present data in Fig. 2, in which the black circles represent the values of $\overline{L}_2$ given in Table II. With the possible exception of a few of the points, the deviations found are within the estimated accuracy of the e. m. f. method. The value obtained in the present work at 4 *m* is subject to greater doubt than those at lower concentrations, since this point is near the end of the concentration range studied and the slope is therefore more poorly defined.

Gucker and Pickard[10] have pointed out recently that experiments in which a relatively large volume of air is contained in the dilution cup over a concentrated solution may be subject to significant errors arising from distillation of water from the diluent into this air space after mixing has taken place. This correction and the correction for the condensation of water vapor from the air over the diluent have been applied throughout, the necessary vapor pressure data being taken from the work of Åkerlöf and Kegeles.[9] Unfortunately, the work of Gucker and Pickard was noted at too late a date to allow correction of the curves in Figs. 1 and 2, though all the data given in the tables are corrected. The dilution heats were lowered on the average approximately 3 joules per mole by these corrections, so that most of the changes are practically invisible on the small scale of Figs. 1 and 2.

Corrections of this type have no significant effect in the case of the data on the heats of dilution of aqueous glycine solutions previously published,[11] but cause changes somewhat larger than the estimated uncertainty in some of the data on hydrochloric acid.[1] It is hoped that a recalculation of the latter data will be published in the near future.

Summary

The heat of dilution of aqueous solutions of sodium hydroxide has been determined at 25° up to a concentration of 4 *m*. From these data have been calculated the apparent and partial relative molal heat content of the solute, and the partial relative molal heat content of the solvent.

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(10) Gucker and Pickard, THIS JOURNAL, **62**, 1464 (1940).

(11) Sturtevant, *ibid.*, **62**, 1879 (1940).

NEW HAVEN, CONN. RECEIVED JUNE 24, 1940

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Thermodynamics of the Silver Bromide–Mercurous Bromide Cell[1]

BY THOMAS W. DAKIN[2] AND D. T. EWING

A measurement of the simple cell

$$\mathrm{Hg/Hg_2Br_2,\ MBr\ (aq.\ soln.),\ AgBr/Ag} \qquad (1)$$

where MBr is either hydrogen bromide or potassium bromide and its concentration immaterial, leads directly to the difference between the standard electrode potentials of the silver bromide and the mercurous bromide electrodes and the difference between the free energies of formation of silver bromide and mercurous bromide. A measurement of the temperature coefficient of this cell leads to the difference between the heats and entropies of formation of silver bromide and mercurous bromide. Using the comparatively accurate values of these constants for silver bromide which are in the literature, the corresponding constants for mercurous bromide may be calculated. The present investigation was carried out to redetermine by measurement of the above cell at three temperatures the standard electrode potential of the mercurous bromide electrode and the thermodynamic functions of the formation of mercurous bromide.

The values found in the literature[3] for the standard electrode potential of the mercurous bromide electrode at 25° vary over a range from 0.1385 v. to 0.1400 v. and for the most part are based on somewhat deviating values for the activity coefficients of hydrobromic acid solutions. Larson[4] measured a cell similar to the one reported in the present paper, using potassium bromide solutions exclusively, and at the temperatures 20, 25 and 30°. He obtained a value for the standard electrode

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(1) This paper was presented at an Ohio–Michigan regional meeting of the A. C. S. in October, 1939.

(2) The material of this paper has been abstracted from a thesis submitted to the faculty of the Graduate School of Michigan State College by T. W. Dakin in September, 1938, in partial fulfillment of the requirements for the M. S. degree. The present address of the junior author is Harvard University.

(3) Gerke and Geddes, *J. Phys. Chem.*, **31**, 886 (1927); Matthews, Ph.D. Thesis, Michigan State College (1930); Larson, M. S. Thesis, Michigan State College (1931); Gerke, "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, Vol. VI, p. 332; Ishikawa and Ueda, *J. Chem. Soc. Japan*, **51**, 59 (1930).

