

increase with p_{O_2} and to decrease as p_{O_2} increases. More evident, however, is the tendency for ϕ to decrease as P increases, suggesting that a three-body collision involving regeneration of ozone from oxygen molecules and oxygen atoms is important.

Summary

Carefully purified ozone was photolyzed at λ 280, 254 and 210 $m\mu$ in the presence of saturated water vapor at 2 and 20°. Partial pressures of ozone ranged from 10 mm. to one atmosphere. The observed quantum yields, ϕ , determined with numerous precautions, ranged from

1.6 to 130, indicating a chain mechanism. Increase in p_{O_2} raised ϕ rather noticeably while increase in total pressure or in p_{O_2} depressed it.

At any given wave length, ϕ was found to be inversely proportional to a fixed power of light intensity. This power was 0.37 at λ 210 $m\mu$ independent of partial pressures, and 0.24 at both λ 254 and 280 $m\mu$ in spite of marked differences in absorption coefficients.

Over the temperature interval 2 to 20°, ϕ , adjusted as above, was found proportional to the square root of the concentration of water molecules. The implications of this fact are suggested.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Thermodynamics of Aqueous Barium Chloride Solutions from Electromotive Force Measurements¹

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The thermodynamic properties of aqueous barium chloride solutions have been determined from e. m. f. measurements on cells of the type Ba (two-phase amalgam) | BaCl₂ (*m*) | Hg₂Cl₂ | Hg, at 0, 15, 25, 35 and 45°. The activity coefficients calculated by Pearce and Gelbach² from e. m. f. data at 25°, and those calculated by Hepburn³ from vapor pressure measurements at 25°, show large deviations in the more concentrated regions from the accepted values of Lucasse⁴ calculated from e. m. f. data at the same temperature. Furthermore, preliminary measurements⁵ indicated that the activity coefficient, as a function of temperature for given molality, passes through a maximum at about 20°. These factors all indicated the desirability of a comprehensive study of the thermodynamic behavior of barium chloride in aqueous solution at various temperatures.

Materials and Apparatus

The materials used in this investigation were purified with utmost care. The water used for making the barium chloride solutions was prepared by successive distillation of laboratory distilled water from alkaline permanganate, barium hydroxide and finally from a silica still from which the water was collected in a silica receiver.

(1) Based upon a thesis submitted by Emerson A. Tippetts to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

(2) Pearce and Gelbach, *J. Phys. Chem.*, **29**, 1023 (1925).

(3) Hepburn, *J. Chem. Soc.*, 1284 (1932).

(4) Lucasse, *THIS JOURNAL*, **47**, 743 (1925).

(5) Newton and Tippetts, *ibid.*, **54**, 3779 (1932).

The barium chloride was purified by three recrystallizations from water purified as described. A concentrated stock solution was made from this salt, and solutions for the cells were made by diluting this stock solution. These solutions were analyzed by evaporating weighed portions to dryness in a weighing bottle at about 100° and subsequent heating to about 150° for several hours. This is a very satisfactory method for analysis as the salt has no tendency to creep out of the vessel during the evaporation process. The residue is anhydrous and is allowed to cool in the closed weighing bottle in a desiccator before weighing.

The mercury used in making the barium amalgam and calomel was purified by washing with nitric acid and distilling three times under reduced pressure in a current of air.

The calomel was prepared by electrolysis of redistilled hydrochloric acid. Calomel thus prepared was washed, shaken with mercury and allowed to stand for several days before being used.

The barium amalgam was prepared by electrolysis of a saturated solution of barium chloride. Electrolysis was continued until two phases were present, at which time the solution was drawn off and the amalgam washed repeatedly with 95% ethyl alcohol and finally with anhydrous ether until dry. The amalgam was then covered with a layer of light mineral oil and kept in glass-stoppered weighing bottles until used. This layer of oil prevented excessive reaction with oxygen or carbon dioxide of the air. The oil was previously saturated with beeswax, since beeswax was used to coat the amalgam compartment of the cell to prevent creeping of the liquid around the amalgam. It was important that the oil adhering to the amalgam should not dissolve this film of beeswax.

The constant temperature baths were controlled within $\pm 0.01^\circ$ at 15, 25 and 35°, and within $\pm 0.02^\circ$ at 0 and

45°, the temperatures being established with a thermometer calibrated by the U. S. Bureau of Standards.

