thought that perhaps the increase in molecular conductivity in alcohol with rise in temperature, is a parabolic function, as in aqueous solutions; and that the Euler equation

$$\mu v = \mu o + \alpha t + \mu t^2$$

applies to both.

This will be tested in the later work by determining the conductivities of some of the acids at temperatures other than the three already named, and comparing the results obtained, with those calculated from this equation. The most striking feature of the conductivities of the organic acids in alcohol, as compared with the conductivities of the same acids in water, is *their very small value*. When we consider the relative powers of alcohol and water to dissociate salts, the above fact does not at present seem to admit of any very satisfactory explanation. Alcohol has from one-fourth to one-fifth the dissociating power of water, as shown by their dissociation of salts. With the organic acids the conductivities in alcohol are often several hundred times smaller than in water. It is hoped that the further work which is now in progress in this laboratory on this problem may throw some light on this relation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

# THE FREE ENERGY OF IODINE COMPOUNDS.

BY GILBERT N. LEWIS AND MERLE RANDALL.

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## Elementary Iodine.

The elementary forms of iodine which we shall consider are solid and liquid iodine, $I_2$ in aqueous solution, and the two gaseous modifications, $I_2$ and I. Solid iodine is taken as the standard state.

$I(s) = I(l)$.—The free energy of liquid iodine is obtained directly from the melting point of solid iodine, which was found by Ramsay and Young[1] to be 114°, a value which is in good agreement with those given by Regnault and by Stas. From the vapor pressure measurements of Ramsay and Young the heat of vaporization of liquid iodine has been calculated by Baxter, Hickey and Holmes[2] and shown to be 5250 cal. per g. atom. From their own measurements, which we shall presently discuss more fully, the heat of sublimation of $I(s)$ at the same temperature, 114°, is 7270 cal. Subtracting, we find in round numbers for our reaction[3] $\Delta H = 2000$ cal.

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[1] Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).

[2] Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907).

[3] Favre and Silbermann obtained the value 1500 cal., but only made one determination.

We have no safe means of estimating the heat capacity of liquid iodine. We will therefore write $\Delta\Gamma = 0$. This assumption may be quite erroneous and therefore we must not attempt to use over too wide a range of temperature, the free energy equation[1] which we thus obtain, namely,

$$I(s) = I(l);\quad \Delta F^\circ = 2000 - 5.17T, \qquad (1)$$

where the value $I = -5.17$ is found directly by writing $\Delta F^\circ = 0$ at 114° C. Hence, $\Delta F^\circ_{298} = 460$.

*$2I(s) = I_2(g)$*.—The heat capacity, per gram atom, of $I(s)$ was found by Nernst, Koref, and Lindemann[2] to be 6.6 at room temperature. The value will doubtless be higher at higher temperatures, but we have no data upon which to determine the temperature coefficient above room temperature. We shall therefore treat $C_p$ as constant. The value of $C_p$ for the gas $I_2$ we have given in another place[3] as

$$C_p(I_2) = 6.5 + 0.0040T.$$

We thus find[4] for the reaction in question

$$\Delta\Gamma = -6.7 + 0.0040T. \qquad (2)$$

The heat of sublimation was calculated by Baxter, Hickey and Holmes[5] to be about 15100 cal. at 30°, whence $\Delta H_0 = 16900$ and

$$\Delta F^\circ = 16900 + 6.7T \ln T - 0.0020T^2 - 78.73T \qquad (3)$$

where the value of $I = -78.73$ is calculated from the vapor pressure measurements of Baxter, Hickey and Holmes, who find the vapor pressure

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[1] For a discussion of the general form of the free energy equation see Lewis, THIS JOURNAL, **35**, 1 (1913).

[2] Nernst, Koref and Lindemann, *Sitz. Kgl. preuss. Akad. Wiss.*, **12**, **13**, 261–282 (1910).