(4) Larson, THIS JOURNAL, **62**, 764 (1940).

potential of the mercurous bromide electrode of 0.13970 v. at 25° based on Harned and Donelson's[5] value of 0.07131 v. for the standard potential of the silver bromide electrode.

Reports in the literature of the heat and the entropy of formation of mercurous bromide are less numerous. The value of the heat of formation in the "International Critical Tables" is based on the early work of Thomsen[6] and Nernst,[7] and is −49,210 cal./mole at 18°. Ishikawa and Ueda[3] also measured the temperature coefficient of the cell

$$\text{Pb (2 phase amal.)/PbBr}_2\text{ (satd. soln.), Hg}_2\text{Br}_2\text{/Hg} \quad (2)$$

and on the basis of the corresponding values for the lead bromide, calculated the heat of formation of Hg_2Br_2 as −48,940 cal./mole at 25° and the entropy of formation as −21.0 cal./deg./mole. Larson[4] does not report a value for the heat of formation of mercurous bromide, but calculations from his temperature coefficient give a value of −50,216 cal./mole at 25°. He reports implicitly an entropy of formation of mercurous bromide of −25.1 cal./deg./mole. Both of these values are considerably higher than the work of Ishikawa and Ueda indicates.

Experimental

Mercury used in the preparation of the mercurous bromide electrodes was purified first by making it the anode in a shallow dish using 3% nitric acid as the electrolyte. Electrolysis was continued for six to eight hours under an outside e. m. f. of 7.5 v., and the large surface of the mercury was stirred continuously. A cup beneath the cathode caught any of the metallic deposit dropping off. The mercury was then twice distilled in a vacuum and kept under an atmosphere of nitrogen until used.

The hydrobromic acid used in the cells and in the precipitation of mercurous bromide was prepared from Baker Analyzed hydrobromic acid by making a constant boiling solution by fractional distillation in an all-Pyrex still. The approximately constant boiling solution was redistilled four times, retaining only the middle portion each time. The final product was water white and boiled at 123.6° at 74.21 cm. pressure. To prevent photochemical decomposition it was kept in the dark. All hydrobromic acid solutions used in the cells were prepared from this by dilution.

Mercurous bromide was prepared by precipitation from approximately 0.1 *M* solutions of hydrobromic acid and mercurous nitrate. Previous to precipitation the solutions were prepared oxygen free by evacuation and gentle heating and were kept under an atmosphere of nitrogen during the precipitation, which was carried out with a slight excess of hydrobromic acid. It was washed by decantation eight times with evacuated conductivity water and five times with the solution of hydrobromic acid or potassium bromide which was to be used in the cell, the last portion remaining over it for at least eighteen hours with frequent shaking to attain equilibrium. It was then transferred with some of the precipitate to the cell where it was placed over the mercury electrode. Solutions were kept under an atmosphere of nitrogen and transferred to the cell without contact with the air. Preliminary experiments had indicated that electrodes prepared from mercurous bromide made in the above manner came to equilibrium much more readily than when using mercurous bromide prepared from potassium bromide in the air as recommended by Larson[3,4] and Matthews.[3]

The potassium bromide which was used in a few cells was thrice recrystallized from the Baker Analyzed product and contained no detectable chlorine. It was not used in the preparation of the mercurous bromide or the silver bromide, so a trace of chloride could not affect the results, and no special precautions were taken to eliminate it, other than that mentioned.

Silver bromide electrodes were of two types. Most of the cells were made using the plated type, in a manner exactly similar to the way recommended by Brown[8] for silver chloride electrodes. Silver was plated on 2-cm., no. 23 platinum wires from a pure $KAg(CN)_2$ solution, after which the wires were washed and a layer of silver bromide put on. Two cells included in the average were made up using the Keston[9] fused type of silver bromide electrode. Usually six electrodes were prepared at the same time, at least five of which differed from each other by less than 0.1 mv., two of these being used in a single cell. The plated type electrodes were found unsatisfactory for use in hydrobromic acid solutions more concentrated than 0.2 *M*.

