*, **34**, 173 (1911).

pacities of water vapor and liquid water between 0° and 100°, the heat of vaporization at 0° becomes 10690. Combining this with the heat of formation of liquid water we find for the heat content of water vapor, $H_{273} = -57780$ cals. We have for the heat capacities of the other gases

$$H_2O;\ C_p = 8.81 - 0.0019T + 0.00000222T^2$$

$$H_2;\ C_p = 6.5 + 0.0009T$$

$$^1/_2O_2;\ C_p = 3.25 + 0.0005T$$

hence

$$\Delta\Gamma = -0.94 - 0.0033T + 0.00000222T^2; \qquad (40)$$

and

$$\Delta H = \Delta H_o - 0.94T - 0.00165T^2 + 0.00000074T^3. \qquad (41)$$

Substituting the above value for ΔH_{273} in this equation,

$$\Delta H_o = -57410 \text{ cals.},$$

and our free energy equation is

$$\Delta F^\circ = -57410 + 0.94T \ln T + 0.00165T^2 - 0.00000037T^3 + IT. \quad (42)$$

For determining the value of I in the above equation several direct determinations of the dissociation of water vapor at high temperatures are available. Nernst and von Wartenberg[1] were the first to investigate this important equilibrium, and later measurements by different methods were made by Löwenstein,[2] von Wartenberg[3] and Langmuir.[4] The measurements of Holt[5] were obviously lacking in self-consistency and can be given no weight.[6] The results obtained by these investigators are given in Table III. The first column indicates the names of the investigators, the second the absolute temperature, the third the measured percentage dissociation, and the fourth the equilibrium constant $K_p = [H_2O]/[H_2][O_2]^{1/2}$, where the brackets indicate the pressure of the gases in question.

From each of these values of K_p we may determine a value for I. Thus, the measurements of Nernst and von Wartenberg give I = 3.81, 3.94, 3.67, respectively, average 3.81. Langmuir's values lead to the average value I = 3.55, with about the same mean deviation. Löwenstein's results show greater variation and lead to the average value I = 3.71, while von Wartenberg's two measurements at the highest temperatures

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[1] Nernst and von Wartenberg, *Z. physik. Chem.*, 54, 715 (1905).

[2] Löwenstein, *Ibid.*, 54, 715 (1905).

[3] von Wartenburg, *Ibid.*, 56, 513 (1906).

[4] Langmuir, THIS JOURNAL, 28, 1357 (1906).

[5] Holt, *Phil. Mag.*, [6] 13, 630 (1907).

[6] In a case of this kind, where a large number of data for a given equilibrium at different temperatures are available, a very good idea of the consistency of the various determinations may be obtained by plotting log K_p against 1/T.

TABLE III.

	T.	Per cent. dissoc.	K$_p$.	Log K$_p$.
Nernst and von Wartenberg	1397	0.0078	2.05×10^6	6.312
	1480	0.0184	5.66×10^5	5.753
	1561	0.0340	2.26×10^5	5.354
Löwenstein	1705	0.0326	2.3×10^4	4.362
	1783	0.0778	1.82×10^4	4.260
	1863	0.211	6.70×10^3	3.826
	1968	0.373	3.79×10^3	3.579
von Wartenberg	2155	1.18	1.094×10^3	3.039
	2257	1.77	0.590×10^3	2.771
Langmuir	1325	0.00325	7.65×10^6	6.884
	1354	0.0049	4.13×10^6	6.616
	1393	0.0069	2.47×10^6	6.393
	1433	0.0103	1.35×10^6	6.129
	1455	0.0142	8.35×10^5	5.922
	1474	0.0141	8.45×10^5	5.927
	1531	0.0255	3.47×10^5	5.540
	1550	0.0287	2.91×10^5	5.464

give 3.67 and 3.57, average 3.62. We may take as the weighted mean[1] of all these results I = 3.66. Substituting this value of I in our equation we find

$$\Delta F^\circ_{298} = -54590 \qquad (43)$$

We shall not, however, regard these values of ΔF°_{298} and of I as final, since there are other important methods of determining the free energy of formation of water still to be considered.

$H_2O(g) = H_2O(l)$.—The free energy of formation of liquid water from gaseous water may be obtained from the vapor pressure. According to Scheel and Heuse[2] the vapor pressure of water at 25° is 23.8/760 atms. Assuming that water vapor at this temperature and pressure is sufficiently near to a perfect gas,

$$\Delta F^\circ_{298} = -R'T \ln \frac{760}{23.8} = -2053 \qquad (44)$$

$H_2 + {}^1/_2O_2 = H_2O(l)$.—Combining (43) and (44) gives

$$\Delta F^\circ_{298} = -56640 \text{ cals.}$$

We shall not accept this as the final value but proceed to the discussion of the other methods of determining this quantity.

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[1] We have not included in this calculation measurements of the electromotive force of the oxygen, hydrogen, water vapor cell by Haber and his students. These experiments, although not capable of being carried out with the same accuracy as the equilibrium measurements, furnish a further important check upon the correctness of the results obtained by the latter methods.