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

[4] It may at first sight seem absurd to introduce into Equation 2 a term involving the change in specific heat of $I_2$ with the temperature when we have neglected a similar term, possibly greater than this, in the heat capacity of solid iodine. This is, however, by no means the case. In the handling of free energy equations it proves to be as important to use consistent values as to use true ones, and any attempt to round off in the course of a calculation data which have previously been decided upon leads to the utmost confusion. The reason for this will become obvious if we consider a simple example. Suppose that we know accurately the heat capacities of the gases $I_2$ and I, while the heat capacity of $I(s)$ is not accurately known. Since, however, $I(s)$ is taken as the standard form, the free energy equations to be considered are those corresponding to the two reactions, $2I(s) = I_2(g)$ and $I(s) = I(g)$. No matter how inaccurate the thermal data may be which are used for $I(s)$, if we use these values consistently and have kept in our equations the accurate equations for $I_2$ and I, then by subtracting the two free energy equations we will have an exact equation for the reaction $I_2 = 2I$. It is therefore of the highest importance that when values of $\Delta\Gamma$ or $\Delta H$ or the constant I are once adopted for one reaction that the data on which these values are based be used in exactly the same form in all other equations. In our first free energy calculations an immense amount of time was lost through neglect of this principle.

[5] Baxter, Hickey and Holmes, *loc. cit.*

to be 0.305 mm. at 25° and 2.154 mm. at 50°. Whence, assuming that the vapor obeys the gas law, $\Delta F^\circ_{298} = 4630$ and $\Delta F^\circ_{323} = 3770$ cal. These lead respectively to the values —78.76 and —78.71 for I. We will take $I = -78.73$ and $\Delta F^\circ_{298} = 4640$. (4)

$I_2(g) = 2I(g)$.—The heat capacity of the monatomic gas I is undoubtedly that of other monatomic gases; $C_p = 5.0$, that of $I_2$ is given in Equation 2. Hence

$$\Delta\Gamma = 3.5 - 0.0040T$$
$$\Delta H = \Delta H_0 + 3.5T - 0.0020T^2$$

The heat of the reaction can be obtained only from the equilibrium measurements of Starck and Bodenstein,[1] from which we have constructed Table I.

TABLE I.

| T. | K. | ΔF°. | ΔH. | I. |
|---|---|---|---|---|
| 1073 | 0.0114 | 9550 | | —2.04 |
| | | | 35670 | |
| 1173 | 0.0474 | 7115 | | —1.94 |
| | | | 37000 | |
| 1273 | 0.165 | 4560 | | —1.94 |
| | | | 37840 | |
| 1373 | 0.492 | 1940 | | —2.01 |
| | | | 39640 | |
| 1473 | 1.23 | —614 | | —2.02 |
| | | | Mean, 36860 | —1.99 |

The first column gives the absolute temperature, the second the equilibrium constant,[2] the third gives the corresponding free energies, the fourth gives the values of ΔH calculated from consecutive pairs of K, and the fifth the values of I, which are ultimately obtained from the several values of K. The mean value of ΔH at the average temperature of 1273° A leads to $\Delta H_0 = 35650$ cal. Hence,

$$I_2(g) = 2I(g);\ \Delta F^\circ = 35650 - 3.50T\ln T + 0.0020T^2 - 1.99T \quad (5)$$

This equation agrees at least as well with the experimental data of Bodenstein and Starck as the equation which they use. From our equation we find

$$\Delta F^\circ_{298} = 29290 \text{ cal.} \quad (6)$$

$I(s) = I(g)$.—Combining (4) and (6); (3) and (5), $\Delta F^\circ_{298} = 16965$,

$$\Delta F^\circ = 26275 + 1.60T\ln T - 40.36T. \quad (7)$$

$2I\ (s) = I_2(aq.)$.—The free energy of formation of a molal solution of iodine in water can readily be determined from solubility measure-

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[1] Starck and Bodenstein, *Z. Electrochem.*, **16**, 961 (1910).

[2] The equilibrium constant here given is, as usual, the one involving gaseous pressures (sometimes designated as $K_p$). It has been calculated from the values of $K_c$ given by Bodenstein.

ments. Jakowkin[1] found the solubility of iodine at 25° to be $0.001334M$. This value is corroborated by the work of Hartley and Campbell.[2] Bray and MacKay[3] show that some of the iodine dissolved is not present as such owing to hydrolysis, and they give the true solubility as $0.00132M$.

