slope of our curve covering the same pressure difference, namely, 40 mm. It is apparent that the composition is not a linear function of the pressure under which distillation is accomplished. The same thing is apparent in the work of Roscoe and Dittmar[5] which is the only work covering a long pressure range. The importance of these solutions of constant boiling point is such that this work of Roscoe and Dittmar should be repeated with all possible precision. We hope to undertake this in this Laboratory during the coming year.

Summary

A precise determination of the compositions of hydrochloric acid of constant boiling point is given for pressures near 640 mm. It is pointed out that the composition of these acids is not a linear function of the pressure.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM BROMIDES AND IODIDES IN CONCENTRATED AQUEOUS SOLUTIONS

BY HERBERT S. HARNED AND STUART M. DOUGLAS

RECEIVED AUGUST 9, 1926 PUBLISHED DECEMBER 16, 1926

The activity coefficients of some alkali metal halides have been obtained from measurements of electromotive forces of cells of the type, $Ag \mid AgX \mid MX(m) \mid M_xHg \mid MX(m_0) \mid AgX \mid Ag$, by a number of investigators. Thus, MacInnes and Parker[1] and MacInnes and Beattie[2] have determined the activity coefficients of potassium chloride and lithium chloride in concentrations ranging from 0.01 to 0.5 *M* and from 0.01 to 3 *M*, respectively. Allmand and Polack[3] have measured the activity coefficient of sodium chloride by a similar cell in dilute and concentrated solutions, and Pearce and Hart[4] have studied potassium bromide solutions. With the idea of making these data more complete, we have undertaken an investigation of the activity coefficients of concentrated aqueous solutions of potassium and sodium bromides and potassium and sodium iodides and for this purpose have measured the cells

$$Ag \mid AgBr \mid NaBr(m_2) \mid Na_xHg \mid NaBr(m_1) \mid AgBr \mid Ag$$
$$Ag \mid AgBr \mid KBr(m_2) \mid K_xHg \mid KBr(m_1) \mid AgBr \mid Ag$$
$$Ag \mid AgI \mid NaI(m_2) \mid Na_xHg \mid NaI(m_1) \mid AgI \mid Ag$$
$$Ag \mid AgI \mid KI(m_2) \mid K_xHg \mid KI(m_1) \mid AgI \mid Ag$$

---

[5] Roscoe and Dittmar, *J. Chem. Soc.*, **12**, 128 (1860); *Ann.*, **112**, 343 (1859). Roscoe, *Ann.*, **116**, 213 (1860).

[1] MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

[2] MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).

[3] Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

[4] Pearce and Hart, THIS JOURNAL, **43**, 2483 (1921).

Experimental Part

Potassium and sodium amalgams of 0.01% alkali metals were employed. These were made according to the method frequently described.[1,5]

The salt solutions were prepared by introducing a calculated amount of salt into a weighed flask and adding a slight excess over the calculated amount of water. They were then boiled under reduced pressure and reweighed. Corrections were applied for the loss of water. The solutions were transferred to the cell without exposure to air.

In making the silver-silver bromide electrodes and the silver-silver iodide electrodes, the technique of Noyes and Ellis[6] was followed. A platinum helix sealed through a glass tube was plated with silver and coated with a well-washed silver oxide paste which was converted to spongy silver in an electric furnace at 450°. The bromide electrodes were coated with silver bromide by making them the anodes in a solution of 0.75 *N* hydrobromic acid using a current of 10 ma. each for two hours. The iodide electrodes were made in a similar manner from a fresh hydriodic acid solution which was prepared by slowly dropping water onto a mixture of iodine and red phosphorus and passing the evolved hydriodic acid gas over phosphorus into a weighed amount of distilled water. This solution was disconnected from the generator from time to time and weighed until a solution of the desired strength was obtained. From this solution the silver-silver iodide electrodes were immediately prepared.

