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

THE ELECTROMOTIVE FORCES OF UNI-UNIVALENT HALIDES IN CONCENTRATED AQUEOUS SOLUTIONS

BY HERBERT S. HARNED

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Measurements of flowing amalgam cells of the type

$$\mathrm{Ag} \mid \mathrm{AgX} \mid \mathrm{MX}(m_2) \mid \mathrm{M_xHg} \mid \mathrm{MX}(m_1) \mid \mathrm{AgX} \mid \mathrm{Ag}$$

in which MX is an alkaline halide, have been made by a number of investigators.[1] Accurate results of this character are of fundamental importance since they measure the partial free energy of the solute relative to a given concentration directly, and thus afford a means of computing the activity coefficients. Further, these electromotive forces are of considerable use for the calculation of other quantities, as, for example, the dissociation of water in salt solutions.[2] For these reasons, a more searching, precise and thorough study than heretofore made of the cells containing potassium and sodium chlorides and bromides will be presented, as well as results of less accuracy with cells containing lithium chloride and bromide. Certain experimental difficulties which were encountered will be pointed out and the concentration range in which these measurements may be expected to be valid will be indicated.

Materials and Electrodes.—The mercury employed was distilled three or more times. All the salts were purified by recrystallization of high grade analyzed chemicals. The sodium and potassium chlorides were precipitated by hydrochloric acid gas and then fused. The recrystallized sodium and potassium bromides were dried for two days or more at a temperature of 200–250°. Solutions of these salts were made by direct weighing of both salt and water. Concentrated solutions (approximately 12 *M*) of lithium chloride and bromide were made from the recrystallized salts and analyzed gravimetrically. These stock solutions were diluted to the desired strength by mixing with the required weight of water.

The amalgams of potassium and sodium were made by the method described by Harned[3] and always contained approximately 0.01% of the alkali metal. Lithium amalgam of approximately 0.003% as recommended by Harned and Swindells[4] was employed. It was made by the electrolysis of a solution of the hydroxide. We have never encountered serious difficulties in the use of sodium or potassium amalgams. Lithium amalgam, however, is much more difficult to control and consequently results obtained with it are considerably less reliable than those obtained with the sodium and potassium amalgams.

Three kinds of silver-silver chloride electrodes have been employed. Type 1.

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[1] (a) MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915); (b) MacInnes and Beattie, *ibid.*, **42**, 1117 (1920); (c) Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919); (d) Pearce and Hart, THIS JOURNAL, **43**, 2483 (1921); (e) Harned and Douglas, *ibid.*, **48**, 3095 (1926).

[2] Harned, *ibid.*, **47**, 930 (1925).

[3] Harned, *ibid.*, **47**, 676 (1925).

[4] Harned and Swindells, *ibid.*, **48**, 126 (1926).

A platinum spiral filled with a paste of silver oxide was heated to 450°. The silver electrode thus obtained was surrounded by crystalline silver chloride, obtained by the slow evaporation over sulfuric acid of an ammoniacal silver chloride solution. This type of crystalline silver chloride was recommended by Güntelberg[5] for this purpose. Type 2. A platinum spiral which held silver obtained from heating the oxide paste was made the anode in a normal hydrochloric acid solution and the chloride was formed by slow electrolysis at low current densities (20 ma. per cc. electrode for two hours). Type 3. These electrodes were the same as recommended by Noyes and Ellis,[6] and were the same as Type 2 with the exception that a layer of electrolytic silver was deposited upon the spiral by electrolysis of a potassium silver cyanide solution before the silver oxide paste was put on.

Apparatus and Methods of Measurement.—The cell finally employed (Fig. 1) was of a very simple design. It could be filled readily through the tubes DD with solutions which had been previously boiled *in vacuo*. It also could be completely emptied by suction through the outlets OO. This method of filling and emptying the apparatus has been sufficiently described elsewhere.[7] A Type 1 electrode is represented by C. A small ball of glass wool at the narrow opening in the tube was used to hold the crystalline silver chloride. Electrodes of Types 2 and 3 are represented by A. In the actual measurements, electrodes of the same type were used in each of the two cell compartments. The stopcocks SS which had to be manipulated during the course of a measurement are shown to contain grease cups at the two ends. By filling these with a rubber–vaseline–paraffin mixture, they could be manipulated under the water in the thermostat without danger of electrical leakage. The amalgam reservoirs, B, were of the design used by MacInnes and Beattie. In the cases of potassium and sodium chlorides and bromides, and lithium bromide, three amalgam reservoirs were employed. A measurement would be made with the first, then the cell emptied and refilled with the same solution. The second amalgam reservoir was then introduced and another measurement obtained. This manipulation was repeated until all three amalgam reservoirs were used. Reservoir No. 1 delivered 1 cc. of amalgam in fifteen seconds from the left capillary and 1 cc. in twenty-five seconds from the right capillary. Reservoir No. 2 delivered 1 cc. in fifteen seconds from both capillaries. Reservoir No. 3 delivered 1 cc. in twenty-five seconds from the left and the same amount from the right capillary in fifteen seconds. Two ways of forming the amalgam electrodes were employed when using potassium and sodium amalgams. One was to allow the jets of amalgam from the capillaries to break in the solution. This could be done by removing the amal-