Assuming now that the activity of $I_2$ in solution is proportional to its concentration, the free energy of a molal solution is given by the equation

$$\Delta F^{\circ}_{298} = -R'T \ln 0.00132 = 3926 \text{ cal.} \qquad (8)$$

## Hydrogen Iodide.

$^1/_2H_2 + {}^1/_2I_2(g) = HI(g)$.—This reaction was carefully studied by Bodenstein,[4] and the work has been subjected to a careful critique by Haber in his "Thermodynamics of Technical Gas Reactions." Haber expresses Bodenstein's data by the free energy equation

$$\Delta F^{\circ} = -89.575 - 1.575T \ln T + 0.00549T^2 + R'T \ln \frac{p_{HI}}{(p_{I_2}\, p_{H_2})^{1/2}} + 2.67T.$$

From this equation $\Delta H_{298} = -96$ cal. and $\Delta F^{\circ}_{298} = -1480$ cal.

This equation, as we shall see, gives values of $\Delta F^{\circ}$, $\Delta H$, and $\Delta \Gamma$, which are by no means consistent with those obtained in other ways. Haber suggested the possibility that the dissociation of iodine into monatomic vapor might have caused some error in the calculations based upon Bodenstein's measurements. Since then, the investigation of Bodenstein and Starck has permitted us to calculate the actual dissociation of $I_2$ at the various temperatures and pressures used by Bodenstein. Thus, from Equation 5 of this paper we have calculated the fraction of $I_2$ dissociated at the four absolute temperatures given in Table II.

TABLE II.

| T. | 553. | 633. | 713. | 793. |
|---|---|---|---|---|
| Fraction $I_2$ dissociated ($p_{I_2} = 1$) | $1.50 \times 10^{-5}$ | $1.35 \times 10^{-4}$ | $0.65 \times 10^{-3}$ | $2.45 \times 10^{-3}$ |
| Fraction $I_2$ dissociated ($p_{I_2} = {}^1/_4$) | $3.01 \times 10^{-5}$ | $2.51 \times 10^{-4}$ | $1.31 \times 10^{-3}$ | $4.90 \times 10^{-3}$ |

From this table we may make the small corrections to Bodenstein's equilibrium constants at the four temperatures which we have chosen as representative. In Table III the value of ln K, which Haber gives, are shown in the second column, the values of ln K corrected for the dissociation of the iodine in the third, and in the fourth the values of $\Delta F^{\circ}$ obtained from ln K (cor.).

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[1] Jakowkin, *Z. phys. Chem.*, **18**, 590 (1895).

[2] Hartley and Campbell, *J. Chem. Soc.*, **93**, 741 (1908).

[3] Bray and MacKay, THIS JOURNAL, **32**, 914 (1910); **33**, 1485 (1911).

[4] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899), and earlier papers.

TABLE III.

| T. | ln K (Haber). | ln K (cor.). | $\Delta F^\circ$. | I. |
|---|---|---|---|---|
| 553 | 2.2229 | 2.2229 | —2440 | —2.40 |
| 633 | 2.0983 | 2.0984 | —2640 | —2.52 |
| 713 | 1.9631 | 1.9638 | —2780 | —2.51 |
| 793 | 1.8195 | 1.8219 | —2870 | —2.50 |

From these data it is theoretically possible to repeat Haber's procedure and obtain a free energy equation with four constants, representing the values of $\Delta H_0$, $\Delta\Gamma_0$, $\Delta\Gamma_1$, and I, and we thus find for $\Delta H_0$, 465.2, instead of Haber's —89.6; for $\Delta\Gamma_0$, —0.246 instead of 1.575, and for $\Delta\Gamma_1$ —0.008 instead of —0.011. Now this work of Bodenstein is perhaps the most careful investigation of a gaseous equilibrium that is to be found in the literature, and the calculation that we have just made shows how impossible it is to use any such body of data, obtained over a small temperature range, for the calculation of such quantities as $\Delta\Gamma_0$ and $\Delta\Gamma_1$, since the corrections which we made amounted to hardly more than the probable experimental error and yet have produced enormous changes in the calculated thermal quantities.