The cell was of the type developed by Knobel and by Harned but so modified by Åkerlöf as to permit washing and filling without removal from the thermostat.[5,7]

All traces of air were excluded from the cell solutions and apparatus. Because of this all solutions had to be boiled in a vacuum, and it was there-

Table I

Activity-Coefficient Ratios of Potassium and Sodium Bromides and Iodides at 25°

Sodium Bromide

m_1	m_2	E	ΔE	$E_{\text{corr.}}$	m	$\gamma_m/\gamma_{0.1}$
0.1011	0.03008	−0.05763	+0.00043	−0.0572	0.03	1.095
.1046	.05065	− .03432	+ .00165	− .0327	.05	1.059
.1	.1	.00000	.00000	.0000	.1	1.000
.1010	.3052	.05276	.00051	.0524	.3	0.924
.1027	.5038	.07631	.00101	.0773	.5	.901
.1010	1.011	.11239	− .00005	.1123	1	.880
.1046	1.544	.13374	.00083	.1345	1.5	.915
.1015	2.032	.15086	− .00005	.1508	2	.941
.1021	2.569	.16620	− .00033	.1659	2.5	1.009
.1002	3.021	.17818	− .00026	.1779	3	1.064

---

[5] (a) Knobel, This Journal, **45**, 70 (1923). (b) Harned, *ibid.*, **47**, 676 (1925).

[6] Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[7] Åkerlöf, *ibid.*, **48**, 1160 (1926).

TABLE I (*Concluded*)

m_1	m_2	E	ΔE	$E_{\text{corr.}}$	m	$\gamma_m/\gamma_{0.1}$
		POTASSIUM BROMIDE				
.1012	0.0505	− .03224	− .00015	− .0324	.05	1.064
.1	.1	.00000	.00000	.0000	.1	1.000
.1009	.3028	.05133	− .00002	.0513	.3	0.905
.1026	.5158	.07492	− .00028	.0746[a]	.5	.855
.1012	1.007	.10656	.00026	.1068[a]	1	.799
.1007	1.516	.12684	− .00019	.1266	1.5	.784
.1004	2.000	.14081	.00020	.1410	2	.778
.1010	2.512	.15284	.00027	.1531	2.5	.787
		SODIUM IODIDE				
.1037	.0307	− .05791	+ .00069	− .0572	.03	1.094
.1	.1	.00000	.00000	.0000	.1	1.000
.1008	.3020	.05360	.00009	.0537	.3	0.946
.1003	.4970	.07818	.00046	.0786	.5	.924
.0997	1.003	.11500	− .00031	.1147	1.1	.932
		POTASSIUM IODIDE				
.1	0.1	.00000	.00000	.0000	0.1	1.000
.1008	.3017	.05204	.00015	.0522	.3	0.920
.1020	.5103	.07587	− .00004	.0758	.5	.875
.1052	1.017	.10747	.00174	.1092	1.0	.837
.0988	2.004	.14532	− .00074	.1447	2.0	.834

[a] Pearce and Hart obtained 0.0750 and 0.1066 for these cells, respectively.

fore impracticable to attempt to obtain values of m_1 and m_2 at exactly round concentrations. Corrections to round concentrations were made upon the assumption that over the small concentration ranges involved, the activity coefficients were constant. To this end, the equations

$$\Delta E = 0.1183 \log (m_1/0.1);\ \Delta E = -0.1183 \log (m_2/m) \qquad (1)$$

were employed. Table I contains the experimental data, the correction ΔE, the corrected electromotive forces, $E_{\text{corr.}}$, and the activity coefficients, at round concentrations, m, relative to 0.1 M.

The values of $\gamma_m/\gamma_{0.1}$ were computed by means of the equation

$$E = 0.1183 \log \gamma_m m/\gamma_{0.1}\, 0.1 \qquad (2)$$

Calculation of the Activity Coefficients

In order to obtain the activity coefficients from the electromotive-force data, we have employed Hückel's equation,[8]

$$\log \gamma = -\frac{0.354\sqrt{2c}}{1 + A\sqrt{2c}} + B(2c) - \log (1 + 0.036\ m) \qquad (3)$$

were c is the normal concentration, m the molal concentration and A and B are constants. The constants A and B were evaluated from the electromotive force data by the method employed by Hückel (p. 123).[9] The

---

[8] Hückel, *Physik. Z.*, **26**, 93 (1925).

[9] See also (a) Scatchard, THIS JOURNAL, **47**, 2098 (1925). (b) Harned, *ibid.*, **48**, 326 (1926). (c) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

values of the electromotive forces used for this calculation were read off large scale plots of the data in Table I. This calculation was made only in the cases of the bromide solutions where accurate data were available over a considerable concentration range. Since it is more difficult to obtain accurate values with the iodide solutions and since the high solubility of silver iodide in the alkali metal iodide solution above 1 *M* throws some doubt on the accuracy of these measurements above this concentration, we have not calculated the results by Equation 3.