[2] Scheel and Heuse, *Ann. Physik,* [4] **31,** 715 (1910). See also the very recent determination of Derby, Daniels and Gutsche, THIS JOURNAL, **36,** 793 (1914).

The Free Energy of Water from the Dissociation of Silver Oxide.—From measurements at higher temperatures, Lewis[1] calculated the decomposition pressure of silver oxide at 25° to be 5×10^{-4}, whence we calculate

$$2Ag + {}^1/_2O_2 = Ag_2O;\ \Delta F^\circ_{298} = -2250. \qquad (45)$$

According to the measurements of Böttger, silver oxide is in equilibrium with water containing Ag^+ and OH^- at $1.4 \times 10^{-4}\ M$.[2] Assuming that, at this concentration, the activity of the ions is proportional to their concentration,

$$Ag_2O + H_2O = 2Ag^+ + 2OH^-;\ \Delta F^\circ_{298} = 21040. \qquad (46)$$

Finally we need for this calculation the free energy of formation of Ag^+. The cell Ag, $AgNO_3$, (0.1*M*), KNO_3 (0.1*M*), KCl (0.1*M*), HgCl, Hg was investigated by Lewis[3] who found $\mathbf{E}_{298} = -0.399$. Noyes and Brann[4] have studied this same cell more recently and find $\mathbf{E} = -0.3992$. Eliminating the liquid potentials (—0.0025; +0.0018) and referring to the normal electrode by (11)

$$Ag,\ AgNO_3\ (0.1M)\ \|\ N.E.;\ \mathbf{E} = -0.4515 \qquad (47)$$

There is no way of calculating directly from existing data the activity or the corrected concentration of 0.1*M* $AgNO_3$. But, if we assume that the properties of silver nitrate are approximately the same as those of the analogous thallous nitrate, we may estimate this quantity. Noyes[5] found that the lowering of the solubility of TlCl by KCl (0.1*M*) and $TlNO_3$ (0.1*M*) indicated a concentration of Tl^+ 10% less than the concentration of K^+. Lewis[6] showed by a combination of conductivity and transference data the degree of dissociation of $TlNO_3$ and $AgNO_3$ to be 8% less than that of KCl at this concentration. Taking the corrected concentration of K^+ in KCl (0.1*M*) as 0.074 we will therefore, conclude that that of Ag^+ in $AgNO_3$ (0.1*M*) is 0.067. Hence

$$Ag,\ Ag^+\ (M)\ \|\ AgNO_3\ (0.1M),\ Ag;\ \mathbf{E} = -0.0694. \qquad (48)$$

From (47), (48) and (18) we therefore find for the potential of silver against (hypothetical) molal silver ion

$$Ag,\ Ag^+\ (M)\ \|\ H^+\ (M),\ H_2;\ \mathbf{E}^\circ_{298} = -0.7985 \qquad (49)$$

and

$$Ag + H^+ = {}^1/_2H_2 + Ag^+;\ \Delta F^\circ_{298} = 18424. \qquad (50)$$

We may now combine[7] (45), (46), (50) and (36), namely,

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[1] Lewis, THIS JOURNAL, **28**, 139 (1906).

[2] Lewis, "The Potential of the Oxygen Electrode," *Ibid.*, **28**, 164 (1906).

[3] Lewis, *Ibid.*, **28**, 167 (1906).

[4] Noyes and Brann, *Ibid.*, **34**, 1026 (1912).

[5] Noyes, *Z. physik. Chem.*, **9**, 603 (1892).

[6] Lewis, THIS JOURNAL, **34**, 1641 (1912).

[7] The last three of the four equations used above may be combined to give the equation $Ag_2O + H_2 = H_2O + 2Ag$. In place of the laborious and perhaps somewhat doubtful calculations used in these three reactions, a determination of the e. m. f. of

$$\begin{aligned}
2Ag + {}^1/_2O_2 &= Ag_2O; & \Delta F^\circ_{298} &= -\ 2250\\
Ag_2O + H_2O &= 2Ag^+ + 2OH^-; & \Delta F^\circ_{298} &= \ 21040\\
2Ag^+ + H_2 &= 2H^+ + 2Ag; & \Delta F^\circ_{298} &= -36848\\
2OH^- + 2H^+ &= 2H_2O; & \Delta F^\circ_{298} &= -38470.
\end{aligned}$$

