[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND OF THE WEST VIRGINIA GEOLOGICAL SURVEY]

THE IODIDE, IODINE, TRI-IODIDE EQUILIBRIUM AND THE FREE ENERGY OF FORMATION OF SILVER IODIDE

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RECEIVED FEBRUARY 23, 1928 PUBLISHED JULY 6, 1928

Introduction

U. Fischer,[1] and Braune and Koref,[2] working in Nernst's laboratory, have made measurements of the free energy of formation (A) and heat of formation (U) of silver iodide from its elements. Nernst[3] has measured the specific heat of silver, iodine and silver iodide down to the temperature of liquid hydrogen. Fischer and Nernst regard the agreement between the measured heat of formation and the value computed indirectly from the free energy and specific heats by the aid of the Third Law of Thermodynamics as sufficiently close to furnish support for the Law.

Grinnell Jones and M. L. Hartmann[4] made measurements of the potential of cells of the type Ag, AgI, xKI, xKI + I_2 sat., Pt (similar in principle to the cell used by Fischer but differing in details) at both 25 and 0°. They were thus enabled to obtain a value for dA/dT, or the entropy of the reaction directly from their electromotive force measurements without using thermochemical measurements. They found a value for the entropy nearly twice that found by Fischer and criticize Fischer's work; they also point out that their results and Nernst's data on the specific heats of these substances are not reconcilable by the Third Law of Thermodynamics.

The essence of the Third Law of Thermodynamics is that, for a reaction between solids, the temperature coefficient of the free energy, dA/dT, or the entropy (S) of the reaction is a function solely of the specific heats of the substances involved and can be computed quantitatively if these specific heats are accurately known from absolute zero up to the working temperature. Therefore, as is pointed out by Jones and Hartmann, the sharpest test of the validity of the theory is obtained by comparing the values of dA/dT experimentally determined with that computed from the specific heats of the substances involved. Fischer's method of testing the theory, referred to above, requires not only accurate data on the specific heats and on the free energy of the reaction at one temperature but in addition requires accurate measurements of the heat of the reaction. Therefore, the unavoidable experimental errors in the calorimetric work increase the difficulty of testing the theory by this method. Electromotive force measurements are in

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[1] U. Fischer, *Z. anorg. Chem.*, **78**, 41 (1912).

[2] H. Braune and F. Koref, *Z. anorg. Chem.*, **87**, 175 (1914).

[3] W. Nernst, *Ann. Physik.*, [4] **7**, 36, 395 (1911).

[4] Jones and Hartmann, THIS JOURNAL, **37**, 752 (1915).

general more precise than calorimetric measurements and in the comparison of very similar measurements made at a slightly different temperature, the effect of systematic errors on the temperature coefficient may be largely eliminated.

This point of view is supported by the publications of G. N. Lewis, and especially by the work of R. H. Gerke,[5] which is in our opinion the most rigid test of the validity of the Third Law yet published, and which is based solely on the comparison of measurements of the temperature coefficient of the electromotive force of galvanic cells with the computations based on measurements of specific heat from absolute zero up to the usual working temperature. In the application of this method errors in the potential measurements which vary with the temperature should be guarded against with special care.

If the data of Nernst on the specific heats of silver iodine and silver iodide are correct, and if the Third Law is valid, the value of dA/dT should be 2.19 calories per degree.

H. S. Taylor[6] and Taylor and Anderson[7] have discussed this discrepancy between the data of Jones and Hartmann and of Fischer but without definitely locating the cause of the discrepancy. In the meantime G. N. Lewis and his associates have published papers too numerous to refer to in detail which furnish stronger evidence of the validity of the Third Law of Thermodynamics than the numerous papers from Nernst's laboratory. The paper of Gerke[5] referred to above is especially significant. A recent paper by Webb[8] which summarizes and extends the work done on this subject at Princeton also supports the validity of the Third Law.

The discrepancy between the results of Fischer and of Jones and Hartmann has been studied by O. Gerth,[9] a student of Nernst, who duplicated the cells of Jones and Hartmann and of Fischer and repeated the measurements of electromotive force (E_1), and in both cases obtained results which agreed within a few tenths of a millivolt with those of the original authors and also checked the divergent temperature coefficients.

The iodine electrodes prepared either by the procedure of Fischer or by that of Jones and Hartmann were measured by Gerth against each other and agreed within ± 0.02 millivolt. Significant differences were found by Gerth when the two types of silver-silver iodide electrodes were measured against each other. Fischer used pure electrolytic crystals of silver. His silver iodide had been previously fused and then allowed to crystallize on cooling and then broken up into small pieces and added to the silver

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[5] R. H. Gerke, THIS JOURNAL, **44**, 1684 (1922).

[6] H. S. Taylor, *ibid.*, **38**, 2295 (1916).

[7] H. S. Taylor and W. T. Anderson, Jr., *ibid.*, **43**, 2014 (1921).

[8] T. J. Webb, *J. Phys. Chem.*, **29**, 816 (1925).

[9] O. Gerth, *Z. Elektrochem.*, **27**, 287 (1921).

electrodes as a depolarizer. The electrolytes were $N/2$, $N/3$ or $N/10$ solutions of potassium iodide. Jones and Hartmann covered a platinum spiral with silver by electroplating from a cyanide bath. The silver was covered with a paste of pure silver oxide in water, and then heated in an electric furnace to a low red heat to convert the silver oxide completely into spongy metallic silver. The electrodes were then coated with a thin layer of silver iodide by making them an anode in a solution of potassium iodide with a very low current density. These electrodes were then allowed to stand in a fresh solution of $N/10$ or $N/20$ potassium iodide.

Gerth measured silver–silver iodide electrodes of these two types against each other in $N/10$ potassium iodide. His measurements showed that the electrodes made according to the specifications of Jones and Hartmann were positive to those prepared according to Fischer by 0.54 millivolt at 25° and in general the difference is represented by the formula $E = 0.00090 - 0.000015\ t$.

This indicates that the crystalline form of silver iodide used by Fischer is more stable than the form used by Jones and Hartmann. Gerth says "The difference in the silver electrodes found by the preceding measurements explains a part of the discrepancy mentioned at the beginning." This conclusion does not seem to us to be justified because the potential readings of Jones and Hartmann are above those of Fischer, whereas if the only difference between the two types of cell had been that Fischer used a more stable form of depolarizer he should have obtained the higher readings. Thus, if to Gerth's value for the complete cell with the J + H type of electrode, $E_1 = 0.6934 + 0.000258\ t$, there is added the difference between the two kinds of electrodes, $E = 0.0009 - 0.000015\ t$, we obtain $E_1 = 0.6943 + 0.000243\ t$, which should be the same as Gerth's directly measured value for the complete cell of the Fischer type whereas the result obtained by Gerth by actual measurement was $E_1 = 0.6921 + 0.000302\ t$. Thus by taking account of the difference between the two types of electrodes as measured by Gerth, the discrepancy between the measurements of Fischer and those of Jones and Hartmann is made worse instead of being partially accounted for.