We must, therefore, proceed in this case as in others and obtain our chief knowledge of the thermal data from calorimetric measurements. We have previously obtained

$$C_p(\text{HI}) = 6.5 + 0.0010T$$
$$C_p(^1/_2\text{H}_2) = 3.25 + 0.00045T$$
$$C_p(^1/_2\text{I}_2) = 3.25 + 0.0020T$$

Hence,

$$\Delta\Gamma = 0.00 - 0.00145T \tag{9}$$

Thomsen gives 6000 and Berthelot 6300 cal. (average 6150) as the value of $\Delta H$ for the formation of HI from solid iodine at room temperature. We have already seen that the heat of sublimation of iodine at room temperature is 7550 cal. Hence for our reaction $\Delta H_{291} = -1400$ and from (9) $\Delta H_0 = -1340$ cal. Thus,

$$^1/_2\text{H}_2 + {}^1/_2\text{I}_2(g) = \text{HI}(g);\ \Delta F^\circ = -1340 + 0.000725T^2 - 2.48T \tag{10}$$

where the value of I is the average obtained from the four values of $\Delta F$ given in Table III.

Hence we find $\Delta F^\circ_{298} = -2010$ cal.

The value of $\Delta F^\circ_{298}$ thus calculated is corroborated by the work of Stegmüller,[1] who measured the electromotive force of a cell with hydrogen and iodine electrodes and hydrogen iodide solution as electrolyte. The pressures of $H_2$, $I_2$ and HI were all measured. His results are given in Table IV, where the first column shows the centigrade temperature, the second the values of $\Delta F^\circ$ obtained from the e. m. f., the third the

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[1] Stegmüller, *Z. Electrochem.*, **16**, 85 (1910).

values of $\Delta F^\circ$ calculated from Equation 10, and the fourth the values of I obtained from Stegmüller's results.

TABLE IV.

| *t*. | $\Delta F^\circ$. | $\Delta F^\circ$ calc. | I. |
|---|---|---|---|
| 31.6 | —2036 | —2028 | —2.5 |
| 55.2 | —2019 | —2073 | —2.3 |
| 81.6 | —1958 | —2130 | —2.0 |

It is evident that some error, perhaps due to the neglect of the liquid potential between the HI solution and the HI solution saturated with $I_2$, has given a false temperature trend to Stegmüller's results, but his value at the lowest temperature is in almost perfect agreement with Equation 10.

$^1/_2H_2(g) + I(s) = HI(g)$.—By combining Equations 3 and 10 we find for this reaction $\Delta F^\circ_{298} = 310$ cal. and

$$\Delta F^\circ = 7110 + 3.35T \ln T - 0.000275T^2 - 41.845T \quad (11)$$

## Iodide Ion.

$^1/_2I_2(aq.) + \ominus = I^-$.—The most accurate investigation of this electrode potential to be found in the literature is that of Maitland,[1] who obtained for the cell $I_2$(aq.),$I^-$ || N.E.; $\mathbf{E}^\circ_{298} = -0.3415$v., $\mathbf{E}^\circ$ being calculated from the measured value of **E** by the equation[2]

$$\mathbf{E} = \mathbf{E}^\circ + \frac{RT}{\mathbf{F}} \ln \frac{(I^-)}{(I_2)^{1/2}}.$$

Some unpublished measurements made by Dr. P. V. Farragher in this laboratory fully corroborate Maitland's experimental work. But the recent investigations of Lewis upon the ratio of activity to concentration show that Maitland's result is subject to a small correction. Instead of attempting to calculate the magnitude of this correction, Farragher has studied the same cell at lower concentrations and has found that with increasing dilution of $I_2$ and of $I^-$ the normal e. m. f. reaches the constant value $\mathbf{E}^\circ_{298} = -0.3407$.