The cell used was essentially of the type described by Danner,⁶ wherein the solution is renewed over the amalgam. Danner found that with a thin layer of oil on the amalgam the electromotive force of such a cell was constant within 0.2 mv. on renewing the solution. In this investigation Danner's cell was modified by sealing the tube, connecting the amalgam compartment with the rest of the cell, in at the side of the compartment rather than at the top, leaving the top open to facilitate the introduction of the amalgam and cleaning of the cell.

Electromotive forces of the cells were measured on a Leeds and Northrup Type K Potentiometer.

Preparation of Cells

Two methods were employed for introduction of the amalgam into the cells. For the lower temperatures hot liquid amalgam was pipetted into the cells. On cooling in the thermostats, solid separated to give a two-phase amalgam. This technique is superior since it was found that amalgams introduced in this manner had least tendency to gas. It was found, however, that on introducing hot liquid amalgam for the cells at 35° and allowing the solid to crystallize at the temperature of the thermostat, a higher e. m. f. was obtained than when a two-phase amalgam was introduced directly. This seems to indicate a phase change in the region of this temperature and that with the cooling of the liquid a different solid phase, probably metastable, settled out. It was feared that the same solid phase could not be reproduced in each cell by this method at 35 and 45°. Therefore the two-phase amalgam with excess solid was introduced for cells measured at these temperatures. At 0, 15 and 25° the e. m. f.'s obtained by either technique were the same although greater time was required for the cells to reach equilibrium if liquid alone was introduced. The final e. m. f.'s obtained for any particular molality when plotted against temperature give a smooth curve with no evidence of a break, indicating that the solid phase of the amalgam was the same at all temperatures.

Equilibrium was usually established within five hours, although in some cells at the lower temperatures where liquid amalgam was introduced, thirty-six hours were required.

In many cases the amalgam reacted with the water of the solution liberating hydrogen, especially for those cells where the two-phase amalgam was introduced directly. This was probably due to the difficulty of transferring solid amalgam into the cells without introducing traces of the scum which formed on the surface of the amalgam in the containers in which it was stored. Cells prepared by pipetting amalgam from below the surface showed practically no tendency to liberate hydrogen. All gassing cells were discarded.

An air-free technique was not employed because in the type of cell used an excess of solid amalgam ensures the same composition in the electrode even though small amounts of barium react with the dissolved air. The solution was renewed at intervals to ensure known concentration at the amalgam surface. The essential agreement of the data at 25° with those of Lucasse⁴ at the same

temperature, using an air-free technique, indicates that the precaution is unnecessary if a two-phase amalgam electrode is used.

Discussion of the Results

The observed e. m. f.'s with corresponding molalities are shown in Table I. It was found that on renewing the solution over the amalgam the e. m. f. dropped about 0.5 mv. and then quickly increased to a maximum value and remained constant for several hours, at which time the value began falling off, due to reaction of barium with the solution. For the concentrated solutions the e. m. f.'s were constant for about two days before they began to fall off. On renewing the solution this maximum value was again established within ± 0.2 mv. These deviations were somewhat greater for the most dilute solutions.

From Table I a series of values of $(E_m - E_{0.05})$ was computed for each temperature. In

TABLE I
ELECTROMOTIVE FORCE OF CELLS
Ba (2-Phase amalgam) | BaCl₂ (m) | Hg₂Cl₂ | Hg

m mole BaCl ₂ 1000 g. H ₂ O	E. m. f., volts				
	0°	15°	25°	35°	45°
0.05000	2.0072	2.0306	2.0453	2.0595	2.0735
.05629			2.0418		
.06897	1.9977		2.0348		2.0625
.07898				2.0439	
.09508				2.0379	
.1159	1.9832		2.0183	2.0317	
.1194	1.9821		2.0175		2.0437
.1303			2.0147		
.1339		2.0004		2.0270	
.1539			2.0094		2.0355
.2293	1.9631	1.9836		2.0090	2.0225
.2373			1.9953		2.0211
.4546	1.9433		1.9738		1.9978
.4575	1.9428			1.9852	
.4786		1.9595		1.9838	
.4856			1.9718		1.9957
.5183		1.9570			
.6931		1.9464		1.9700	
.7021			1.9578		1.9809
.7021			1.9577		1.9812
.8807	1.9199		1.9489	1.9598	1.9715
.9138		1.9360			
.9975			1.9434		1.9650
1.0757		1.9293			
1.4000	1.9007				
1.4000	1.9007				
1.4015	1.9003			1.9392	1.9497
1.4019	1.9006				
1.5271			1.9243		1.9454
1.5465		1.9130			
1.5713				1.9333	
1.7783			1.9166		1.9374
1.7783					1.9375
1.8524					1.9350