The cells themselves were of a double H type with a stopcock having an ungreased central portion intermediate between the two types of electrodes. Since there were two electrodes of each type, an immediate check was permitted on the consistency of one or the other type. When either pair of electrodes of the same type in the cell showed a difference of more than 0.2 mv. the cell was discarded. Four cross measurements could be made on each cell. Cells made up using the mercurous bromide precipitated as described above and kept free from oxygen gave a constant e. m. f. after a few hours, and were measured and found constant over periods of two days to a week. Throughout, procedures were conducted with reasonable care so as to allow only red light to reach the mercurous bromide and the solutions in the cells.

E. m. f. measurements were made for the most part with a Queen–Gray potentiometer. These values were on several occasions checked with a Leeds and Northrup type K instrument which had been certified by the U. S. Bureau of Standards. The voltage standard was a Weston standard cell which had been calibrated and certified by the Bureau of Standards. Cells were thermostated in water thermostats which were controlled to 0.01° and their temperature was determined by a Bureau of Standards calibrated thermometer. Corrections for a small fraction of a degree were made to all e. m. f. values to avoid fractional temperatures. A coefficient of 0.00031 volt/deg. was used for this purpose.

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(5) Harned and Donelson, THIS JOURNAL, **59**, 1280 (1937).

(6) Thomsen, "Thermochemische Untersuchungen," 1882-1886.

(7) Nernst, *Z. physik. Chem.*, **2**, 23 (1888).

(8) Brown, THIS JOURNAL, **56**, 646 (1934).

(9) Keston, *ibid.*, **57**, 1671 (1935).

TABLE I

Temp., °C.	No. cells	E_{cell}, v.	$E^0_{\text{Ag,AgBr}}$, v.	$E^0_{\text{Hg}_2\text{Br}_2\text{,Hg}}$, v.
15.0	5	0.06492 ± 0.00015	−0.07586	0.14078
20.0		(0.06648)	− .07361	.14009
25.0	12	0.06804 ± 0.00012	− .07121	.13925
30.0		(0.06960)	− .06863	.13823
35.0	6	0.07116 ± 0.00010	− .06591	.13707

Results

Measurements were made on cells of type (1) at three different concentrations of hydrobromic acid (0.05, 0.10 and 0.20 *M*) and at one concentration of potassium bromide. The two cells included in the average in which 0.2 *M* potassium bromide was the solution did not deviate from the average of the other cells by more than the average deviation among themselves. The Keston fused type silver bromide electrodes were used in the two cells containing 0.05 *M* hydrobromic acid and these cells also showed no more than the average deviation from the others. They are included in the average. The average values of all the cells at the temperatures indicated are given in column three of Table I. Such an averaging is justified as no trend was shown experimentally in the e. m. f. with changing concentration or cation. The value for each cell consisted of a time average during the period of constancy of an average of each of the four cross measurements possible, each cell actually being equivalent to better than two cells.

The potential values at the three temperatures lie, within the experimental error, on a straight line, and can be represented by the linear equation

$$E_{\text{cell}} = 0.06804 + 0.000312\ (t - 25)\ \text{volts}$$

Values in parentheses in column three, Table I, are interpolated values using this equation. The value of the temperature coefficient of the cell is considerably smaller than that obtained by Larson,[4] which was 0.000418 volt/deg. The value of the e. m. f. of the cell at 25° differs from his value by −0.35 mv. which is almost three times the average deviation reported in either case. The interpolated value at 20° differs from Larson's value at that temperature by only 0.18 mv., but the interpolated value at 30° differs by a millivolt from his value. If we are to assume that the true temperature coefficient is almost linear over the temperature range 15–35°, greater credence should be given to the temperature coefficient reported here, on the basis of the fact that it covers a wider range of temperature by twice, and small experimental errors will affect the value less.