We have found in the preceding paper[3] N.E. || $H^+$, $H_2$; $\mathbf{E}^\circ_{298} = -0.2776$. Hence for the cell $I_2$(aq.),$I^-$ || $H^+$,$H_2$; $\mathbf{E}^\circ_{298} = -0.6183$. This then is the normal potential of an electrode involving dissolved iodine and iodide ion. From the equation $\Delta F = -n\mathbf{E}\mathbf{F}'$, $n$ being in this case —1, we find

$$^1/_2I_2(aq.) + \ominus = I^-;\ \Delta F^\circ_{298} = -14267 \quad (12)$$

$I(s) + \ominus = I^-$. — Combining Equations 8 and 12

$$\Delta F^\circ_{298} = -12304. \quad (13)$$

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[1] Maitland, *Z. Electrochem.*, **12**, 263 (1906).

[2] The conventions employed in such electromotive force equations are stated by Lewis (THIS JOURNAL, **35**, 22 (1913)); see also footnote to the page cited.

[3] Lewis and Randall, THIS JOURNAL, **36**, 1975 (1914), Equation 18.

## Tri-Iodide Ion.

$I^- + 2I(s) = I_3^-$.—The equilibrium between iodide and tri-iodide is one in which some unusually large apparent deviations from the law of the perfect solution are evident, even at high dilutions, as shown by Bray and MacKay.[1] In the presence of solid iodine the ratio of potassium iodide to potassium tri-iodide should be constant, provided that the degree of dissociation of the two salts is the same function of the concentration. As a matter of fact, however, the ratio is not constant even in fairly dilute solutions, as shown by Table V (Bray and MacKay), in which the first row shows the total concentration of potassium salt, and the second the ratio of potassium iodide to potassium tri-iodide in solutions in which the activity of the iodine was kept constant by the presence of an excess of solid iodine. The measurements were at 25°.

Table V.

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| $\Sigma K$ | 0.100 | 0.020 | 0.010 | 0.005 | 0.002 | 0.001 | 0.0 |
| $KI/KI_3$ | 0.99 | 1.04 | 1.06 | 1.08 | 1.11 | 1.14 | 1.16 |

Bray and MacKay assume that the degree of dissociation of these two salts is the same, and that the activity of the tri-iodide ion is abnormal. Making the same assumption here and using the value at infinite dilution, we find for our reaction,

$$\Delta F^\circ_{298} = -R'T \ln (1/1.16) = 88 \text{ cal.} \qquad (14)$$

When working, however, with any appreciable concentration of $I_3^-$ we must, for the present, make use of the empirical tables of Bray and MacKay, and of Jakowkin.[2]

$3I(s) + \ominus = I_3^-$.—Combining (13) and (14) gives

$$\Delta F^\circ_{298} = -12216. \qquad (15)$$

## Hypoiodous Acid.

$I_2(aq.) + H_2O(l) = H^+ + I^- + HIO(aq.)$.—The hydrolysis of iodine leads to the reversible formation of hydriodic and hypoiodous acids, the latter of which, a very weak acid, is present in the un-ionized state. The degree of hydrolysis has been investigated by Bray[3] and by Bray and Connolly[4] through measurements of the conductivity of solutions of iodine in water. They find at 25° for the equilibrium constant,[5]

$$K = (H^+)(I^-)(HIO)/(I_2) = 3 \times 10^{-13}.$$

Hence,

$$\Delta F^\circ_{298} = -R'T \ln (3 \times 10^{-13}) = 17100 \qquad (16)$$

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[1] Bray and MacKay, This Journal, **32**, 914 (1910).

[2] Jakowkin, *Z. physik. Chem.*, **20**, 19 (1896).

[3] Bray, This Journal, **32**, 932 (1911).

[4] Bray and Connolly, *Ibid.*, **33**, 1485 (1911).

[5] Skrabal, *Z. Elektrochem.*, **17**, 665 (1911), by a more indirect method obtained a value between 3 and 4 times as great as this.

$I(s) + {}^1/_2O_2 + {}^1/_2H_2 = HIO(aq.)$.—Combining Equations 8, 13 and 16 of this paper with 8 and 53 of the preceding paper, on oxygen and hydrogen compounds, gives

$$\Delta F^\circ_{298} = -23300 \qquad (17)$$

The degree of dissociation of HIO as an acid is extraordinarily small, and has not been quantitatively determined. It is therefore impossible to calculate the free energy of the hypoiodite ion.