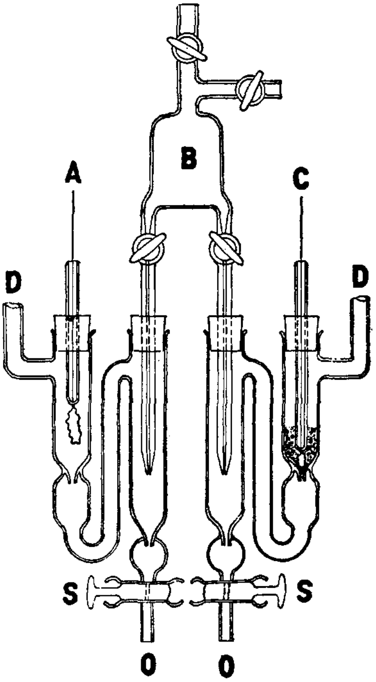

Fig. 1.

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[5] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

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

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

gam quite rapidly through the stopcocks SS. The second way was to form pools of mercury in the electrode vessels by removing the amalgam comparatively slowly at first through SS. The jets from the capillaries were allowed to flow without breaking into the pools of amalgam. This allowed a large amalgam surface. When using potassium and sodium amalgams *both these methods of manipulation gave identical results.* Owing to the high reactivity of lithium amalgam, the pool method was never successful. The first method of the free flowing jet was always employed, but even this was difficult because of the manner in which the lithium amalgam stuck to the sides of the glass walls. Although results were obtainable which could be reproduced to within ±0.3 mv., they were always somewhat erratic. Other forms of amalgam reservoirs with specially designed capillary delivery tubes were tried but none of these was sufficiently applicable to warrant further description. Such a specially designed apparatus was used in the case of some of the lithium chloride cells.

Experimental Results

1. Potassium Chloride.—The most extensive series of measurements was obtained with the cells containing potassium chloride. The three amalgam reservoirs as well as the three types of silver–silver chloride electrodes were employed. In Table I are given the results with the crystalline silver chloride electrodes of Type 1. Two series were obtained without changing the silver chloride electrodes. One compartment of the cell was filled with 0.1 *M* potassium chloride and the other compartment contained the solutions of varying strengths. The first series was started

Table I

Electromotive Forces of the Cells

Ag | AgCl | KCl(m) | K_xHg | KCl(0.1) | AgCl | Ag

Type 1. Silver–silver chloride electrodes. $t = 25°$

m	No. 1	No. 2	No. 3	Δ_I (mv.)	No. 1	No. 2	No. 3	Δ_{II} (mv.)	M_I	M_{II}	*M*	Δ (mv.)
0.01	−0.10885	−0.10902	−0.10906	0.21	−0.10909	−0.10919	−0.10912	0.10	−0.10898	−0.10913	−0.10906	0.15
.02	− .07562	− .07558	− .07569	.11	− .07550	− .07561	− .07556	.11	− .07563	− .07556	− .07559	.06
.05	− .03220	− .03228	− .03227	.08	− .03227	− .03233	− .03227	.06	− .03225	− .03229	− .03227	.04
.1	.00000	.00000	.00000	.00	.00000	.00000	.00000	.00	.00000	.00000	.00000	.00
.2	.03199	.03196	.03201	.05	.03197	.03202	.03193	.09	.03199	.03197	.03198	.02
.5	.07394	.07397	.07389	.08	.07391	.07387	.07381	.10	.07393	.07387	.07390	.06
1	.10562	.10555	.10556	.07	.10558	.10564	.10562	.06	.10558	.10561	.10559	.03
2	.13888	.13880	.13880	.08	.13880	.13876	.13876	.04	.13883	.13877	.13880	.06
3	.15993	.15962	.15983	.31	.15981	.15984	.15972	.12	.15979	.15979	.15979	.00
4	.17537	.17556	.17547	.19	.17539	.17546	.17545	.07	.17547	.17543	.17545	.04