Adding we find

$$H_2 + {}^1/_2O_2 = H_2O(l);\ \Delta F^\circ_{298} = -56530.$$

The Free Energy of Formation of Water from the Dissociation of Mercuric Oxide.—Another similar calculation has been made by Brönsted[1] from the dissociation pressure of mercuric oxide, measured by Pélabon, and from his own measurements of the e. m. f. of the cell, H_2, NaOH (aq), HgO, Hg, which is independent of the concentration of NaOH, provided that this is not great enough to lower materially the activity of the water in which it is dissolved. Brönsted found for this cell (H_2 at one atmosphere), $\mathbf{E}_{298} = 0.9268$, hence,

$$H_2 + HgO = H_2O(l) + Hg(l);\ \Delta F^\circ_{298} = -42770. \qquad (51)$$

Taylor and Hulett[2] have just redetermined the dissociation pressure of HgO. From their measurements it appears that at the boiling point of mercury, 357°, the oxide is in equilibrium with the gas which it produces, when the total pressure is 86 mm. Now one-third of this gas is oxygen and two-thirds mercury. Reducing pressures to atmospheres we find $K = [Hg][O_2]^{1/2} = 0.0146$. At this temperature liquid mercury is in equilibrium with its vapor at 1 atm., therefore, $\Delta F^\circ_{630} = -R'T \ln K = 5290$ is also the free energy change for the reaction $HgO = Hg(l) + {}^1/_2O_2$.

The heat of this reaction was found by Varet[3] as —21,500 and by Brönsted as —21700 cals. We may take the average $\Delta H = 21600$. The change in heat capacity in this reaction is zero, within the limits of accuracy of existing data, and $\Delta F^\circ = 21600 + IT$, hence, from the above value of ΔF°_{630}, $I = -25.9$ and

$$HgO = Hg(l) + {}^1/_2O_2;\ \Delta F^\circ_{298} = 13880. \qquad (52)$$

Combining (51) and (52) gives

$$H_2 + {}^1/_2O_2 = H_2O(l);\ \Delta F^\circ_{298} = -56650.$$

Final Value for the Free Energy of Water and the Electromotive Force of the Hydrogen Oxygen Cell.—We have found above three independent and extraordinarily concordant values for the free energy of formation of liquid water at 25°, namely, —56640, from the measurements of Nernst

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the cell Ag, Ag_2O, NaOH, H_2 should give the desired result. Luther and Pokorny' (*Z. anorg. Chem.*, **57**, 290 (1908)) have measured this cell at 25° and found $\mathbf{E} = 1.172$. This would give for the free energy of liquid water —56335. Their measurements, however, were only certain to within a few millivolts and we shall prefer for the present the calculations which we have used above.

[1] Brönsted, *Z. physik. Chem.*, **65**, 84 and 744 (1909).

[2] Taylor and Hulett, *J. Phys. Chem.*, **17**, 565 (1913).

[3] Varet, *Ann. chim. phys.*, [7] **8**, 100 (1896).

and von Wartenberg, of Löwenstein, and of Langmuir; —56530 from the measurements of Lewis; —56650 from the measurements of Brönsted and of Taylor and Hulett. These values correspond to 1.2275, 1.2250, and 1.2276 volts for the electromotive force of the hydrogen-oxygen cell. We may take, as a kind of *weighted mean, 1.2270 v.* The corresponding *average of the free energy values is*

$$H_2 + {}^1/_2O_2 = H_2O(l);\ \Delta F^\circ_{298} = -56620. \qquad (53)$$

The heat capacity of water is not constant, nor can it be expressed as a linear function of the temperature. However, over the range from 0° to 300°, which alone is of practical importance, we may, with sufficient accuracy, regard the value of $\Delta\Gamma$ as constant and equal to 8.0. We have seen that for this reaction $\Delta H_{273} = -68470$, whence,

$$\Delta F^\circ = -70650 - 8.0T \ln T + 92.64T. \qquad (54)$$

Combining (44) and (53) gives

$$H_2 + {}^1/_2O_2 = H_2O(g);\ \Delta F^\circ_{298} = -54567, \qquad (55)$$

and redetermining the value of I for this reaction in (42) we find

$$\Delta F^\circ = -57410 + 0.94T \ln T + 0.00165T^2 - 0.00000037T^3 + 3.72T. \qquad (56)$$

$H_2O(s)$ = $H_2O(l)$.—Instead of determining the general equation for the free energy of formation of ice it will be more convenient to obtain a simpler equation for the free energy of fusion of ice, valid over a small range of temperature. The best value for the heat of fusion is 79.7 cals. per gram, or 1436 cals. per mol.[1] The difference between the heat capacities of water and ice is neither constant nor accurately known. In the neighborhood of the freezing point we may take this difference as 9.0, and since the free energy of fusion is zero at 0°, we find[2]

$$H_2O(s) = H_2O(l);\ \Delta F^\circ_{298} = -141.6$$

$$\Delta F^\circ = -1022 - 9.0T \ln T + 54.230T. \qquad (57)$$

$H_2 + {}^1/_2O_2 = H_2O(s)$.—Combining with (53) gives $\Delta F^\circ_{298} = -56478$.

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[1] A. W. Smith, *Phys. Rev.*, **17**, 193 (1903); Roth, *Z. physik. Chem.*, **63**, 442 (1908). It is interesting to note that the value now accepted for the heat of fusion of ice is identical with the value 79.7 obtained by Black in 1762.