(6) Danner, THIS JOURNAL, 46, 2385 (1924).

order to extrapolate these values to infinite dilution and to obtain the most probable e. m. f.'s at round concentrations, the Hückel⁷ equation was used and the constants of that equation determined from the experimental data, using the method of least squares. It is necessary to resort to this treatment in this case rather than use the direct method as outlined by Hückel⁷ because of the greater uncertainty attending the e. m. f. measurements of this particular cell. Also the Hückel equation without extension is probably farther from a true representation of the behavior of a salt like barium chloride than it is for a simple 1:1 type salt.

The method used for evaluating the constants of the Hückel equation is similar to that of Jones and Dole.⁸ The concentration cell e. m. f. ($E_1 - E_2$) may be expressed by the equation

$$E_1 - E_2 = \frac{3RT}{2F} \ln \frac{f_2 c_2}{f_1 c_1} \quad (1)$$

where f equals the activity divided by the concentration and c equals the concentration in moles per liter. The Hückel equation for $\log f$ may be written

$$\log f = -\frac{M \sqrt{c}}{1 + N \sqrt{c}} + Pc \quad (2)$$

in which M for barium chloride is equal to $u \sqrt{12}$. The values of u were taken from Table VII of Harned and Ehlers.⁹ The N and P constants have the same significance as in the paper of Jones and Dole.⁸

Combining equations (1) and (2) with $E_{0.05}$ as reference

$$E_m - E_{0.05} = -\frac{3RT}{2F} 2.3026 \left[\left(\log c_m - \frac{M \sqrt{c_m}}{1 + N \sqrt{c_m}} + Pc_m \right) - \left(\log c_{0.05} - \frac{M \sqrt{c_{0.05}}}{1 + N \sqrt{c_{0.05}}} + Pc_{0.05} \right) \right] \quad (3)$$

Abbreviating conveniently

$$E_{i(\text{calcd.})} = -\frac{3RT}{2F} 2.3026 \left(\log c_i - \frac{M \sqrt{c_i}}{1 + N \sqrt{c_i}} + Pc_i \right) - E_s \quad (4)$$

where E_s has the value of the first term calculated for the reference concentration 0.05 M . As first approximation the values of N and P were calculated by the method outlined by Hückel.⁷ It was desired to change N and P by such amounts as to make $E_{i(\text{calcd.})}$ agree as well as possible with $E_{i(\text{obs.})}$. However the $E_{i(\text{obs.})}$ includes any error for cell $m = 0.05$ as well as for the cell with concentration m . The e. m. f.'s for the cells $m = 0.05$ are

(7) Hückel, *Physik. Z.*, **26**, 93 (1925).

(8) Jones and Dole, *This Journal*, **51**, 1084 (1929).

(9) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

probably the most uncertain of the whole series. Hence it is also desirable to change E_s as well as N and P to get the most consistent values of $E_{i(\text{calcd.})}$. As a first approximation E_s takes the value already defined.

The quantity to be minimized is

$$\Sigma [E_{i(\text{obs.})} - (E_{i(\text{calcd.})} + \Delta E_{i(\text{calcd.})})]^2 \quad (5)$$

in which

$$E_{i(\text{calcd.})} + \Delta E_{i(\text{calcd.})} = -\frac{3RT}{2F} 2.3026 \left(\log c_i - \frac{M \sqrt{c_i}}{1 + N \sqrt{c_i}} + Pc_i \right) - E_s - \Delta E_s - \frac{3RT}{2F} 2.3026 \left(\frac{Mc_i}{(1 + N \sqrt{c_i})^2} \Delta N + c_i \Delta P \right)$$