Even more important than the discrepancy between the experimental results of Fischer and of Jones and Hartmann is the difference in the computed corrections to allow for the disturbing effect of the formation of tri-iodides in the solution.

The iodide–iodine–tri-iodide equilibrium has been much studied in the past but a detailed review of this earlier work must be omitted to save space.[10] These researches have established that when free iodine is added

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[10] (a) J. L. Gay-Lussac, *Ann. de chemie*, **91**, 72 (1814); (b) E. Baudrimont, *Compt. rend.*, **51**, 827 (1860); (c) L. Dossios and W. Weith, *Z. fur Chemie*, **5**, 380 (1869); (d) M. LeBlanc and A. A. Noyes, *Z. physik. Chem.*, **6**, 401 (1890); (e) A. A. Jakowkin,

to a solution of an iodide the principal reaction that occurs is the formation of a tri-iodide according to the reaction $I^- + I_2 \rightleftharpoons I_3^-$. The equilibrium constant of this reaction, $(I^- \times I_2)/I_3^- = k$, is a true constant if the solution is sufficiently dilute in free iodine and iodide, but if the solution is saturated with iodine, especially if the iodide is 0.1 N or stronger, there is a decrease in the constant which indicates that some higher complex is present. The iodine electrode is reproducible, constant and reversible to an unusual degree, but in the interpretation of measurements made with it proper allowance must be made for the formation of tri-iodides and the conditions should be so chosen that the formation of higher polyiodides is negligible.

As a result of the formation of the tri-iodides, there is a difference in the concentration of the iodide ion in the two halves of the cell which requires that an osmotic work correction be applied by the Nernst Equation $E_o = RT/F \ln c_2/c_1$. Fischer not only omitted the liquid junction entirely but applied the osmotic work correction in a crude manner because of a lack of accurate knowledge of the tri-iodide equilibrium at the odd temperatures of his measurements. Jones and Hartmann utilized the results of Bray and MacKay[10g] on the tri-iodide equilibrium at 25° and made a study of this equilibrium at 0° themselves[10i] for the purpose. From their measurements with 0.1 N potassium iodide solutions, they found $dA/dT = 3.7$ cal. per degree; and from their measurements with 0.05 N potassium iodide solutions they found $dA/dT = 4.5$ cal. per degree. They regard the latter as the more reliable.

Gerth made new measurements of the potential of silver–silver iodide–iodine cells similar to those of Jones and Hartmann, using $N/20$, $N/40$ and $N/60$ potassium iodide solutions (E_1) and the results show the same systematic change with concentration.

Gerth then undertook to reduce the disturbing effect of tri-iodides by working with solutions unsaturated with respect to iodine but having a known vapor pressure of iodine. The osmotic work correction and the liquid junction correction are thus substantially reduced and replaced by a correction which can be computed by the Nernst equation $E_p = RT/2F \ln p_2/p_1$, from the vapor pressure of iodine from the solution actually

ibid., **13**, 539 (1894); **18**, 585 (1895); **20**, 19 (1896); (f) A. A. Noyes and J. Seidensticker, *ibid.*, **27**, 357 (1898); (g) W. C. Bray and G. M. J. MacKay, THIS JOURNAL, **32**, 914 (1910); (h) W. C. Bray, *ibid.*, **32**, 932 (1910); W. C. Bray and E. L. Connolly, *ibid.*, **33**, 1485 (1911); (i) Grinnell Jones and M. L. Hartmann, *ibid.*, **37**, 241 (1915); (j) R. Abegg and A. Hamburger, *Z. anorg. Chem.*, **50**, 426 (1906); (k) C. L. Parsons and C. F. Whittemore, THIS JOURNAL, **33**, 1934 (1911); (l) G. A. Linhart, THIS JOURNAL, **40**, 162 (1918); (m) G. S. Johnson, *J. Chem. Soc.*, **1877**, p. 249; (n) H. L. Wells and H. L. Wheeler, *Z. anorg. Chem.*, **1**, 448 (1892); (o) H. W. Foote and W. C. Chalker, *Am. Chem. J.*, **39**, 561 (1908); (p) C. L. Parsons and H. P. Corliss, THIS JOURNAL, **32**, 1367 (1910); (q) E. W. Washburn and E. K. Strachan, *ibid.*, **35**, 691 (1913); (r) P. P. Fedotieff, *Z. anorg. Chem.*, **69**, 32 (1911).

used (p_1) and the vapor pressure of solid iodine at the temperature of the cell (p_2). This is fundamentally a good idea because as a general rule the activity of un-ionized molecules such as I_2 is very nearly proportional to the vapor pressure and only slightly if at all influenced by the concentration of the ions present, whereas the activity coefficient of the ions is appreciably different from the degree of dissociation as estimated from the conductivity even in solutions as dilute as 0.05 N and widely discrepant in solutions as concentrated as 0.5 N. But if the unsaturated iodine solution can be made sufficiently dilute to reduce the osmotic work correction and the liquid junction to a small figure of the order of one or two millivolts the error in this correction is probably negligible.

To prepare potassium iodide solutions with a small known iodine vapor pressure, Gerth passed nitrogen through a U-tube containing iodine maintained at 0°, thus saturating the nitrogen with iodine vapor at the vapor pressure of solid iodine at 0°. This nitrogen was then bubbled through a potassium iodide solution of known concentration at some higher temperature, until equilibrium had been established. The voltage of a platinum electrode in this solution against a platinum electrode in a solution of the same strength in potassium iodide but saturated with solid iodine was then measured (E_2). The measured potential includes the potential due to difference in iodide ion concentration (osmotic work) and to the liquid junction between the saturated and unsaturated solution as well as the potential due to the difference in the activities of the free iodine in the two solutions. If the vapor pressures are accurately known the latter potential can be computed with precision. This permits the sum of the osmotic work correction and the liquid junction correction to be determined experimentally with a precision greater than they can be computed from the theoretical formulas as was done by Fischer and by Jones and Hartmann. This method does not entirely eliminate the necessity of applying a computed correction for the osmotic work and liquid junction due to the formation of tri-iodides because there still remains a difference in the iodide ion concentration in the pure potassium iodide solution containing no iodine which surrounds the silver iodide electrode and in the solution which is unsaturated with iodine, used by Gerth in his measurements. This potential (E_4) must be computed by the methods criticized above. Gerth attempted to make the unsaturated iodine solution sufficiently dilute so that the error in this correction would be negligible.