Within the last five years three values of the standard electrode potential of the silver bromide electrode have been reported from the laboratories at Yale,[5,10] which cover the temperature range considered here (15–35°). They show a maximum deviation of only 0.3 mv. from each other at any one of the temperatures. The values from these three papers have been averaged with equal weight to each and are tabulated in column 4 of Table I, and are made the basis of the calculation of the standard potentials of the mercurous bromide electrode in column 5 of Table I. The e. m. f. of the cell (1) is related to the standard potentials of the silver bromide and mercurous bromide electrodes according to the equation

$$E_{\text{cell}} = E^0_{\text{Ag,AgBr}} + E^0_{\text{Hg}_2\text{Br}_2\text{,Hg}}$$

where the E_{cell} is taken positive.

The standard potential of the mercurous bromide electrode over this temperature range may be represented by the equation

$$E^0 = 0.13925 - 0.000186(t - 25) - 0.0000032(t - 25)^2$$

which fits the above data to within 0.02 mv. These data are not in very serious disagreement with Larson[4] except in the value at 30° and in the temperature coefficient, the latter of which is decidedly different. At 25° the value of the standard potential of the mercurous bromide electrode here obtained lies about in the middle of the range of values reported in the literature.[3,4]

The Entropy, Heat and Free Energy of Formation of Mercurous Bromide.—The decrease in free energy accompanying the reaction

$$2\text{Ag} + \text{Hg}_2\text{Br}_2 \longrightarrow 2\text{AgBr} + 2\text{Hg}$$

which is the reaction in the cell (1), is equal to $2FE/4.186$ cal./mole, where F is the faraday and E the e. m. f. of the cell. At 25° the decrease in free energy for the above reaction is found to be 3137 cal. Now the following relationship holds

$$\Delta F = 2\Delta F_{\text{AgBr}} - \Delta F_{\text{Hg}_2\text{Br}_2}$$

where ΔF is the free energy change in the above reaction, ΔF_{AgBr} is the free energy of formation of AgBr from Ag and $^1/_2\text{Br}_2$, and $\Delta F_{\text{Hg}_2\text{Br}_2}$ is the

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(10) Harned, Keston and Donelson, THIS JOURNAL, **58**, 989 (1936); Owen and Foering, *ibid.*, **58**, 1575 (1936).

free energy of formation of Hg_2Br_2 from 2Hg and Br_2. Using the free energy of formation of silver bromide obtained by Jones and Baeckstrom[11] ($-\Delta F = 22{,}935$ cal./mole), we can calculate the free energy of formation of mercurous bromide as $-\Delta F = 42{,}733$ cal./mole at 25°. This agrees well with the value reported by Ishikawa and Ueda[3] of 42,700 cal., obtained from a different cell measurement. Calculations from the data of Larson[4] indicate a value of 42,716 cal., which is very nearly the same.

The heat of the reaction in the cell (1) may be calculated using the well-known thermodynamic equation

$$\Delta H = \frac{2F}{4.186}\left(T\frac{\mathrm{d}E}{\mathrm{d}T} - E\right)$$

where E is the e. m. f. of the cell (1) and $\mathrm{d}E/\mathrm{d}T$ is its temperature coefficient (0.000312 volt/deg.). Then $\Delta H = 1150$ calories at 25° for the reaction in the cell, which value is less than half the one calculated from the data of Larson,[4] which yields a value of 2591 cal. This is of course due to the fact that he obtained a much higher temperature coefficient. Values for the heat of formation of silver bromide at 25° have been determined by Webb[12] from thermal measurements and Woitinek[13] from cell measurements, which values differ by only five calories and whose average is $\Delta H = -23{,}813$ cal./mole. This value and the value above for the heat of reaction in the cell (1) are combined to give a value for the heat of formation of mercurous bromide at 25° of $\Delta H = -48{,}776$ cal./mole, which agrees fairly well with the value of Ishikawa and Ueda, but not that of Larson (see above). According to the relationship $\Delta S = (-\Delta F + \Delta H)/T$, we can calculate the entropy of formation of mercurous bromide at 25° from the above values for the heat and free energy of formation, and we obtain $\Delta S = -20.4$ cal./deg./mole. Adding to this the values for the standard third law entropies of mercury and bromine given by Latimer[14] and based on the data of Kelley[15] and Latimer and Hoenshel,[16] we obtain 53.4 calories/deg./mole for the entropy of mercurous bromide at 25°. This is in disagreement by about five entropy units with the value given by Larson[4] (48.7 cal./deg./mole), but agrees within 0.6 entropy unit with that obtained by Ishikawa and Ueda.[3]