Quantity (5) then becomes

$$\Sigma \left[E_{i(\text{obs.})} + \frac{3RT}{2F} 2.3026 \left(\log c_i - \frac{M \sqrt{c_i}}{1 + N \sqrt{c_i}} + Pc_i \right) + E_s + \Delta E_s + \frac{3RT}{2F} 2.3026 \frac{Mc_i}{(1 + N \sqrt{c_i})^2} \Delta N + \frac{3RT}{2F} 2.3026 c_i \Delta P \right]^2$$

The first three members are equivalent to $E_{i(\text{obs.})} - E_{i(\text{calcd.})}$ and for convenience are designated by y_i . If the coefficients of ΔN and ΔP are designated by a_i and b_i , respectively, by summing and squaring, the quantity to be minimized becomes

$$\Sigma (y_i + \Delta E_s + a_i \Delta N + b_i \Delta P)^2 \quad (6)$$

By differentiation with respect to ΔE_s , ΔN and ΔP , there result three linear equations which are solved for ΔE_s , ΔN and ΔP . E_s , N and P are then changed by the corresponding Δ quantities and the whole process repeated until the Δ quantities become negligible.

This method of calculating the N and P constants differs from that of Jones and Dole in that the reference e. m. f. is allowed to change by such an amount as to give the best possible agreement between the concentration cell e. m. f.'s determined by experiment and those calculated by use of the Hückel equation. This treatment is preferable because it does not give undue weight to the reference e. m. f. The actual disagreement between $E_{0.05(\text{calcd.})}$ and $E_{0.05(\text{obs.})}$ ranged from +0.09 mv. for 15° to +0.52 mv. for 45°. The average deviation of $E_{i(\text{obs.})}$ from $E_{i(\text{calcd.})}$ for all calculations was about ± 0.2 mv. with maximum deviation of ± 0.5 mv.

The values of c corresponding to m for the above calculations were determined from the corresponding densities calculated from the data listed in the "International Critical Tables."¹⁰

(10) "International Critical Tables," McGraw-Hill Book Co., New York, 1928, Vol. III, p. 75.

Using the values of E_s , N and P thus determined a series $E_{i(\text{calcd.})}$ was calculated for each temperature at round concentrations from 0.05 M to 0.9 M , the latter being the concentration at which the Hückel equation began to give values of E_i significantly different from the experimental, for all temperatures except 45°. For concentrations greater than this the concentration cell e. m. f.'s were read off from a large plot of the original data against $m^{1/2}$. This method of plotting was chosen because for concentrations greater than 0.4 M it yields a practically straight line. Thus for each temperature a series of $(E_{0.05} - E_m)$ values was prepared at round concentrations from $m = 0.05$ practically to saturation. Each series was corrected by the deviation of $E_{0.05}$ determined as already described.

It was found that an equation of the form

$$E_i = a + bt + ct^2 \quad (7)$$

expressed with an average deviation of ± 0.1 mv. the concentration cell e. m. f.'s for the various temperatures at constant composition. The constants a , b and c were calculated by the method of least squares and are listed in Table II. For the purpose of brevity the e. m. f.'s are omitted and only the constants of equation (7) given. Smoothed values of c , designated as c' , obtained from a plot of c against m , are also listed in Table II.

TABLE II

CONSTANTS OF EQUATION (7)				
m	a	$b \times 10^4$	$-c \times 10^6$	$-c' \times 10^6$
0.1	0.01957	1.162	0.96	0.96
.2	.03928	2.366	1.97	1.97
.3	.05121	3.066	2.51	2.51
.4	.06002	3.519	2.76	2.76
.5	.06714	3.837	2.86	2.86
.6	.07320	4.047	2.82	2.82
.7	.07852	4.192	2.71	2.71
.8	.08340	4.228	2.44	2.55
.9	.08788	4.322	2.50	2.38
1.0	.09216	4.334	2.29	2.20
1.1	.09596	4.327	1.93	2.01
1.2	.09973	4.423	1.95	1.85
1.3	.10307	4.426	1.71	1.74
1.4	.10634	4.510	1.68	1.67
1.5	.10945	4.584	1.64	1.64

Activity Coefficients

The activity coefficient f was calculated at 0.05 M for each temperature using equation (2). The value thus obtained was changed to activity coefficient γ by multiplying by the corresponding factor c/m . From the smoothed e. m. f. values using the 0.05 M solution as reference the activity

coefficients of Table III were calculated. Equation (2) gives values of f which, when converted to the corresponding γ , are in agreement to about 1 M . At 45° the agreement extends to 1.2 M .