## Iodate Ion.

In order to determine the free energy of formation of the iodate ion we may consider the following subsidiary reactions:

$3I_2(aq.) + 3H_2O + 5AgIO_3(s) = 5AgI(s) + 6H^+ + 6IO_3^-$.—This reaction is one which was studied by Sammet,[1] who investigated the equilibrium at 25° in a system comprising a solution of $HIO_3$ and $I_2$, and solid AgI and $AgIO_3$, the concentration of the $I_2$ being determined by shaking out with carbon tetrachloride, that of $HIO_3$ by analysis. The equilibrium constant is

$$K = \frac{(H^+)^6(IO_3^-)^6}{(I_2)^3}.$$

It is in just such a reaction as this where ions enter only on one side of the reaction that we might expect a great variability of $K$ with the concentration, if the ion concentrations are calculated from the conductivities by Kohlrausch's rule. By a curious chance, however, Sammet, using old and unquestionably incorrect conductivity values, obtained degrees of dissociation identical with our calculated corrected degrees of dissociation of substances of the type of $HIO_3$. Consequently, $K$ was found to be a constant, and its average value, in the five cases in which the concentration of acid did not exceed $0.1M$, was 0.000853. Hence,

$$\Delta F^\circ_{298} = 4190 \qquad (18)$$

$AgIO_3 = Ag^+ + IO_3^-$.—We may employ the solubility product of $AgIO_3$, which, at 25°, is found to be $3.5 \times 10^{-8}$ by Noyes and Kohr;[2] $3.1 \times 10^{-8}$ by Hill and Simons;[3] and about $3.2 \times 10^{-8}$ by Kohlrausch.[4] The value of $4.5 \times 10^{-8}$ obtained by Sammet is doubtless quite erroneous. We may take as the average of the first three, $3.3 \times 10^{-8}$, whence

$$\Delta F^\circ_{298} = 10220 \qquad (19)$$

$AgI + {}^1/_2H_2 = Ag + H^+ + I^-$.—On account of the extreme discordance of the values given in the literature for the solubility of silver iodide we shall, instead of making use of the free energy of solution of

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[1] Sammet, *Z. physik. Chem.*, **53**, 641 (1905).

[2] Noyes and Kohr, *Ibid.*, **42**, 338 (1903).

[3] Hill and Simons, *Ibid.*, **67**, 602 (1909).

[4] Kohlrausch, *Ibid.*, **64**, 151 (1908).

AgI, employ the results of Danneel,[1] who studied the reversible reaction between hydrogen and silver iodide. The temperature of his measurements was variable, ranging from 13° to 17°. Fortunately the equilibrium constant of this reaction changes little with the temperature, and we may conclude from his measurements that at 25° Ag and AgI are in equilibrium with hydrogen at 1 atms. and HI at $0.05M$. Taking the corrected degree of dissociation at this concentration as 0.82, the concentration of $H^+$ and of $I^-$ is $0.041M$ and

$\Delta F^\circ_{298} = -2R'T \ln 0.041 = 3800$[2] (20)

We have found in Equations 13 and 8 the free energy of iodide ion, and of aqueous iodine; and in the preceding paper on oxygen and hydrogen compounds the free energy of water, of silver ion, and of hydrogen ion, Equations 53, 50, and 8. We may combine all these equations as follows:

$5AgIO_3 + 3I_2(aq.) + 3H_2O(l) = 5AgI + 6H^+ + 6IO_3^-; \quad \Delta F^\circ_{298} = 4190$

$5Ag^+ + 5IO_3^- = 5AgIO_3; \quad \Delta F^\circ_{298} = -51100$

$5AgI + 5/2H_2 = 5Ag + 5H^+ + 5I^-; \quad \Delta F^\circ_{298} = 19000$

$5I^- + 5\oplus = 5I(s); \quad \Delta F^\circ_{298} = 61520$

$6I(s) = 3I_2(aq.); \quad \Delta F^\circ_{298} = 11780$

$3H_2 + 3/2O_2 = 3H_2O(l); \quad \Delta F^\circ_{298} = -169860$

$11H^+ = 11/2H_2 + 11\oplus; \quad \Delta F^\circ_{298} = 0$

$5Ag + 5\oplus = 5Ag^+; \quad \Delta F^\circ_{298} = 92120$

$I(s) + 3/2O_2 + \ominus = IO_3^-; \quad \Delta F^\circ_{298} = -32350$

The eight equations are added as they stand to give the equation for the free energy of the iodate ion. We shall not, however, number this equation as there is another, presumably more accurate, method of determining this free energy which we shall consider presently. It is difficult to estimate the accuracy of the calculation which we have just made. Each of the individual measurements seems fairly reliable, but there is large opportunity for the multiplication and accumulation of errors in the whole calculation.