Although the basic idea of Gerth's method is good, he lacked the data necessary for its successful execution. This method requires an accurate knowledge of the vapor pressure of iodine at each of the temperatures used in the experiments. Gerth did not determine the vapor of iodine at each of his working temperatures and does not even state directly the values which he used, but he refers to Abegg's "Handbuch," Vol. 4, part 2, p. 350 (1913), where a table of vapor pressures of iodine at various temperatures is given. These data by many different experimenters are obviously inconsistent and lacking in the precision needed for the purpose, as may be readily seen by plotting them on the same sheet with the data given in the "International Critical Tables," Vol. III, p. 201, which are based chiefly on the work of Baxter and Grose. The vapor pressure at 0° is especially important for Gerth's calculations but is so low (0.03 mm. of mercury) that it is difficult to determine with precision and is recorded to only one significant figure. It would seem to be over sanguine to claim that the figures used by Gerth are reliable within 10% and yet an error of 10% makes an error in the computed potential of 1.2 millivolts, whereas Gerth computes the corrections to tenths of millivolts.

Gerth still omits the liquid junction correction (E_j) on the assumption that the potential between the pure potassium iodide around the silver iodide electrode and the unsaturated iodine solution around the platinum electrode is negligible, but this is by no means true as may be seen by inspection of Tables I–V below. Moreover, since these solutions at 11.5° are approximately one-third saturated, and at 25° are only one-tenth saturated, the error due to this omission will have a marked temperature coefficient.

The essential idea of Gerth's new method is to replace the osmotic work correction, E_o, and liquid junction, E_j, which are computed by the Nernst and Planck equations, respectively, involving the concentration of the ions, by a direct measurement, E_2, and a computed correction, E_p, based on the vapor pressure of iodine. This change is partial only and the fraction of the total correction obtained by the old and by the new methods is different at different temperatures. A reference to Table 6 of Gerth's paper will show that at 25° the total correction is -0.0152 volt, of which -0.0133 is obtained by the new method and -0.0019 (or 12% of the total) is computed by the old method. At 11.5° the total correction is -0.0126, of which -0.0056 or 44% is obtained by the old method.

It is apparent that Gerth's new method would fail utterly at 0°, as at this temperature E_2 and E_p would become zero and the total correction would be E_o as computed by the old method (plus the liquid junction correction which Gerth omits). This in effect amounts to applying the correction by the new method at 25° and by the old method at 0° and if the two methods are different in effect, as Gerth contends, this procedure must introduce an error in dE/dT and in dA/dT or the entropy; but as was pointed out above it is especially important to avoid errors in dA/dT in attempts to test the validity of the Third Law of Thermodynamics.

More recently Gerke[11] has made measurements on three different cells

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[11] R. H. Gerke, This Journal, **44**, 1703 (1922).

which can be combined so that the following results may be obtained indirectly for the reaction Ag + $^1/_2$ I_2 = AgI, at 25°; electromotive force, 0.6858 volt; free energy, 15,825 calories; heat of formation, 14,814 calories; entropy, 3.4 calories per degree. Gerke, unlike any of the investigators referred to above, used precipitated silver iodide. Webb[8] has measured the heat of formation of silver iodide calorimetrically and obtained 14,975 calories. He combines this with the value of 15,767 calories for the free energy (based on the average of the data of Gerke, Gerth, Braune and Koref, Taylor, and Jones and Hartmann) and hence computes the entropy to be 2.6 calories per degree.

Experimental Part

Gerth's fundamental idea of using solutions unsaturated in iodine, thereby replacing the osmotic work correction and the liquid junction correction by another correction dependent on the vapor pressure (or activity) of the iodine, seemed to be a good one if it could be done in a way free from the objections pointed out above in Gerth's procedure. In particular we regard it as essential to use a method equally applicable at 0° and at 25°. We, therefore, undertook a new investigation of the iodine–iodide–tri-iodide equilibrium with special attention to dilute solutions (down to 0.01 *N* potassium iodide and from 2 to 33% of the amount of iodine necessary to saturate the solution with iodine). The results have been used in a redetermination of the normal potential of the iodine electrode.

Titration gives the sum of the free iodine and of the tri-iodide but does not distinguish between them. Earlier studies of this equilibrium discussed above have been based on the determination of the free iodine either by (1) distribution experiments with a non-miscible solvent such as carbon bisulfide or carbon tetrachloride, interpreted with the aid of data on the distribution of iodine between the solvent and pure water, or (2) analyses of potassium iodide solution saturated with solid iodine interpreted on the assumption that the concentration of the free iodine in the solution containing potassium iodide is the same as the solubility of iodine in water (corrected for hydrolysis).

Since we were interested in studying solutions containing very little free iodine, the second method was inapplicable. The first method was objectionable because the other solvent used is not entirely soluble in the water and thus changes the nature of the medium, and because the distribution ratio is extremely unfavorable. The distribution ratio of iodine between carbon tetrachloride and water is high and varies with the concentration (85–87.9) so that the merest trace of emulsified carbon tetrachloride in the water layer makes serious errors in the analysis. With carbon bisulfide this ratio is even more unfavorable and variable (585–652).[12]

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[12] Jakowkin, *Z. physik. Chem.*, **18**, 586, 588 (1895).

These difficulties were overcome by the invention of a device which we call an equilibrator, which has been described in a separate article because of its suitability for the investigation of many similar problems.[13]

A potassium iodide solution of the desired concentration was prepared by weight, its density and conductivity were determined and one tube of the equilibrator (A) was filled with the solution. Sufficient dry iodine was then added to give approximately the concentration desired. A mixture of water and a saturated solution of iodine in water in the proper proportion to give approximately the desired concentration was placed in the other tube (B) of the equilibrator, and one drop of dilute sulfuric acid was added to prevent hydrolysis. Portions of the potassium iodide solution containing iodine were then blown from tube (A) into a pycnometer to determine its density, into a conductivity cell, into the electromotive force cell and into a weight buret. In a similar fashion the liquid from the water side of the apparatus (tube B) was blown into a pycnometer and weight buret.

The titrations for iodine were made by the Washburn method[14] using arsenite solutions and phosphate buffers with a starch indicator. The end-point is sensitive to 0.01 mg. of iodine. Its principal drawback is that the arsenite solution, if exposed to air, slowly changes its factor by oxidation. We, therefore, found it necessary to maintain an oxygen free atmosphere in the stock bottle. Compressed nitrogen from a steel tank passed through a suitable purifying train to remove all oxygen, then through a wash bottle containing some of the standard arsenite solution to bring it to the proper aqueous vapor pressure and then was delivered to the top of the stock bottle containing the reserve stock of standard arsenite solution.