TABLE III

ACTIVITY COEFFICIENTS (γ) OF BARIUM CHLORIDE

m	0°	15°	25°	35°	45°
0.01	0.725	0.727	0.723	0.720	0.710
.05	.555	.565	.559	.554	.536
.1	.483	.498	.492	.487	.467
.2	.422	.442	.436	.431	.409
.3	.394	.416	.411	.405	.383
.4	.379	.400	.397	.391	.370
.5	.371	.395	.390	.382	.363
.6	.367	.391	.386	.378	.360
.7	.365	.390	.384	.376	.359
.8	.367	.390	.384	.375	.360
.9	.371	.391	.386	.375	.362
1.0	.377	.395	.389	.381	.365
1.1	.381	.399	.393	.385	.370
1.2	.389	.405	.399	.392	.375
1.3	.395	.411	.404	.395	.378
1.4	.402	.417	.411	.401	.383
1.5	.410	.425	.417	.409	.390
1.6	-	.433	.425	.417	.397
1.7	-	-	.434	.423	.404
1.8	-	-	-	-	.424

Constants of Equation (2)

N	1.9294	2.3214	2.3306	2.4047	2.1749
a (Å.)	3.43	4.10	4.09	4.20	3.77
P	0.1575	0.1293	0.1318	0.1188	0.1596

The N of equation (2) is related to the Hückel constant A by the equation $N = \sqrt{6} A$. The mean distance of approach of the ions " a " was computed from the equation $a = Ax$ employing the values of x given in Table IV of Harned and Hecker.^{11a} The results of these computations are listed in Table III. The value of " a " while not exactly constant may be considered so within experimental error and to have a value of 3.9 Å. The low values at 0 and 45° are accompanied by an increase in the P constant which is proportional to $1/a$.

The value of γ for the 0.01 M solution at 25° is 0.723. This is in agreement with all calculations based on Lucasse's data.^{4,8,12,13} This agreement is considered significant because Lucasse's data extend to 0.01 M while the data of this investigation extend only to 0.05 M . The value of 0.716 calculated by Lewis and Linhart¹⁴ from the freezing point measurements of Hall and Harkins,¹⁵

(11) Harned and Hecker, (a) THIS JOURNAL, **55**, 4838 (1933); (b) *ibid.*, **56**, 650 (1934).

(12) Scatchard and Tefft, *ibid.*, **52**, 2272 (1930).

(13) Harned, *ibid.*, **48**, 326 (1926).

(14) Lewis and Linhart, *ibid.*, **41**, 1952 (1919).

(15) Hall and Harkins, *ibid.*, **38**, 2658 (1916).

TABLE IV
RELATIVE PARTIAL MOLAL HEAT CONTENT OF BARIUM CHLORIDE

<i>m</i>	\bar{L}_2 (cal./mole)				
	0°	15°	25°	35°	45°
0.01	-200	+60	+275	+505	+725
.05	-930	-150	+450	+1085	+1710
.1	-1490	-340	+525	+1430	+2330
.2	-2100	-550	+580	+1770	+2965
.3	-2430	-675	+600	+1935	+3285
.4	-2595	-745	+605	+2010	+3435
.5	-2670	-775	+605	+2035	+3490
.6	-2650	-775	+610	+2035	+3470
.7	-2590	-750	+610	+2005	+3410
.8	-2450	-670	+630	+1985	+3340
.9	-2320	-580	+660	+1965	+3260
1.0	-2130	-490	+700	+1945	+3190
1.1	-1980	-425	+720	+1925	+3120
1.2	-1880	-365	+750	+1915	+3070
1.3	-1780	-305	+770	+1905	+3030
1.4	-1700	-270	+780	+1895	+2990
1.5	-1650	-240	+790	+1875	+2970

Constants of Equation (9)

$K \times 10^{-4}$	-6.15	-3.08	-0.39	2.46	4.88
$K' \times 10^{-3}$	4.38	1.20	-0.23	-1.64	-3.55

differs somewhat from the corresponding value 0.725 of this investigation at 0°. It is to be noticed that the activity coefficient for constant composition varies appreciably with temperature, and shows the highest value at 15°, in accord with the preliminary indications that γ passes through a maximum.