[2] In order to use such an equation as (57) over a small range from a melting point or a transition point with the accuracy justified by experiments, it is necessary to use 7 or 8-place logarithm tables in many cases. In order to avoid this we may substitute in such an equation as (57), $\Theta + t$ for T, where t is the temperature above the transition temperature Θ. Expanding the various terms and neglecting all terms of higher order than t^3 gives

$$\Delta F = -\frac{\Delta H_\theta}{\Theta}t - \frac{\Delta\Gamma}{2\Theta}t^2 + \frac{\Delta\Gamma}{6\Theta^2}t^3. \qquad (58)$$

In this particular case Θ is 273.1° and t is the centigrade temperature. Substituting the numerical values,

$$\Delta F = -5.26t - 0.0165t^2 + 0.00002t^3. \qquad (59)$$

This equation will be found especially useful in determining the free energy of solutions from freezing point data.

Hydrogen Peroxide.

The oxidizing potential of an oxygen electrode is diminished by the addition of hydrogen peroxide. Measurements[1] of such an electrode potential have been supposed to give material for the calculation of the free energy of hydrogen peroxide, but in this case, as in the case of ozone, there is no satisfactory evidence that the electromotive force is due to a single definite reversible reaction.

Traube[2] obtained a yield of 0.74% of H_2O_2 by directing an oxyhydrogen flame against water. The temperature of the flame was probably between 2000° and 3000°, but it is obviously impossible to obtain any quantitative estimate of the free energy of formation of hydrogen peroxide from this observation. We shall obtain a moderately accurate solution of this problem by considering the dissociation pressure of barium peroxide, and the equilibrium between barium peroxide hydrate and water.

$BaO + {}^1/_2O_2 = BaO_2$.—According to Berthelot, $\Delta H_{291} = -17200$. The later measurements of de Forcrand[3] give $\Delta H = -18400$. We will use the value —18000. The change in heat capacity in this reaction is small and will be neglected. Hence

$$\Delta F^\circ = -18000 + IT. \qquad (60)$$

We may calculate the value of I from the dissociation pressures given by Le Chatelier.[4] Except at the lower temperatures, his pressures lead to a constant value of I, namely, 16.8, whence $\Delta F^\circ_{298} = -13000$.

Hildebrand[5] made a careful investigation of the dissociation of barium peroxide and found that the reaction did not occur except in the presence of water (and, therefore, barium hydroxide) as catalyzer. His results apparently indicated a considerable mutual solubility of BaO in BaO_2, but an inspection of his curves makes it seem equally probable that the $Ba(OH)_2$ was largely responsible for the phenomena which he attributed to solid solution, and that in his univariant system the BaO and BaO_2 behave as nearly pure substances. We shall, therefore, calculate I directly from Hildebrand's several oxygen pressures and obtain very constant results, average I = 16.1, whence we find as final value

$$BaO + {}^1/_2O_2 = BaO_2;\ \Delta F^\circ_{298} = -13200 \qquad (61)$$

$BaO_2.10H_2O = BaO_2 + 10H_2O(g)$.—In the presence of water at ordinary temperatures, BaO_2 forms a hydrate, which, according to the work of de Forcrand,[6] is $BaO_2.10H_2O$. In order to complete the necessary free energy

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[1] Haber and Grinberg, *Z. anorg. Chem.*, **18**, 37 (1898); Haber, *Z. Elektrochem.*, **7**, 441, 1043 (1901); Nernst, *Z. physik. Chem.*, **46**, 720 (1903).

[2] Traube, *Ber.*, **18**, 1890 (1885).

[3] de Forcrand, *Ann. chim. phys.*, [8] **15**, 433 (1908).

[4] Le Chatelier, *Compt. rend.*, **115**, 654 (1892).

[5] Hildebrand, THIS JOURNAL, **34**, 246 (1912).

[6] de Forcrand, *Compt. rend.*, **130**, 778, 834 (1900).

equations we have, therefore, measured the pressure of water vapor over a mixture of BaO_2 and $BaO_2.10H_2O$. The measurements were made with a differential mercury manometer so arranged that either limb could be exhausted at will. The vapor pressure proved to be only slightly less than that of pure water. The mean results of several determinations were 15 mm. at 22°, 18.6 mm. at 25°, 28.3 mm. at 31°. Hence

$$\Delta F^\circ_{298} = 22000.$$

$H_2O_2\ (aq) = H^+ + HO_2^-$.—Hydrogen peroxide in aqueous solution is a weak acid. Joyner[1] found its ionization constant to be $K = 0.67 \times 10^{-12}$ at 0°, and $K = 2.4 \times 10^{-12}$ at 25°. Hence

$$\Delta F^\circ_{273} = 15{,}220;\ \Delta F^\circ_{298} = 15860. \qquad (63)$$

$H_2O_2\ (aq) + OH^- = HO_2^- + H_2O$.—When hydrogen peroxide combines with an alkali it is merely a matter of preference whether we regard H_2O_2 as an acid forming a salt with the alkali, or consider that the H_2O_2 forms a complex with OH^- according to the reaction $OH^- + H_2O_2 = H_3O_3^-$. This last ion differs only in hydration from HO_2^-, and the equation may equally well be written as above. The equilibrium constant of this reaction $(HO_2^-)/(OH^-)(H_2O_2)$ is obtained by dividing the above values of K by K_w obtained from (36). Hence