The results of the calculation of the bromide solutions are compiled in Table II. The first and second columns contain the normal and molal concentrations. The third column contains the activity coefficients calculated from the activity coefficient ratios in Table I and the calculated values of 0.783 and 0.768 for the activity coefficients of sodium bromide and potassium bromide, respectively, at 0.1 *M* concentration. The fourth column contains the values of γ calculated by Equation 3 using the constants given in Table II. The fifth column contains the deviations in millivolts of the calculated from the observed values.

TABLE II

OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS OF POTASSIUM AND SODIUM BROMIDES AT 25°

SODIUM BROMIDE

$A = 0.915 \quad B = 0.04$

c	m	γ (obs.)	γ (calcd.)	Deviations in mv.
0.03	0.03	0.858	0.853	0.29
.0499	.05	.829	.825	.25
.0997	.1	(.783)	(.783)	.0
.2975	.3	.723	.723	.0
.494	.5	.705	.704	.07
.978	1	.697	.701	− .29
1.43	1.5	.716	.714	.14
1.895	2	.737	.747	− .68
2.34	2.5	.790	.781	.56
2.775	3	.832	.819	.80

POTASSIUM BROMIDE

$A = 0.78 \quad B = 0.022$

c	m	γ (obs.)	γ (calcd.)	Deviations in mv.
0.0499	0.05	0.816	0.816	0.0
.0996	.1	(.768)	(.768)	.0
.296	.3	.695	.689	.45
.490	.5	.656	.655	.08
.962	1	.613	.618	.41
1.409	1.5	.602	.605	− .25
1.86	2	.598	.601	− .34
2.287	2.5	.604	.602	.16

Since we find that the activity coefficients of these four salts are greater at a given concentration in the order potassium bromide, potassium iodide, sodium bromide, sodium iodide, we have arbitrarily selected 0.775 and 0.788

for the activity coefficients of potassium iodide and sodium iodide, respectively, at 0.1 *M*. These must be very nearly correct since the first lies about half way between the values for potassium bromide and sodium bromide, and the second lies somewhat higher than the activity coefficient of sodium bromide at this concentration. By employing these values at 0.1 *M* concentration, the values of γ of sodium iodide and potassium iodide were computed from the activity coefficient ratios in Table I. These are given in Table III.

TABLE III

ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM IODIDES AT 25°

m	0.03	0.1	0.3	0.5	1	2
NaI, γ	.861	(.788)	.746	.721	0.734	...
KI, γ	...	(.775)	.715	.678	.649	0.646 (?)

Discussion

In Fig. 1, the values of γ given in Tables II and III are plotted against the square root of the molality as well as corresponding values for potassium

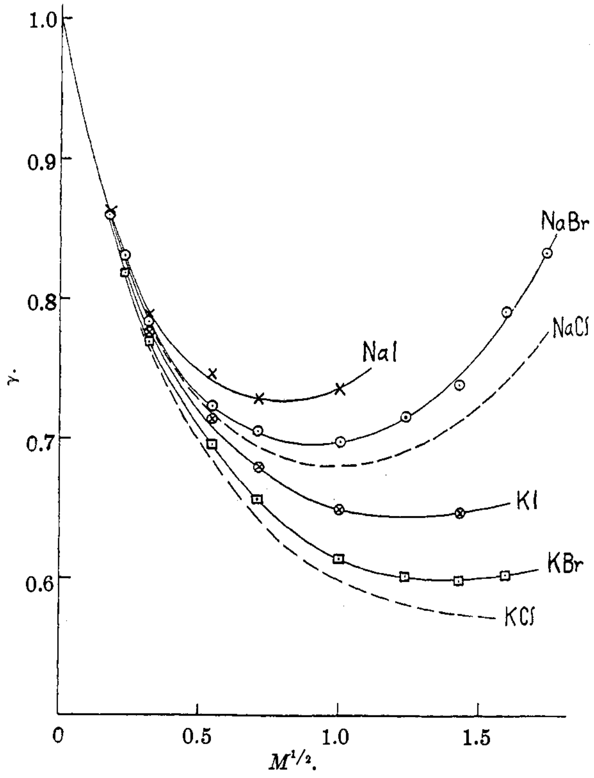

Fig. 1.—The activity coefficients of sodium and potassium bromides and iodides.

and sodium chlorides (shown by dashed lines). It is seen that in both cases, the activity coefficient of the iodide is higher than that of the bromide at a given concentration. It is also true that the activity coefficient of the bromide is higher than that of the corresponding chloride, and that the activity coefficients of the halogen acids are greater in the order hydrochloric, hydrobromic, hydriodic at a given concentration. This very simple fact is of considerable importance when we come to consider the theoretical aspects of concentrated halide solutions.