The titration of the potassium iodide solution from tube (A) gives the sum of the free iodine (I_2) and the tri-iodide ($\Sigma I_3 = I_3^- + KI_3$). The titration of the water from the other tube gives the free iodine (I_2) which at equilibrium is the same in the two tubes. Hence the tri-iodide may be obtained by a simple subtraction, and the iodide remaining may be readily obtained by subtracting the tri-iodide from the original concentration of the solution. The equilibrium constant of the reaction $K^+ + I^- + I_2 \rightleftharpoons K^+ + I_3^-$ may then be readily calculated. This calculation assumes that the activity of the uncharged molecule I_2 is the same as its concentration in the dilute water solution in the other tube of the equilibrator with which it is in equilibrium, and that the activity coefficients of the iodide ion and the tri-iodide ion in the same solution are identical, so that the ratio of the activity of these ions in the common solution is the same as the ratio of their concentrations.

The electromotive force measurements were made in cells of the ground stopper type introduced by Laurie[15] and similar to those used by Jones and Hartmann except that the upper joints were glass stoppers. This type of cell has several important advantages over the other types in common use.

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[13] Jones and Kaplan, THIS JOURNAL, **50**, 1600 (1928).

[14] E. W. Washburn, *ibid.*, **30**, 31 (1908); Washburn and Bates, *ibid.*, **34**, 1341 (1912).

[15] A. P. Laurie, *Proc. Roy. Soc. Edinburgh*, **28**, 383 (1908); *Z. physik. Chem.*, **67**, 627 (1909).

(1) It requires only a small amount of the solution used and makes good thermal contact with the constant temperature bath.

(2) It gives readings which are constant for long periods and easily reproducible.

(3) The liquid junction formed by diffusion in the ground joint realizes experimentally the theoretical conditions assumed by Planck in the derivation of the formula for the liquid junction potential and therefore this formula may be used with greater confidence for the computation of the diffusion potential than is possible with other types of liquid junctions which are not so well defined. This type of cell has the disadvantage of a high internal resistance, which greatly diminishes the sensitiveness of the galvanometer, especially if dilute solutions are used. This drawback is probably mainly responsible for the fact that this type has been comparatively little used in the past.

We have invented an improvement in the potentiometer which overcomes this difficulty entirely and makes the sensitiveness of the voltage measurement practically independent of the internal resistance. This improvement consists in adding a large electrostatic condenser in parallel with the galvanometer and its tapping key. Then with the tapping key open, the condenser will be charged to a potential equal to the difference between the potential of the cell and the setting of the potentiometer. A high resistance in the cell cannot prevent this charging of the condenser but can only delay it slightly. If the cell has a resistance of the order of one million ohms it is well to wait about one minute for the condenser to become charged. Then on closing the tapping key the condenser will discharge through the galvanometer but not through the cell and therefore a deflection of the galvanometer will not be influenced by the high resistance of the cell, but will show any slight error in the adjustment of the potentiometer in spite of the high resistance of the cell.

Of course this procedure requires a sensitive ballistic galvanometer in place of the dead-beat instrument commonly used. To bring the instrument quickly and conveniently to its zero reading it is advisable to shunt the galvanometer by a resistance equal to the critical damping resistance of the galvanometer and another tapping key.

The condenser actually used was made by soldering together in parallel enough Western Electric paraffined paper condensers to give a capacity of 44 microfarads (these cost approximately fifty cents per microfarad) mounted in a suitable wooden box carrying a double pole, single throw switch by which the condenser may be disconnected or connected as desired. It is well to have this switch open until an approximate balance (within a few millivolts) has been secured because if a high charge is impressed on the condenser it does not discharge itself completely on a single contact of the discharge key, since with paper condensers the charge is partly "absorbed" in the dielectric and can only be completely removed by tapping the key several times at intervals of a few seconds. Then the switch is closed and the key tapped several times to remove the absorbed charge. The galvanometer is brought to rest at its zero by the key in the critical damping circuit. After waiting a short time for the condenser to become charged (in extreme cases up to one minute) the key is tapped and the deflection of the galvanometer, if any, noted. Then the potentiometer is adjusted until the galvanometer reads zero when the key is tapped.

The effectiveness of the condenser is shown by a typical example. These measurements were made on a cell Ag, AgI, 0.01 *N* KI, 0.01 *N* KI + I_2, Pt at 0° in which the liquid junction was made inside of a well ground stopper which was pushed in tightly. The internal resistance of the cell was measured and found to be approximately 1,600,000 ohms, an exceptionally high value.

When the condenser was not used it was necessary to change the setting of the potentiometer by 3 millivolts in order to cause a deflection of 1 mm. on the scale and it was concluded that the potential of the cell was 0.646 volts with an uncertainty of 1 millivolt.

The condenser of 44 microfarads was then connected. It was found that a change in the setting of the potentiometer of 0.1 millivolt made a difference in the galvanometer reading of 3 mm. on its scale—a ninety-fold increase in sensitiveness. At balance the potentiometer reading was 0.64555, volt which was probably correct within 0.02 millivolt. With the condenser the sensitiveness of the potential measurement was found to be nearly independent of the internal resistance. With our potentiometer and galvanometer, which were high-resistance instruments, the condenser is not needed to measure the potential of cells having an internal resistance of 10,000 ohms or less. This modification of the potentiometer overcomes the principal difficulty in the use of cells of the Laurie type for measurement of electromotive force.

The results of the experiments with the equilibrator and the electromotive force measurements are recorded in Tables I–VI, in which the abbreviations have the following significance: ΣK is the concentration of the potassium iodide solutions used; *M* is the sum of the concentration of the free iodine (I_2) plus the iodine equivalent of the polyiodides present in the potassium iodide solution which is unsaturated with respect to iodine, as determined by titration of the liquid from one tube of the equilibrator; I_2 is the concentration of free iodine in each tube of the equilibrator as found by titration of the tube containing water (plus a trace of sulfuric acid to prevent the reaction $I_2 + H_2O = H^+ + I^- + HIO$). In the later calculations polyiodides higher than I_3, if present, are neglected; $\Sigma I_3 = M - I_2$, $\Sigma I = \Sigma K - \Sigma I_3$, $k = (\Sigma I \times I_2)/\Sigma I_3$, the equilibrium constant of the reaction $KI + I_2 \rightleftharpoons KI_3$.

If it be assumed that the activity coefficient of the iodide ion and of the tri-iodide ion in the common solution is the same, then $k = (I^- \times I_2)/I_3^-$, where the symbols represent the activities of the respective molecular species. This assumption finds support in the following considerations. (1) There seems to be much evidence that activity coefficients are functions primarily of the valence of the ion and of the total ion concentration[16] and there is no change in valence and in total ion concentration due to the reaction $I^- + I_2 = I_3^-$. (2) There is no change in freezing point when iodine is added to a solution of potassium iodide. (3) The degrees of dissociation as computed from the conductivity of KI and of KI_3 are very nearly the same (probably equal within the experimental error as has been shown by Jones and Hartmann, see THIS JOURNAL, **37**, 250–251 (1915)).