$$K_{273} = 720,\ K_{298} = 300.$$

$BaO_2.10H_2O = Ba^{++} + 2OH^- + H_2O_2\ (aq) + 8H_2O$.—We have attempted to determine the equilibrium corresponding to this reaction, when the hydrated barium peroxide is shaken up with water. Unfortunately the solution of the peroxide hydrate, notwithstanding the large surface exposed, is very slow, and the rate of decomposition of hydrogen peroxide in alkaline solution is appreciable. In order to obviate these difficulties as far as possible, the mixture was vigorously stirred in a bath at 0°. The analysis of the resulting solutions is given in Table IV (Experiments 8 and 9). The equilibrium was also approached from the other side. Solutions of $Ba(OH)_2$ and H_2O_2 were mixed and stirred in the absence of

TABLE IV.

	Time. Hours.	$Ba(OH)_2$. Millimols per l.	H_2O_2. Millimols per l.
1	5	2.68	5.44
2	8	2.74	5.36
3	6	2.78	2.06
4	5	107.0	<0.05
5	7	2.66	5.36
6	7	3.29	12.50
7	6	2.98	8.60
8	6	2.87	1.56
9	24	6.38	0.20

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[1] Joyner, *Z. anorg. Chem.*, 77, 103 (1912).

carbon dioxide and the resulting solutions were filtered by forcing the solution through an asbestos filter, and analyzed (Experiments 1–7), Table IV gives the results of the analyses.

At the time when these measurements were made it was not possible to interpret them, but the recent determination by Joyner of the ionization constant of H_2O_2, to which we have already referred, enables us to calculate the concentrations of the various constituents of the solution which we analyzed. We have seen in a previous section that at 0°, $(HO_2^-)/(H_2O_2)(OH^-) = 720$. Assuming that the activity of the ions in these pretty dilute solutions is proportional to the concentrations as ordinarily determined by conductance measurements, and taking the degree of ionization of $Ba(OH)_2$ and of $Ba(HO_2)_2$ as 0.86 when the barium concentration is $0.06M$, and 0.90 at $0.0027M$, and solving by a series of approximations,[1] we find the concentrations in millimols per liter of the various constituents as given in Table V.

TABLE V.

	(Ba^{++}).	(HO_2^-).	(OH^-).	(H_2O_2).	$K \times 10^{12}$.
1	2.41	2.94	1.88	2.17	18.5
2	2.47	2.96	1.97	2.07	19.8
3	2.50	1.38	3.62	0.52	17.1
5	2.40	2.90	1.89	2.14	18.4
6	2.95	4.93	0.97	7.02	19.5
7	2.68	4.01	1.35	4.15	20.3
8	2.58	1.08	4.08	0.36	15.5
9	5.50	0.15	10.80	0.02	13.0

The equilibrium constant $K = (Ba^{++})(OH^-)^2(H_2O_2)$ is given in the last column. The constancy of this product is far better than could have been anticipated. The calculation is necessarily such as to magnify greatly the experimental errors, and this is especially true in Experiments 3, 8, and 9, where the H_2O_2 was nearly all combined. Excluding these three measurements the average is $K_{273} = 19.3 \times 10^{-12}$.

From the thermochemical investigations of de Forcrand, we find for the above reaction $\Delta H = 23700$, and applying the Van't Hoff equation $K_{298} = 7.48 \times 10^{-10}$, whence

$$BaO_2.10H_2O = Ba^{++} + OH^- + H_2O_2(aq) + 8H_2O;\ \Delta F^\circ_{298} = 12450. \qquad (64)$$

$BaO + H_2O(l) = Ba^{++} + 2OH^-$.—In order to determine the free energy of formation of hydrogen peroxide from the preceding equations it remains to determine the free energy of solution of barium oxide. An inspection of the literature seems to show the availability of two different

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[1] The equations used in this calculation are $2(Ba^{++}) = (HO_2^-) + (OH^-)$, $\Sigma(H_2O_2) = (H_2O_2) + (HO_2^-)/\alpha$, where α is the degree of ionization of $Ba(OH)_2$ or $Ba(HO_2)_2$, and $(HO_2^-)/[(H_2O_2)(OH^-)] = 720$.