*$I(s) + 3H_2O(l) + 5\oplus = 6H^+ + IO_3^-$.*—A more accurate method of determining the free energy of the iodate ion is furnished by the e. m. f. measurements of Sammet, who determined the potential corresponding to the above reaction. A platinum electrode in contact with $0.001M$ $HIO_3$ and solid iodine, against the normal calomel electrode at 25° gave

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[1] Danneel, *Z. physik. Chem.*, 33, 439 (1900).

[2] By combining this value with the free energy of formation of $H^+$, of $I^-$ and of $Ag^+$ we find for the free energy of formation of AgI, $F^\circ_{298} = -16100$ and for the solubility of AgI at 25°, $7.2 \times 10^{-9}M$. This is only about 70% of the solubility obtained by Goodwin and by Thiel from e. m. f. measurements. A far more accurate value could be readily obtained by a repetition of Danneel's work at 25°.

$E = -0.665$, exclusive of liquid potentials. The potential of the normal calomel electrode we have found in the preceding paper to be $-0.2776$. The absolute potential, therefore, of the above electrode is $-0.943$. Hence we may obtain the normal potential of this electrode from the equation $-0.943 = E^\circ_{298} - (0.05915/5)\log(H^+)^6(IO_3^-)$. Assuming the degree of dissociation of $0.001M$ $HIO_3$ to be 0.97, the concentration of each ion is $0.00097M$;

$$E^\circ_{298} = -1.193;\ \Delta F^\circ_{298} = -5EF' = 137590. \qquad (21)$$

$I(s) + 3/2O_2 + \ominus = IO_3^-$ —Combining Equation 21 with the value we have used above for the free energy of formation of liquid water and of hydrogen ion, we find

$$\Delta F^\circ_{298} = -32270 \qquad (22)$$

This value is in surprisingly good agreement with the one obtained above. The latter calculation is by far the more reliable of the two and can hardly be in error by more than 200 calories.

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

## Summary.

We shall not summarize here the various subsidiary calculations used in this paper, but merely repeat the final values of the free energy of formation of the iodine compounds investigated.

TABLE VI.

| Substance. | $\Delta F^\circ_{298}$. | Equation. | Substance. | $\Delta F^\circ_{298}$. | Equation. |
|---|---|---|---|---|---|
| $I(s)$ | 0 | | $HI(g)$ | 310 | 11 |
| $I(l)$ | 460 | 1 | $I^-$ | —12304 | 13 |
| $I_2(g)$ | 4640 | 4 | $I_3^-$ | —12216 | 15 |
| $I(g)$ | 16965 | 7 | $HIO(aq.)$ | —23300 | 17 |
| $I_2(aq.)$ | 3926 | 8 | $IO_3^-$ | —32270 | 22 |

BERKELEY, CALIFORNIA.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

# A SENSITIVE CRITERION OF THE PRECISION AND OF CONSTANT ERRORS IN THE CONDUCTANCE DATA OF WEAK ELECTROLYTES, THE DETERMINATION OF THE MOLAR CONDUCTANCE OF ORGANIC ELECTROLYTES AT ZERO CONCENTRATION AND A STUDY OF THE CORRECTION FOR THE SPECIFIC CONDUCTANCE OF THE CONDUCTIVITY OF WATER.

BY C. G. DERICK.

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## I. "Calculated" $\lambda_0$ as a Criterion of Precision.

If the ideal mass law for weak electrolytes is given the form $k = (\alpha^2/1 - \alpha)$ or $k = c\lambda/\lambda_0(\lambda_0 - \lambda)$, since $\alpha = \lambda/\lambda_0$, is assumed to hold