The percentage of saturation is obtained by dividing the free iodine (I_2) by 0.00132 at 25° and by 0.000635 at 0°.[17]

E_1 (J. and H.) is the measured potential of the cell of the type, Ag, AgI, 0.1 *N* KI, 0.1 *N* KI + I_2 sat., Pt taken from the paper of Jones and Hartmann. E_2 is the result of our new measurement of the potential of cells of the type, Pt, 0.1 *N* KI + I_2 sat., 0.1 *N* KI + I_2 unsat., Pt, in which the solution unsaturated with respect to iodine was taken from the equilibrator and is a portion of the same solution whose analysis is recorded in the upper part of the table, and the solution saturated with iodine was made from the same original potassium iodide solution. By adding these two potentials, the osmotic work correction and the liquid junction correction applied by Jones and Hartmann is largely although not entirely eliminated, but a new correction (E_c) must be applied owing to the fact that the iodine around the electrode is unsaturated. This correction is computed by the Nernst formula, $E_c = RT/2F \ln I_2 \text{ (sat.)}/I_2 \text{ (unsat.)}$.

This computation assumes that the activity of the iodine is proportional to its concentration in its water solution. These solutions are dilute (0.00132 at a maximum) and contain no ions, and therefore the errors involved in this calculation are believed to be less than in the best estimate that can be made in regard to the activities of iodide ions in solutions of potassium iodide up to one-tenth normal.

E_o is the remaining osmotic work correction referred to above, which must be applied because the concentration of the iodide ion in the pure

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[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1st ed., **1921**, p. 374; E. Hückel, *Ergebnisse der exakten Naturwissenschaften*, **3**, 243 (1924).

[17] Jones and Hartmann found the solubility of iodine in water to be 0.0006383 mole of I_2 per liter at 0°. From the conductivity of the solution they determined that the hydrolysis of iodine, $I_2 + H_2O = H^+ + I^- + HIO$, is responsible for the solution of 3.2×10^{-6} mole of iodine. Therefore the solubility of iodine as such (I_2) is 0.0006383 − 0.0000032 or 0.000635. The figure 0.000638 given by Jones and Hartmann is incorrect owing to an arithmetical error made by them in this calculation.

potassium iodide solution used around the silver iodide electrode is not the same as the concentration of the iodide ion in the unsaturated iodine electrode. It is computed by the formula $E_o = (RT/F) \ln (C_2f_2/C_1f_1) = RT/F \ln \Sigma K/\Sigma I$, where C_2 ($= \Sigma$K) is the concentration of the iodide in the original potassium iodide solution and C_1 represents the concentration of the iodide in the solution containing some free iodine (ΣI). It is assumed that the conversion of a part of the iodide into tri-iodide does not change the activity coefficient ($f_2 = f_1$).

E_j is the correction for liquid junction potential because the liquid junction potentials in the two cells measured although nearly equal are not exactly so (Gerth makes an error in assuming them to be equal). The correction which must be applied is the potential between a pure potassium iodide solution and the same solution after a part of the iodide has been converted into the slower moving tri-iodide ion. It is computed by the

TABLE I

EXPERIMENTAL DATA, N/10 KI

	At 25°		At 0°			
Expt. no.	25	26	20	21	22	23
ΣK, g. mol./l.	0.10000	0.10000	0.10017	0.10017	0.10017	0.10017
M, g. mol./l.	.008246	.0048655	.003673	.003562	.006964	.01139
I_2, g. mol./l.	.00012413	.000070864	.000027008	.00002624	.00005241	.00009328
ΣI_3, g. mol./l.	.0081219	.0047946	.0036460	.0035358	.0069116	.011297
ΣI, g. mol./l.	.091878	.095205	.096524	.096634	.093258	.088873
$k = (\Sigma I \times I_2)/\Sigma I_3$	.001403	.001407	.000715	.000717	.000707	.000734
% sat. with I_2	9.4	5.4	4.2	4.1	8.3	14.7
E_1 (J. and H.), volts	+.7000	+.7000	+.69360	+.69360	+.69360	+.69360
E_2, volts	−.0424	−.0503	−.04780	−.04833	−.03905	−.03170
E_c, volts	+.03037	+.03757	+.03716	+.03750	+.02936	+.02258
E_o, volts	−.00218	−.00126	−.00087	−.00085	−.00168	−.00282
E_j, volts	+.00050	+.00029	+.00021	+.00021	+.00040	+.00066
E, volts	.68629	.68630	.68230	+.68213	.68263	+.68231
k, average =	0.001405			.000718		
E, average =	0.6863			.6823		
A, calories =	15,835			15,744		

$dE/dT = 0.000160$. $dA/dT = 3.64$ calories per degree.

TABLE IIA

EXPERIMENTAL DATA, N/20 KI at 25°

Expt. no.	1	2	3	6	10	13
ΣK, g. mol./l.	0.05019	0.04994	0.04994	0.04977	0.04998	0.05000
M, g. mol./l.	.012687	.012496	.012078	.002670	.0011534	.001364
I_2, g. mol./l.	.000452	.000441	.000419	.00007647	.000031518	.000031105
ΣI_3, g. mol./l.	.012235	.012055	.011659	.0025935	.0011219	.0011053
ΣI, g. mol./l.	.037955	.037885	.038281	.047176	.048858	.048895
$k = (\Sigma I \times I_2)/\Sigma I_3$	.001403	.001387	.001375	.001391	.001372	.001376
% sat. with I_2	34.2	33.4	31.7	5.8	2.4	2.35
E_1, volts		+ .69920		+ .69920	+ .69920	+ .69920
E_2, volts		− .02250		− .0495	− .06160	− .06180
E_c, volts		+ .01407		+ .03659	+ .04798	+ .04814
E_o, volts		− .00710		− .00137	− .00058	− .00057
E_j, volts		+ .00150		+ .00031	+ .00014	+ .00014
E, volts		+ .68517		.68523	.68514	.68511

k, average = 0.001386. E, average = 0.68516. A, calories = 15,809.