Larson states that he agreed with Ishikawa and Ueda in respect to their temperature coefficients and suggested that the large difference between his value for the entropy of mercurous bromide and that calculated from the data of Ishikawa and Ueda was due to an error in the other entropy data used, namely, of bromine. Such error is not indicated in the present work. The fact that there is considerable difference between the values for the heat of formation of mercurous bromide calculated from his data and from that of Ishikawa and Ueda would indicate their temperature coefficients did not agree. The accuracy of the reference entropy data used can be checked by using one of the methods employed by Larson[4] to calculate the entropy. The entropy change in the cell reaction above is

$$\Delta S = \frac{2F}{4.186}\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right) = \frac{2F}{4.186}(0.000312) = 14.3 \text{ cal./deg./mole}$$

Combining this value then with the third law entropies at 25° of Ag[17], Hg[15] and AgBr,[18] the other constituents involved in the reaction

$$S_{Hg_2Br_2} = -\Delta S - 2S_{Ag} + 2S_{Hg} + 2S_{AgBr} = 53.5 \text{ cal./deg./mole}$$

which agrees with the value calculated by the other method, and which indicates that the entropy of bromine and of the formation of silver bromide implicit in the two different sets of reference data agree.

Summary

The standard electrode potential of the mercurous bromide electrode has been evaluated over the temperature range 15–35° by reference to the better established value for the standard potential of the silver bromide electrode, and has been found to be 0.13925 v. at 25°. The free energy of formation of mercurous bromide has been found to be −42,733 cal./mole, the heat of formation as −48,776 cal./mole, and the entropy of formation as −20.4 cal./deg./mole, while the standard entropy of Hg_2Br_2 is calculated to be 53.4 cal./deg./mole, all values being at 25°. The potential and free energy values are not seriously different from the values given either by Ishikawa and Ueda or by Larson, but whereas agreement is

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[11] Jones and Baeckstrom, THIS JOURNAL, **56**, 1524 (1934).

[12] Webb, *J. Phys. Chem.*, **29**, 827 (1925).

[13] Woitinek, *Z. Elektrochem.*, **38**, 359 (1932).

[14] Latimer, "Oxidation Potentials," Prentice–Hall, N. Y., 1938.

[15] Kelley, "U. S. Bureau of Mines Bulletin 394," 1935.

[16] Latimer and Hoenshel, THIS JOURNAL, **48**, 19 (1926).

[17] Rodebush and Rodebush, "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1930.

[18] Eastman and Milner, *J. Chem. Phys.*, **1**, 444 (1933).

maintained with entropy and heat values obtained by Ishikawa or by Ueda who measured the temperature coefficient of a different cell, disagreement is found with entropy and heat values obtained by Larson.

East Lansing, Michigan Received June 20, 1940

[Contribution from the Division of Industrial and Cellulose Chemistry, McGill University]

Studies on Lignin and Related Compounds. L. Fractionation of Acetylated Cell Wall Constituents of Red Oak Wood[1]

By Quintin P. Peniston, Joseph L. McCarthy and Harold Hibbert

It is not yet known whether in the plant cell wall the lignin exists in the free state or whether it is in partial or complete chemical combination with carbohydrate substances. Considerable indirect evidence[2] is at hand indicating the presence of such a combination although Klason,[3a] Freudenberg,[3b] and Brauns[3c] have shown independently that a very small part of what is apparently protolignin can be extracted from wood by neutral organic solvents at room temperature, indicating that this extracted fraction probably has a relatively simple structure and is not combined with carbohydrates.