The Relative Partial Molal Heat Content

Harned and Hecker¹¹ have developed a method for extrapolating heat data to infinite dilution. In the case of sodium hydroxide their results agree closely with the calorimetric data. Their method has been adopted here.

The partial molal heat content relative to the 0.05 M solution was computed by the Gibbs-Helmholtz equation

$$(\bar{H}_m - \bar{H}_{0.05}) = NF(E - TdE/dT) \quad (8)$$

The $(\bar{H}_m - \bar{H}_{0.05})$ quantities were computed from equation (8), using equation (7) and the constants *a*, *b* and *c* of Table II for evaluating the temperature coefficients. The average deviation of the quantities given by equation (8) from a smooth curve is ± 50 cal., and the maximum deviation is ± 100 cal. As stated by Harned and Hecker,^{11b} this deviation corresponds to an error of less than ± 0.01 mv. in the temperature coefficient.

For extrapolation purposes, the semi-empirical equation

$$\bar{L}_2 = \frac{\nu z_+ z_- L \sqrt{\Gamma}}{1 + A \sqrt{\Gamma}} + \frac{Kc}{(1 + A \sqrt{\Gamma})^2} + K'c \quad (9)$$

of Harned and Hecker was employed. The values of *L* were taken from Table IV of their paper.^{11a}

The final values of \bar{L}_2 are given in Table IV together with the constants of equation (9). \bar{L}_2 as a function of $m^{1/2}$ for the various temperatures is shown in Fig. 1 together with the values of \bar{L}_2 calculated by a suitable graphical method from the calorimetric data of Richards and Dole¹⁶ at 25°. The agreement is excellent but is admitted to be somewhat fortuitous, as it is better than the uncertainty attending the values of \bar{L}_2 from this investigation.

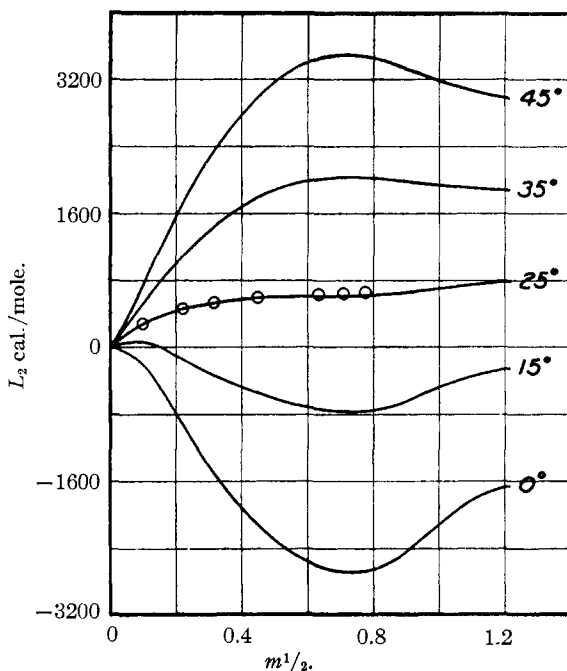


Fig. 1.—The relative partial molal heat content of barium chloride in aqueous solution. (The circles represent points calculated from the calorimetric data of Richards and Dole.)

The Relative Partial Molal Heat Capacity

The smoothed values of *c'* are given in Table II for the purpose of calculating the relative partial molal heat capacity by use of the equation

$$(\bar{C}_p - \bar{C}_{p0.05}) = -2NFTc \quad (10)$$

The value of the temperature coefficient of \bar{L}_2 at 25° amounts to 61 cal./mole deg., which added to the values of $(\bar{C}_p - \bar{C}_{p0.05})$ gives the partial molal heat capacity relative to the infinitely

(16) Richards and Dole, THIS JOURNAL, 51, 794 (1929).

dilute solution. The values of $(\bar{C}_p - \bar{C}_{p0})$ calculated in this manner are in all probability only approximate. It is doubted whether the accuracy of the experimental data warrants the rigorous treatment necessary for this calculation.

Summary

1. Using cells of the type Ba (2-phase amalgam) | BaCl₂ (m) | Hg₂Cl₂ | Hg, e. m. f. measurements have been made at 0, 15, 25, 35 and 45°.

2. A modification of the method of Jones and Dole for the calculation of the constants of the Hückel equation, by the method of least squares, has been developed and applied to the data obtained.