TABLE IIB

EXPERIMENTAL DATA, $N/20$ KI at 0°

Expt. no.	16	17	18
ΣK, g. mol./l.	.05000	0.05000	0.05000
M, g. mol./l.	.001824	.001984	.002004
I_2, g. mol./l.	.00002712	.000030255	.00002935
ΣI_3, g. mol./l.	.0017969	.0019537	.00197465
ΣI, g. mol./l.	.048203	.048046	.048025
$k = (\Sigma I \times I_2)/\Sigma I_3$	.0007275	.000744	.000714
% sat. with I_2	4.3	4.8	4.6
E_1, volts	+ .6920	+ .6920	+ .6920
E_2, volts	− .04890	− .04740	− .04750
E_c, volts	+ .03711	+ .03582	+ .03618
E_o, volts	− .00086	− .00094	− .00095
E_j, volts	+ .00021	+ .00023	+ .00023
E, volts	.67956	+ .67971	.67996

k, average = 0.000729. E, average = 0.67974. A, calories = 15,684.
dE/dT = 0.000217. dA/dT = 5.0.

TABLE III

EXPERIMENTAL DATA, $N/50$ KI

	At 25°		At 0°
Expt. no.	28	29	39
ΣK, g. mol./l.	0.02000	0.02000	0.02000
M, g. mol./l.	.0023668	.001194	.0016505
I_2, g. mol./l.	.0001745	.00008353	.000062015
ΣI_3, g. mol./l.	.0021923	.0011105	.0015885
ΣI, g. mol./l.	.017808	.0188895	.0184115
$k = (\Sigma I \times I_2)/\Sigma I_3$	.001417	.001421	.000719
% sat. with I_2	13.2	6.3	9.8
E_u, volts	+ .66110	+ .65040	.6537
E_c, volts	+ .02599	+ .03546	+ .02738
E_o, volts	− .00298	− .00147	− .00194
E_j, volts	+ .00067	+ .00034	+ .00047
E, volts	.68478	.68473	.67961
k, average, 0.00142			.000719
E, average = 0.6847_5			6796
A, calories = 15,800			15681

dE/dT = 0.000206. dA/dT = 4.74 cal. per degree.

formula $E_j = RT/F \ln \Sigma C_A \Lambda_A / \Sigma C_B \Lambda_B$ where $\Sigma C_A \Lambda_A$ is the sum of the product of the concentration and the mobility of each of the ions in the pure potassium iodide solution and $\Sigma C_B \Lambda_B$ is the corresponding value for the solution containing free iodine. The addition of all of these potentials gives the effective electromotive force, E, of the cell Ag, AgI, I_2.

The results obtained with the tenth normal solution were still different from the results obtained with the twentieth normal solution. Therefore it seemed desirable to work with still more dilute solutions. Jones and Hartmann had made an attempt to do this but had abandoned it owing to the

TABLE IV

EXPERIMENTAL DATA, $N/100$ KI

	At 25°		At 0°	
Expt. no.	33	34	35	36
ΣK, g. mol./l.	0.010274	0.010274	0.010300	0.010300
M, g. mol./l.	.00065807	.0006422	.0005672	.0007245
I_2, g. mol./l.	.00008283	.00008168	.00003832	.00005006
ΣI_3, g. mol./l.	.00057524	.00056058	.00052888	.00067444
ΣI, g. mol./l.	.0096988	.0097134	.0097711	.0096256
$k = (\Sigma I \times I_2)/\Sigma I_3$	.001397	.001415	.000708	.000714
% sat. with I_2	6.3	6.2	6.0	7.9
E_u, volts	+ .65010	+ .65010	+ .64740	+ .65060
E_c, volts	+ .03556	+ .03574	+ .03304	+ .02990
E_w, volts	− .00148	− .00144	− .00124	− .00159
E_l, volts	+ .00034	+ .00033	+ .00030	+ .00036
E, volts	$.6845_2$	$.6847_3$	+ $.6795_0$	$.6792_7$
k, average	0.00141		.000711	
E, average	= 0.6846_2		0.67939	
A, calories	= 15,797		15,676	

$dE/dT = 0.000209$. $dA/dT = 4.83$ cal. per degree.

fact that their cells containing dilute solutions had such a high resistance that their galvanometer was not sufficiently sensitive. This difficulty we have overcome by the invention of an improvement to the potentiometer system described above. In this work with more dilute solutions the iodine solutions containing dilute solutions from the equilibrator were measured directly against the silver–silver iodide electrode prepared by the method of Jones and Hartmann without using saturated iodine electrodes. The electromotive force, E_u, thus obtained is equivalent to $E_1 - E_2$ shown in the table above.

These experiments using unsaturated iodine solutions show a reduction in the osmotic work correction and liquid junction correction as compared with all previous work in this field. With saturated solutions the osmotic work correction is about 18 millivolts at 25° and 15 millivolts at 0°, whereas in some of the above experiments the osmotic work correction was reduced to 0.6 millivolt while the average of all at 25° was 2.04 millivolts and at 0°, 1.3 millivolts. These averages include some experiments in which the solutions were purposely made stronger in iodine than is necessary in order to detect a possible trend, but there is no evidence of such a trend. In Gerth's experiments the osmotic work correction was of about the same magnitude at 25° and from 5.1 to 5.6 millivolts at 11.5°. Gerth does not give data as to tri-iodide formation, so that it is impossible to check his calculations. The liquid junction potential has been reduced from about 3.0 millivolts with saturated solutions to less than one-tenth of this value in our unsaturated solutions but it is not negligible as is assumed by Gerth. A comparison of the results for the equilibrium constant, k, the electromotive force, E, and free energy, A, and its temperature coefficient, dA/dT, indicates that there is no systematic variation with the concentration in the range 0.05 to 0.01 N, but the data obtained with 0.1 N appear significantly different, thus indicating that higher polyiodides are present in sufficient amount to invalidate the results with the more concentrated solutions. In order to test this hypothesis and check still further the work of Fischer it was decided to work with $N/3$ KI also.

Cells of the type Ag, AgI, $N/3$ KI, $N/3$ KI + I_2 sat., Pt were prepared and the potential measured at 25 and 0°. Some of the $N/3$ solution was also used in the equilibrator with less iodine than required for saturation and the distribution constant determined at 25°. Unfortunately, the electromotive force measurements on these dilute solutions were lost owing to an accident and there was no time available to repeat them. The results are shown in Table V.

TABLE V

EXPERIMENTAL DATA, $N/3$ KI

	At 25°		At 0°
Expt. no.	30	31	40
ΣK, g. mol./l.	0.32975	0.33333	0.32386
M, g. mol./l.	.18016	.0034913	.16253
I_2, g. mol./l.	.00132	.00001471	.000635
ΣI_3, g. mol./l.	.17884	.0034766	.161895
ΣI, g. mol./l.	.15091	.32985	.161965
$k = (\Sigma I \times I_2)/\Sigma I_3$	.001113	.001396	.000635
% sat. with I_2	100	1.11	100
E_1, volts	+.70150		.6960
E_a, volts	−.02036		−.01656
E_j, volts	+.00349		+.00309
E, volts	.68463		.68253
A, calories = 15,797			15,748 calories

$dE/dT = 0.000084$. $dA/dT = 1.94$ calories per degree.