We may state the above group of facts in the following simple manner: $\gamma_{Li} > \gamma_{Na} > \gamma_K$ and $\gamma_I > \gamma_{Br} > \gamma_{Cl}$. That is to say, the activity coefficients of the alkali metal ions decrease, those of the halide ions increase with the number of electron layers in their structure. It would seem that a clue to an important factor for the answer to this interesting problem may be found by considering the effects of the halide electrolytes and their ions on the solvent. It has been found[6,10] that at a given concentration of salt, the electrolyte which possesses the greatest activity coefficient at a given concentration causes the greatest dissociation of water into hydrogen and hydroxyl ions. We may think of this in terms of the influence of the ions in deforming the water molecules to different extents. Those ions which would cause the least expansion of the water molecules would dissociate them to the least extent. That the actual deformation brought about by the ions may be considerable is witnessed by the thermodynamic behavior of the hydroxyl ion, which if the theory discussed by Harned and Åkerlöf[9c] is correct can be deformed to considerably different extents in the presence of the different ions.

If such a deformation of the water molecules takes place, that electrolyte which produces the greatest dissociation of water should cause the least contraction of the water molecules by its solution in water. It is difficult to judge this matter exactly but in general this seems to be the case. According to the data of Baxter and Wallace,[11] all the halides cause a contraction in forming the solution except lithium bromide and iodide. These latter cause an expansion which is in very good accord with our conception of the phenomenon. However, the values of the contraction effects produced by the ions do not in all cases parallel the expected behavior. From Baxter and Wallace's data, we may say that the contraction is greater in the order iodide, bromide, chloride ions in all cases and lithium, sodium and potassium in the cases of the iodide solutions. This agrees well with our prediction. In chloride solutions, however, the effect is in the order lithium, potassium, sodium ions, and in bromide solutions in the order lithium, sodium, which latter produces nearly the same effect as the potas-

---

[10] Harned, This Journal, **47**, 930 (1925). Harned and Swindells, *ibid.*, **48**, 126 (1926). Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

[11] Baxter and Wallace, This Journal, **38**, 70 (1916).

sium ion. This discrepancy is not so surprising since we should hardly expect the deformation of the water to be the only cause of the contraction or expansion.

Thus, we find that the increase in activity coefficients of the halide ions in a concentrated solution of a given strength parallels the effect of the ions on the dissociation of water and also approximately the effect on the contraction or expansion of the water molecule. These facts lead us to the conclusion that the specific action of the ions in deforming the water molecules plays a very important role in determining the free energy and activity coefficient of an ion.

Summary

1. The activity coefficients at 25° of potassium bromide, sodium bromide, potassium iodide, and sodium iodide at high concentrations as determined from the electromotive forces of suitable cells are presented.

2. A comparison of the activity coefficients of the alkali halides in aqueous solutions with the effects they produce on the electrolytic dissociation of water, and also with the contraction effects produced by the solution of these electrolytes in water, leads to the conclusion that the specific deformability of the water molecules brought about by the electrical fields of the different ions is an important factor in determining the differences in free energies of the ions in concentrated solutions.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CRYOGENIC RESEARCH LABORATORY OF THE BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE CALIBRATION OF RESISTANCE THERMOMETERS AT THE OXYGEN BOILING POINT AND THE CARBON DIOXIDE SUBLIMATION POINT[1]

BY A. G. LOOMIS AND J. E. WALTERS

RECEIVED AUGUST 11, 1926 PUBLISHED DECEMBER 16, 1926

Introduction

It has now been well established that the temperature scale to —193° may be accurately defined in terms of platinum-resistance thermometers, and that pure platinum as a thermometric resistance wire is entirely reproducible when used under strain-free conditions at low temperatures.[2] To express the temperature in terms of the resistance of platinum wire we may employ the equation of Henning and Heuse,[2] $R = r/r_0 = 1 + at$

---

[1] Published with the approval of the Director, U. S. Bureau of Mines.

[2] Henning, *Ann. Physik,* [4] **40,** 635 (1913). Also *Z. Instrumentenk.,* **44,** 349 (1924). Henning and Heuse, *Z. Physik,* **23,** 95 (1924). Also Heuse, *ibid.,* **37,** 157 (1926). Van Dusen, THIS JOURNAL, **47,** 326 (1925). Loomis and Walters, *ibid.,* **47,** 2851 (1925).