3. Calculations have been made of the activity coefficients, relative partial molal heat contents and heat capacities of barium chloride in aqueous solution.

WEST LAFAYETTE, INDIANA

RECEIVED MAY 7, 1934

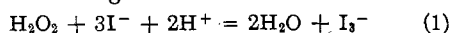
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Kinetics of the Reduction of Hydrogen Peroxide by the Halides

BY ALI MOHAMMAD AND HERMAN A. LIEBHAFSKY

Introduction

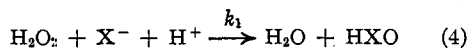
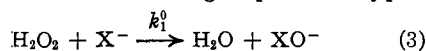
A recent investigation¹ of the reaction



has shown, in agreement with older results, that its rate law has the form

$$-d(\text{H}_2\text{O}_2)/dt = k_1^0(\text{H}_2\text{O}_2)(\text{X}^-) + k_1(\text{H}_2\text{O}_2)(\text{X}^-)(\text{H}^+) \quad (2)^2$$

and this confirms the conclusion that Reaction 1 involves two rate-determining steps of the types



proceeding simultaneously and independently. k_1^0 and k_1 may be measured over a rather large temperature range if suitable experimental conditions are chosen; the equations

$$-d \log k_1^0/d(1/T) = 2943, \text{ and } k_1^0 = 4.91(10^9) e^{-13,400/RT} \text{ from } 0 \text{ to } 50^\circ \quad (5a)$$

$$-d \log k_1/d(1/T) = 2271, \text{ and } k_1 = 4.58(10^8) e^{-10,450/RT} \text{ from } 0 \text{ to } 40^\circ \quad (5b)$$

adequately summarize the accurate experimental results obtained with iodide as reducing agent.¹

Compounds of the halogens often show strikingly analogous kinetic behavior, and it is thus not surprising that the rate laws for the reduction of hydrogen peroxide by bromide and by chloride should each be formally identical with Equation 2. For these halides, however, the specific rates of the steps not involving hydrogen ion (*cf.* Reaction 3) are very much smaller³ than 0.69, the value at 25°

(1) Liebhafsky and Mohammad, *THIS JOURNAL*, **55**, 3977 (1933).

(2) As in previous communications, () will be used to denote concentrations in moles per liter, \longrightarrow will be restricted to reactions that may be rate-determining, and unit time will be the minute. X will be employed as a general symbol for I, Br or Cl.

(3) Liebhafsky has found 2.3 (10^{-6}) (bromide) and 2 (10^{-7})

of k_1^0 for the iodide reaction. Certain difficulties attending the study of these reactions become more marked as the specific rates decrease, and render highly accurate measurements difficult in the case of bromide and impossible in the case of chloride. Nevertheless, we have made measurements involving these halides over a range of temperatures in order that the results might be tabulated with those of Equations 5 to reveal any significant regularities. A complete absence of such regularities where reactions so closely related as these are concerned would indicate that a general theoretical treatment of ionic reactions in solution can scarcely hope for success—in any event, data such as ours are necessary to test whatever theoretical treatment is proposed.

The rates at which bromide and chloride reduce hydrogen peroxide were measured by following the rates at which oxygen was evolved from reaction mixtures in which the steady state had been reached. C. p. sodium salts and perchloric acid, together with concentrated hydrogen peroxide (Merck's "Superoxol"), were employed as reagents. The apparatus and its manipulation have been described previously.⁴ The rate at which a halogen-halide couple decomposes hydrogen peroxide governs the rate at which oxygen is evolved, and is twice the rate at which hydrogen peroxide is reduced at the steady state.⁵ The rate of this reduction we shall write

$$-d(\text{H}_2\text{O}_2)/dt = k'(\text{H}_2\text{O}_2) \quad (6)$$

(chloride) to be provisional values of k_1^0 at 25° for these halides (see Ref. 1, footnote 9).

(4) Liebhafsky, *THIS JOURNAL*, **54**, 1792 (1932).

(5) See, for example, (a) Bray and Livingston, *ibid.*, **45**, 1251 (1923); or (b) Livingston and Bray, *ibid.*, **47**, 2069 (1925); or (c) Abel, *Z. physik. Chem.*, **96**, 1 (1920); or Ref. 4.