The data on the equilibrium constant of the reaction $KI + I_2 \rightleftharpoons KI_3$ are summarized in Table VI. The figures are computed on the assumption that higher polyiodides are absent and that the activities of the iodine

TABLE VI

SUMMARY OF EQUILIBRIUM CONSTANTS OF THE IODIDE–IODINE–TRI-IODIDE REACTION

	At 25°		At 0°	
Concn. of KI	Solns. satd. with I_2	Solns. unsatd. with I_2	Solns. satd. with I_2	Solns. unsatd. with I_2
$N/3$	0.00111	0.00140	0.000635	.....
0.1 N	.00131	.00141	.000693	.000718
.05 N	.00137	.00139	.000707	.000729
.02 N	.00137	.00142	.000712	.000719
.01 N	.00139	.00141	.000710	.000711
.005 N	.00142	....	.000711	.....
.002 N	.00147	....	.000706	.....
.001 N	.00150	....	.000694	.....

and tri-iodide ions in their common solution are identical. The data for the saturated solutions (except $N/3$ KI, which are from Table V) are taken from Bray and MacKay at 25° and Jones and Hartmann at 0°, recomputed on the above basis.

The solutions unsaturated with iodine show no evidence of a systematic trend in spite of a variation in iodine content from 2 to 34% of saturation and in KI concentration from 0.01 N to $N/3$; in view of the low concentration of free iodine in some of the solutions the concordance is satisfactory. It is more difficult to secure concordant results at 0° than at 25°, owing to the smaller vapor pressure of iodine, the weaker solutions used and the greater difficulty of maintaining temperature constancy over the longer periods required for the experiments. The equilibrium constant may be taken as 0.00140 at 25° and 0.00072 at 0°, but the solutions which are saturated with iodine show clearly a systematic decrease of the constant with increasing concentration which is clearly evident with the $N/3$ solution. The variation is greater at 25° than it is at 0°. These data emphasize the importance of working with dilute solutions of potassium iodide unsaturated with iodine when using iodine electrodes. The fact that there appears to be a greater tendency to form the more complex polyiodides at 25° than at 0° shows that when working with strong solutions saturated with iodine as Fischer did the error will have a temperature coefficient. The experimentally determined values for E, $\mathrm{d}E/\mathrm{d}T$, A, $\mathrm{d}A/\mathrm{d}T$ and U for the reaction $\mathrm{Ag} + {}^1/_2\ \mathrm{I}_2 = \mathrm{AgI}$ are summarized in Table VII.

TABLE VII

SUMMARY OF DATA FOR THE REACTION $\mathrm{Ag} + {}^1/_2\ \mathrm{I} = \mathrm{AgI}$

	$N/3$	0.1 N	0.05 N	0.02 N	0.01 N
E at 25°	(0.6846_3)	0.6863	0.6851_6	0.6847_5	0.6846_2
E at 0°	($.6825_3$)	.6823	$.6797_4$	.6796	$.6793_9$
$\mathrm{d}E/\mathrm{d}T$	(.000084)	.000160	.000216	.000206	.000209
A at 25°	(15797)	15835	15809	15800	15797
A at 0°	(15748)	15744	15684	15681	15676
$\mathrm{d}A/\mathrm{d}T$	(1.94) cal. per degree	3.64	5.00	4.74	4.83
U at 25°	(15219)	14750	14318	14386	14358

The results with the $N/3$ solutions are not directly comparable with those obtained with the more dilute solutions because no experiments using the equilibrator and dilute solutions were completed with $N/3$ KI, but these data are comparable with Fischer's measurements. These data indicate that the results are unreliable in solutions 0.1 N or stronger, probably owing to the formation of polyiodides more complex than the tri-iodide or possibly a complex formed by action of potassium iodide on silver iodide, but that in solutions as dilute as 0.05 N and below no such disturbing effect is observed. We therefore believe that the new results obtained with dilute solutions unsaturated with iodine are the most reliable.

The results of the different experimenters on the entropy of the reaction $Ag + {}^1/_2 I_2 = AgI$, are summarized in the following table, arranged in chronological order and also arranged to show the influence of the concentration of the potassium iodide on the results, except in the case of Gerke, who did not use potassium iodide at all.

TABLE VIII

SUMMARY OF THE VALUES OF dA/dT OR THE ENTROPY OF THE REACTION $Ag + {}^1/_2 I_2 = AgI$, BY VARIOUS OBSERVERS, IN CALORIES PER DEGREE

Concn. of KI used	Fischer	Jones and Hartmann	Gerth	Gerke	Webb	Jones and Kaplan
$N/2$	2.419	..	..	..	..	
$N/3$	1.267	..	..	..	..	1.96
$N/10$	1.66	3.68	..	..	2.6	3.64
$N/20$	..	4.52	2.22	..	..	5.00
$N/40$	..	..	2.37	..	..	
$N/50$	..	..	..	..	..	4.74
$N/100$	..	..	..	3.4	..	4.83

If the specific heat measurements on silver, iodine and silver iodide determined by Nernst are reliable and the Nernst-Lindemann formula is used to extrapolate the data down to absolute zero, the value 2.19 calories per degree would be a confirmation of the Third Law.

It will be noticed that Fischer's temperature coefficients of the free energy vary greatly with the concentration but in no systematic manner. For the purpose of testing the Third Law, Fischer averages the results obtained with the $N/2$ and $N/3$ solutions and rejects the results obtained with the $N/10$—an objectionable procedure. Moreover, inadequate allowance for the influence of tri-iodides and higher polyiodides in these strong solutions saturated with iodine vitiates the results. Gerth's results come close to the figure 2.19 which, assuming the accuracy of the specific data obtained in the Nernst laboratory, would support the validity of the Third Law; but as has been pointed out in more detail above, Gerth's new method of surmounting the difficulties due to the formation of tri-iodides fails completely at 0°, and at other temperatures the manner of applying the correction varies considerably with the temperature, thus introducing an error into the temperature coefficient, dA/dT. Moreover, the vapor pressure of iodine is not known as a function of the temperature with sufficient accuracy for the purpose. Our new method of using the equilibrator is a considerable improvement over Gerth's method in principle and radically different in technique. It is equally usable at 0° and at 25° and permits working with solutions more dilute in iodine than Gerth's method. The work of Jones and Hartmann, although improved upon, is confirmed and the opinion that they expressed as to the greater reliability of the data obtained with dilute solution is confirmed.