methods for making this calculation from existing data. First, we might combine the following equations:

$$\mathrm{BaO} + \mathrm{CO_2} = \mathrm{BaCO_3} \qquad (a)$$

$$\mathrm{BaCO_3} = \mathrm{Ba^{++}} + \mathrm{CO_3^{--}} \qquad (b)$$

$$2\mathrm{H^+} + \mathrm{CO_3^{--}} = \mathrm{H_2CO_3(aq)} \qquad (c)$$

$$\mathrm{H_2CO_3(aq)} = \mathrm{H_2O} + \mathrm{CO_2} \qquad (d)$$

$$2\mathrm{H_2O} = 2\mathrm{H^+} + 2\mathrm{OH^-} \qquad (e)$$

The free energy of reaction (*a*) at 25° has been calculated by Johnston[1] from the experiments of Finkelstein;[2] that of (*b*) may be obtained from the solubility of $BaCO_3$; (*c*) from the hydrolysis of Na_2CO_3 and $NaHCO_3$; (*d*) from the solubility of carbon dioxide; and (*e*) from results already obtained in this paper. Unfortunately we find by referring to the original paper of Finkelstein that his dissociation pressures are not obtained from a system containing the two solids, BaO and $BaCO_3$, but from one involving a liquid mixture of these two substances, and it is impossible from his data to determine the free energy of reaction (*a*).

The second method consists in the combination of the followinge quations:

$$\mathrm{Ba(OH)_2.8H_2O} = \mathrm{Ba^{++}} + 2\mathrm{OH^-} + 8\mathrm{H_2O}(l) \qquad (f)$$

$$\mathrm{Ba(OH)_2H_2O} + 7\mathrm{H_2O}(g) = \mathrm{Ba(OH)_2.8H_2O} \qquad (g)$$

$$\mathrm{Ba(OH)_2} + \mathrm{H_2O}(g) = \mathrm{Ba(OH)_2H_2O} \qquad (h)$$

$$\mathrm{BaO} + \mathrm{H_2O}(g) = \mathrm{Ba(OH)_2} \qquad (i)$$

$$9\mathrm{H_2O}(l) = 9\mathrm{H_2O}(g) \qquad (j)$$

(*f*) The solubility of barium hydroxide octahydrate in water at 0° is almost exactly $0.1M$.[3] Now, from a consideration of the freezing-point lowering of several uni-bivalent salts, we find, by the method used by Lewis,[4] that the increase in free energy from a $0.1M$ solution to one in which each ion is in hypothetical molal concentration is about 3610 cals. This then is ΔF°_{273} for the above reaction. The heat of solution according to de Forcrand is —14500, whence $\Delta F^\circ_{298} = 2610$.

(*g*) From the vapor pressures at different temperatures over a mixture of $Ba(OH)_2.8H_2O$ and $Ba(OH)_2H_2O$ measured by Lescoeur[5] we find the vapor pressure at 25° to be 9.1 mm., whence $\Delta F^\circ_{298} = -18350$.

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[1] Johnston, THIS JOURNAL, 30, 1357 (1908).

[2] Finkelstein, *Ber.*, 39, 1585 (1906).

[3] Landolt–Börnstein–Roth; Tabellen.

[4] Lewis, THIS JOURNAL, 34, 1635 (1912). The change in free energy between $0.1M$ and $0.001M$ was first determined, namely, 6960. At $0.001M$ intermediate ions were assumed to be absent and the degree of dissociation, 0.96, was taken from conductivity data. The increase in free energy between $0.001M$ and a solution hypothetical molal with respect to each ion is then equal to $-R'T \ln 0.0096 \times (0.00192)^2 = 10570$. See also Lewis and Lacey, THIS JOURNAL, 36, 804 (1914).

[5] Lescoeur, *Compt. rend.*, 103, 1260 (1887).

(*h*) Lescoeur found the vapor pressure over a mixture of $Ba(OH)_2H_2O$ and $Ba(OH)_2$ at 100° to be 45 mm. According to the work of de Forcrand the heat of this reaction is 14800, whence $p_{298} = 0.3$ mm., and $\Delta F^\circ_{298} = -4650$.

(*i*) The thermal dissociation of barium hydroxide has been investigated by Johnston,[1] who calculated from his data the free energy of the reaction at 25°. This calculation, however, was based on the assumption that the barium hydroxide was solid at the temperatures investigated. The melting point of barium hydroxide has apparently not been accurately determined, but several observers state that it melts at a dull red heat. We may assume, therefore, that the difference in free energy between liquid and solid $Ba(OH)_2$ is small at the lowest temperature investigated by Johnston, namely 647°, at which temperature the pressure obtained from his curve is 12 mm. Assuming, further, that BaO at this temperature is not sufficiently soluble in $Ba(OH)_2$ to lower materially the activity of the latter, we find for reaction (*i*) $\Delta F^\circ_{920} = -7590$. The heat of this reaction according to measurements of de Forcrand is 34700 and the change in heat capacity is very nearly zero. Hence $\Delta F^\circ_{298} = -25900$.

(*j*) The free energy of this reaction from (44) is $\Delta F^\circ_{298} = 18480$.