It is possible that a chemical combination between lignin and carbohydrate exists, perhaps as a glycosidic or an ether linkage between a phenolic hydroxyl group of the lignin and some hydroxyl grouping in the pentosans or cellulose. The acetolysis of such a compound might be expected to result in changes in general similar to those experienced in the case of acetolysis of cellulose wherein a simultaneous acetylation and hydrolytic reaction occurs, so that the resulting degree of polymerization depends upon the extent to which the acetolysis change has proceeded.[4]

Several previous investigators[5] elsewhere and in these Laboratories have studied the acetylation of wood from the point of view of preventing complex condensation or polymerization changes in the individual cell wall constituents by means of a prior acetylation of reactive hydroxyl groups. Success in application of the method in this connection, a matter of considerable importance in the investigation being reported, is shown by the preparation of an oak lignin soluble in sodium bisulfite solution[6] and also partially convertible into lignin building units on ethanolysis.[7]

In the present research an attempt has been made to employ a hydrolytic acetylation, *i. e.*, an acetolysis reaction, in order to obtain an acetylated oak wood, soluble in organic solvents, which by mixed solvent fractionation could be examined for the presence of a lignin–carbohydrate complex. It was hoped that fission of any existing linkages would not proceed to the extent of rupture of all bonds, and that at least a small fraction of a lignin carbohydrate compound would be preserved in the soluble state. It also was desirable to devise a method of purification of acetylated lignin which would avoid the laborious and inefficient acetone extraction step of Suida and Titsch.[5d]

Thus resin-free, alkali-extracted red oak wood meal was acetylated with acetic anhydride in glacial acetic acid solution, using sulfuric acid as the catalyst. The "crude acetylated wood" was recovered by pouring the reaction mixture into water.

In a series of experiments in which the maximum temperature of acetylation was varied, it was established that the solubility of "crude acety-

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(1) From a thesis presented to the Faculty of Graduate Studies and Research, McGill University, by Quintin P. Peniston, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, May, 1939.

(2) (a) Erdmann, *Liebigs Ann. Chem. Suppl.*, **5**, 223 (1867); (b) Cross, *J. Chem. Soc.*, **55**, 199 (1889); (c) Klason, *Ber.*, **56**, 300 (1923); (d) Harris, Sherrard and Mitchell, This Journal, **56**, 889 (1934); (e) Norman and Shrikhande, *Biochem. J.*, **29**, 2259 (1935). See also recent reviews: (f) Hägglund, "Holzchemie," Akad. Verlag., Leipzig, 1939, p. 206; (g) Norman, "The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.," Clarendon Press, Oxford, 1937, p. 59; (h) compare Freudenberg, "Tannin, Cellulose, Lignin," J. Springer, Berlin, 1933, p. 145; (i) Cross and Bevan, "Researches on Cellulose," Vol. 4, Longmans, Green, London, 1922, pp. 152, 170.

(3) (a) Klason, "Beitrage zur Kenntnis der chemische Zusammensetzung des Fichtenholzes," Berlin, 1911, pp. 34–36; (b) Freudenberg, Janson, Knopf, and Haag, *Ber.*, **69**, 1415 (1936); (c) Brauns, This Journal, **61**, 2120 (1939).

(4) Freudenberg, *Ber.*, **54**, 767 (1921).

(5) (a) Fuchs, *ibid.*, **61**, 948 (1928); (b) Horn, *ibid.*, **61**, 2542 (1928); (c) Suida and Titsch, *ibid.*, **61**, 1599 (1928); (d) Suida and Titsch, *Monatsh.*, **54**, 700 (1929); (e) Lieser and Schwind, *Ann.*, **532**, 104 (1937); (f) Steeves, Ph.D. Thesis, McGill University, 1936; (g) Lieff, *ibid.*, 1938; (h) Hawkins, *ibid.*, 1938.

(6) (a) Hibbert and Steeves, This Journal, **59**, 1768 (1937); (b) Steeves and Hibbert, *ibid.*, **61**, 2194 (1939); (c) Hawkins, Wright and Hibbert, *ibid.*, **59**, 2247 (1937).

(7) Peniston, McCarthy and Hibbert, *ibid.*, **61**, 530 (1939).