Since the papers of Fischer and of Jones and Hartmann were published, new determinations of the specific heat of iodine at low temperatures have been published by Günther[18] and by Lange.[19] Günther's results agree substantially with the earlier results obtained by Nernst at temperatures above 30° absolute but differ considerably between 20 and 30° absolute. Günther has proved that there is a transition between two allotropic forms of iodine which occurs at some temperature between 20 and 30° absolute but this transition is a slow one and his data do not make it possible to determine the heat of transition, the specific heat of the form stable at the lower temperature, or the exact temperature of transition. Recently, the heat capacity of iodine has been redetermined by Lange within the range 10 to 52° absolute. He obtained lower results than Nernst, and Günther.

Lange obtained no indication of the existence of a transition temperature between allotropic forms within this range but of course that does not disprove the existence of another form more stable at low temperatures. Lange combines his data at low temperatures with Nernst's at temperatures above 52° and gives a table from which the entropy of iodine at 25° may readily be computed to be 13.95 entropy units. If this is correct and if Nernst's data on silver and silver iodide are correct, then the value of the entropy change during the formation of silver iodide which would be predicted from the heat capacities by the Third Law is 26.8 $-13.95-10.25 = 2.6$ instead of 2.19 based on the measurements of Nernst. If Günther's observations are correct, Lange was probably working with an unstable modification of iodine at the lower temperatures and unstable forms commonly have a higher heat capacity than the stable form. Moreover, Lange's work shows that the data of Nernst are too high in the lower range of temperature and makes it probable that they are too high in the upper range also. If this is correct the value 13.95 for the entropy of iodine may be too high and this would make the value 2.6 for the entropy of formation of silver iodide too low.

Therefore the value of 2.19 for the entropy of formation of silver iodide based on the specific heat of measurements of Nernst can no longer be regarded as having a sound experimental basis, and the fact that the electromotive force measurements of Fischer and Gerth, which are shown above to be faulty, agree with this figure cannot furnish proof of the validity of the Third Law of Thermodynamics. But a conclusion that the theorem is not valid cannot be drawn from the available evidence of this case because of the uncertainty as to the entropy of iodine. The essence of the theorem is that at absolute zero temperature the entropy of chemical reactions is zero and therefore the entropy at any other temperature is a

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[18] Günther, *Ann. Physik*, [4] **51**, 839 (1916).

[19] F. Lange, *Z. physik. Chem.*, **110**, 352 (1924).

function of the specific heats alone. In the past decade evidence supporting the validity of the Third Law of Thermodynamics has accumulated, especially by the work of G. N. Lewis and his associates at the University of California and by the work of H. S. Taylor and his students at Princeton, but more extensive and reliable data on the heat capacities from absolute zero to room temperatures and on the heat effect of any changes of crystalline form that occur within this range of temperature are urgently needed to test this very important theoretical principle.

Summary

1. The earlier work on the free energy of formation of silver iodide is reviewed.

2. The equilibrium constant, $(I^- \times I_2)/I_3 = k$, of the reaction $I^- + I_2 \rightleftharpoons I_3$ was found to be 0.00140 at 25° and 0.00072 at 0°. The results show no systematic variation with the concentration of the iodine between the limits of 2 and 33% of saturation and no systematic variation with the concentration of the iodide between the limits 0.01 and 0.1 *N*. Solutions saturated with iodine give a lower value for the constant especially in the more concentrated solutions of iodide. This indicates that in the stronger solutions some higher polyiodides are formed.

3. A modification of the potentiometer by replacing the usual deadbeat galvanometer with a ballistic galvanometer and shunting an electrostatic condenser of high capacity across the galvanometer and its tapping key has made it possible to determine the potential of a cell having an internal resistance of 1,600,000 ohms within 0.02 millivolt. This invention overcomes the principal difficulty in the measurement of the potential of cells having the liquid junction within a ground glass joint.

4. Measurements have been made of the potential of iodide concentration cells with one electrode consisting of a platinum electrode dipping in a solution of potassium iodide saturated with iodine and the other electrode being similar except that it is unsaturated but with the free iodine activity fixed by the equilibrator.

5. Determinations were made of the solubility of iodine in *N*/3 potassium iodide solution at both 25 and 0°.

6. The free energy of formation of silver iodide has been determined by the aid of the equilibrator, using solutions containing much less iodine than is necessary to produce saturation so that disturbances due to the formation of polyiodides are minimized and can be allowed for by the use of the data supplied by the equilibrator. The results show no systematic variation with the concentration within the range 0.01 to 0.05 *N*, but do show a slight variation at the higher concentration.

7. The average results obtained with the most dilute solutions (0.01 to 0.05 *N*) are: free energy at 25°, 15,802 calories; free energy at 0°

15,680 calories; change in free energy per degree, or entropy change, 4.8; heat of formation at 25°, 14,354 calories.

8. The bearing of these data on some earlier attempts to verify the Third Law of Thermodynamics is discussed.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

NOTE ON MEASUREMENTS OF THE RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE AT VERY LOW PRESSURES[1]

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RECEIVED MARCH 7, 1928 PUBLISHED JULY 6, 1928

Introduction

The decomposition of nitrogen pentoxide is one of the most interesting and most extensively studied of the few known unimolecular reactions. Data on the rate of its decomposition are of great importance to the advancement of our knowledge of the mechanism of chemical reaction.

Although the decomposition of nitrogen pentoxide has finally been shown to be strictly unimolecular over a considerable pressure range,[3] the measurements of Hirst and Rideal[4] would seem to indicate a quite unexpected increase in the specific rate of decomposition at very low pressures. These authors state that, after a critical consideration of their data, they are of the opinion that the increase is real and outside of the experimental uncertainty. Just preceding the presentation of our data, Hibben,[5] by a method similar to Hirst and Rideal's, the details of which are not given, fails to agree with Hirst and Rideal and concludes that the normal rate obtains down to very low pressures.

Since Hirst and Rideal's result is totally unexpected and requires a unique theoretical treatment,[6] it was thought advisable to repeat these measurements by the method which would avoid or at least detect the presence or absence of what seemed to us some objectionable features in Hirst and Rideal's experiments. Especially does this seem desirable since another investigator, using a method similar to Hirst and Rideal's, has obtained a totally different result.

The possible objections to Hirst and Rideal's method that occurred to us were the following. First, unless the apparatus were of proper design,

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Michigan, September 5 to 10, 1927.

[2] Physical Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[3] Daniels and Johnston, THIS JOURNAL, **43**, 53 (1921); Lueck, *ibid.*, **44**, 757 (1922); Hunt and Daniels, *ibid.*, **47**, 1602 (1925); White and Johnson, *ibid.*, **47**, 1240 (1925).

[4] Hirst and Rideal, *Proc. Roy. Soc. London*, **109A**, 526 (1925).

[5] Hibben, *Proc. Nat. Acad. Sci.*, **13** (8), 626 (1927).

[6] See Thomson, *Phil. Mag.*, **269**, (7), 241 (1927).