Adding reactions[2] (*f*)–(*j*),

$$BaO + H_2O(l) = Ba^{++} + 2OH^-; \ \Delta F^\circ_{298} = -27870 \qquad (65)$$

$H_2 + O_2 = H_2O_2$ (aq).—We are now in a position to calculate the free energy of formation of aqueous H_2O_2. Equations (61), (62), (64), (65), (53) and (44) give (all at 298° A)

$BaO + {}^1/{}_2O_2 = BaO_2$; $\Delta F^\circ = -13200$

$BaO_2 + 10H_2O(g) = BaO_2.10H_2O$; $\Delta F^\circ = -22000$

$BaO_2.10H_2O = Ba^{++} + 2OH^- + H_2O_2(aq) + 8H_2O(l)$; $\Delta F^\circ = 12450$

$Ba^{++} + 2OH^- = BaO + H_2O(l)$; $\Delta F^\circ = 27870$

$H_2 + {}^1/{}_2O_2 = H_2O(l)$; $\Delta F^\circ = -56620$

$10H_2O(l) = 10H_2O(g)$; $\Delta F^\circ = 20530$

Adding all these equations as they stand gives the final result

$$H_2 + O_2 = H_2O_2\ (aq); \ \Delta F^\circ_{298} = -30970. \qquad (66)$$

In this determination of the free energy of formation of molal aqueous H_2O_2 it is difficult to estimate the probable error. The chief source of error lies in the determination of the free energy of solution of barium oxide.

${}^1/{}_2H_2 + O_2 + \ominus = HO_2^-$.—We may now obtain the free energy of formation of the hydroperoxide ion from (63), (66) and (9).

$$\Delta F^\circ_{298} = -15110.$$

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[1] Johnston, THIS JOURNAL, 30, 1357 (1908).

[2] The corresponding value obtained by adding equations (*a*) to (*e*), on the assumption that the reaction measured by Finkelstein was that between solid BaO and solid $BaCO_3$, is $\Delta F^\circ_{298} = -26730$. The difference is in the direction to be expected as a consequence of this false assumption.

$H_2O_2(aq) = H_2O(l) + {}^1/_2O_2$.—This reaction is important because its free energy shows the tendency for aqueous hydrogen peroxide to decompose. Combining (66) and (53) gives

$$\Delta F^\circ_{298} = -25650. \qquad (67)$$

Nernst, from e. m. f. measurements, obtained the value —17100, differing from the above by 8500 cals. It is extremely improbable that our value can be in error by one-tenth of this difference. This difference makes an enormous change in the calculation of the equilibrium constant in the vapor phase studied by Nernst, namely, $[H_2O_2]^2/[H_2O]^2[O_2]$. If our calculations are correct the value of Nernst for this constant is erroneous by a factor of 10^{12} as will be shown presently.

$H_2O_2(l) = H_2O_2(g)$.—The experiments of Wolffenstein[1] and of Brühl[2] show the vapor pressure of pure H_2O_2 to be 29 mm. at 69° and 65 mm. at 85°. Hence we find the heat of vaporization per mol to be 12300 cals.,[3] whence the vapor pressure at 25° is 2.1 mm. and

$$\Delta F^\circ_{298} = 3500. \qquad (68)$$

$H_2O_2(aq) = H_2O_2(g)$.—If the law of perfect solutions were applicable to a mixture of H_2O and H_2O_2 the vapor pressure of H_2O_2 (M) would be $2.1/56.5 = 0.037$ mm. Some distillation experiments of Nernst[4] seem to indicate that the vapor pressure is, however, only about one-fourth or one-fifth of that corresponding to Raoult's law. We may take 0.01 mm. as a rough approximation, and

$$\Delta F^\circ_{298} = RT \ln (760/0.01) = 6700. \qquad (69)$$

$H_2 + O_2 = H_2O_2(l)$.—Combining (66), (68) and (69),

$$\Delta F^\circ_{298} = -27770. \qquad (70)$$

$H_2 + O_2 = H_2O_2(g)$.—Adding (66) and (69) gives

$$\Delta F^\circ_{298} = -24270. \qquad (71)$$

The value of ΔH for this reaction may be found by combining the above heat of vaporization of H_2O_2 with the thermochemical data of Thomsen and de Forcrand, which gives $\Delta H_{291} = -32600$. The heat capacity of gaseous H_2O_2 has not been determined. We will assume that it is approximately the same as that of ammonia, the only tetratomic gas which has been investigated. Thus

$$H_2O_2;\ C_p = 7.5 + 0.0042T$$
$$H_2;\ C_p = 6.5 + 0.0009T$$

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[1] Wolffenstein, *Ber.*, **27**, 3307 (1894).

[2] Brühl, *Ibid.*, **28**, 2847 (1895).

[3] From these data the boiling point of H_2O_2 is 144°, and the constant of Trouton's rule, $K = \Delta H/T$, is 29.5. This unusually high value was to be expected. Hydrogen peroxide must be a very abnormal liquid, as shown, for example, by the fact that it has the highest of all dielectric constants.

[4] Nernst, *Z. physik. Chem.*, **46**, 720 (1903).

$$O_2;\ C_p = 6.5 + 0.0010T$$
$$\Delta\Gamma = -5.5 + 0.0023T$$

and

$$\Delta F^\circ = -31100 + 5.5T \ln T - 0.00115T^2 - 8.08T \qquad (72)$$

where the value of I is obtained from the above value of ΔF°_{298}.

From this equation, it appears that hydrogen peroxide cannot be formed spontaneously in appreciable amount from oxygen and hydrogen except below 1000°.

$H_2O(g) + {}^1/_2O_2 = H_2O_2(g)$.—The general equation for the free energy of this reaction may be found by combining Equations (56) and (72).

$$\Delta F^\circ = 26310 + 4.56T \ln T - 0.0028T^2 + 0.00000037T^3 - 11.80T. \quad (73)$$

From this equation we calculate that the pressure of H_2O_2 in equilibrium with water vapor and oxygen, each at atmospheric pressure, is 1×10^{-7} atm. at 2000° A, and 3×10^{-6} atm. at 3000° A. The experiment of Traube, already referred to, in which a considerable yield of H_2O_2 is obtained by the rapid cooling of an oxyhydrogen flame cannot, therefore, be explained by assuming that H_2O_2 is largely present in the gases in the hottest portion of the oxyhydrogen flame. It must be explained rather by assuming that in the colder parts of the flame, probably between 500° and 1000° C., hydrogen and oxygen combine directly to form hydrogen peroxide.

In concluding, we wish to express our obligation to the Rumford Fund of the American Academy of Arts and Sciences for financial aid in this investigation.

Summary.

We shall not attempt to summarize further a paper which is itself a summary of numerous investigations, several of which have not hitherto been published. We have, however, collected in Table VI the values for the free energy of formation of eleven substances from the elements in their standard states. The table also shows the number of the equation connecting the free energy of formation and the temperature.

TABLE VI.

Substance.	F°_{298}.	Equation.	Substance.	F°_{298}.	Equation.
O_3	32400	5	$H_2O(g)$	—54567	56
H	30550	7	$H_2O(s)$	—56478	
H^+	0	9	$H_2O_2(aq)$	—30970	
OH^-	—37385		HO_2^-	—15110	
$H_2O(l)$	—56620	54	$H_2O_2(l)$	—27770	
			$H_2O_2(g)$	—24270	

We also append to this paper a short table of numerical constants, which we have found extremely useful in these calculations, and which may be of use to others.

TABLE VII.

		x.	Log x.
1 cc.-atms.	= x joules	0.10133	9.005737
1 cc.-atms.	= x cals.	0.02423	8.384353
1 cal. (15°)	= x joules	4.182	0.621384
Absolute zero	= — x° C.	273.09	2.436306
Molal gas volume (0° C., 1 atms.)	= x cc.	22412	4.350481
R′	= x cals. per degree	1.9885	0.298528
R	= x joules per degree	8.3160	0.919912
R″	= x cc.-atms. per degree	82.07	1.914175
F	= x coulombs per equiv.	96494	4.984500
F′	= x cals. per volt-equiv.	23074	4.363116
ln ( )	= x log ( )	2.3026	0.362216
R′ ln ( )	= x log ( )	4.5787	0.660744
(R/F) ln ( )	= x log ( )	0.00019844	6.297626
25° C.	= x° A	298.1	2.474362
ln 298.1	= x	5.6974	0.755679
298.1 ln ( )	= x log ( )	686.40	2.836578
298.1 R′ ln ( )	= x log ( )	1364.9	3.135106
298.1 ln 298.1	= x	1698.4	3.230041
298.1 (R/F) ln ( )	= x log ( )	0.05915	8.771988

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

A METHOD OF FINDING THE PARTIAL FROM THE TOTAL VAPOR PRESSURES OF BINARY MIXTURES, AND A THEORY OF FRACTIONAL DISTILLATION.

BY M. A. ROSANOFF, C. W. BACON AND JOHN F. W. SCHULZE.[1]

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Section 1. A Relationship between the Total and Partial Pressures of Binary Mixtures.

A simple method of measuring the partial vapor pressures of liquid mixtures was described in another joint communication from these laboratories.[2] The method depends upon the analysis of a series of consecutive distillates from a given mixture, and presents no manipulative difficulties. The fractions are "analyzed" by determining their refractive indices[3] or, in the case of ternary mixtures, by determining the index of refraction and one other physical property, such as the density or the boiling temperature.[4] There are important cases, however, where mixtures cannot be so simply analyzed with any degree of accuracy, and consequently the experimental determination of the partial pressures would be unreliable.

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[1] A brief preliminary account of the contents of this paper was published in the *J. Frank. Inst.*, December, 1911.

[2] Rosanoff, Bacon and White, THIS JOURNAL, **36**, 1803 (1914).

[3] v. Zawidzki, *Z. physik. Chem.*, **35**, 138 (1900); Rosanoff and Easley, THIS JOURNAL, **31**, 968 (1909).

[4] Schulze, *Ibid.*, **36**, 498 (1914).