with the solutions of the lowest concentration and three measurements were taken with the three different amalgam droppers (denoted by Nos. 1, 2 and 3). The solution of the next concentration was then introduced and three measurements were taken. This was repeated through Series I. Then the process was reversed and measurements were taken first with the most concentrated and then with the solution of the next lower strength. The second, third and fourth columns contain the electromotive forces of Series I and the next column the total deviation of this series. Series II is exactly similar. The columns headed M_{I} and M_{II} are the mean values of the first and second series, respectively, and Δ is the total deviation of these mean values. The next to last column contains the mean of all the results.

The results of cells containing the 0.01 or 0.02 molal solutions were much more difficult to obtain. The electromotive force of the 0.01–0.1 *M* cell checked the values obtained by MacInnes and Parker fairly closely. There is considerable doubt as to whether these results are correct. Indeed, Lewis and Randall thought that unavoidable side reactions caused difficulties with these cells, and this opinion has been borne out by more recent investigations. Care therefore should be exercised in attempting to employ these results. On the other hand, the entire cell mechanism works more steadily with solutions of 0.05 *M* and above so that this series is reliable at concentrations of 0.1 *M* and higher. The average deviation between Series I and II in the concentration range of from 0.02 to 4 *M* is 0.04 mv. This is good if it is possible to obtain the same result with other types of silver–silver chloride electrodes.

Table II contains the electromotive forces of the same cells obtained with Type 2 and Type 3 electrodes as well as the mean values of the results with Type 1 electrodes. Those with Type 3 electrodes were obtained by Harned and Douglas and were only single measurements. The measurements obtained with Type 2 electrodes are recent and were made with the

TABLE II

ELECTROMOTIVE FORCES OF CELLS

$Ag \mid AgCl \mid KCl(m) \mid K_xHg \mid KCl(0.1) \mid AgCl \mid Ag$

M	Type 3, Noyes and Ellis	No.	Type 2	Δ (mv.)	Type 1	*M*
0.1	0.0000	0	0.00000	..	0.00000	0.00000
.2	.0320	0	.....	..	.03198	.03198
.5	.0739	0	.....	..	.07390	.07390
1	.1056	3	.10570	0.10	.10559	.10565
1.5	....	3	.12459	.08	.....	.12459
2	.1389	3	.13874	.04	.13880	.13877
2.5	....	3	.15018	.07	.....	.15018
3	.1599	3	.15972	.02	.16979	.15976
3.5	....	3	.16772	.11	.....	.16772
4	.1755	3	.17538	.08	.17545	.17541

three different amalgam droppers. A freshly prepared spiral electrode which had been equilibrated with the cell solution for about two hours was used for each measurement. In Col. 3 the number of results obtained with electrodes of Type 2 are given and in Col. 5 their total deviation in millivolts. It is to be observed that the difference in millivolts between the series with Type 1 and Type 2 silver–silver chloride electrodes is 0.11, 0.06, 0.07 and 0.07 mv. in the cells containing the 1, 2, 3 and 4 *M* solutions, respectively. The results with Type 2 electrodes are all slightly lower than those with Type 1. Further, the agreement with the Noyes and Ellis electrodes (Type 3) is very good.

2. Potassium Bromide, Sodium Chloride and Sodium Bromide.—Cells containing potassium bromide have been previously measured by Pearce and Hart[1d] and Harned and Douglas.[1e] A few results of less accuracy were obtained by Allmand and Polack[1c] from measurements of cells containing sodium chloride. Harned and Douglas also measured the cells containing sodium bromide. The measurements given in Table III are far more extensive and accurate than those previously obtained. Spiral electrodes of Types 2 and 3 were employed. Type 2 electrodes were employed in the case of all three salts. Type 3 or the Noyes and Ellis type were employed in the case of some of the sodium chloride results. This is indicated in the table. A freshly made silver–silver chloride or silver–silver bromide electrode was used in each run of three results.

These electrodes were placed in the cells and in the cell solutions for periods of from three to five hours before readings were taken. In the case of the silver–silver chloride electrodes constant and reproducible values were obtained within two to three hours. Silver–silver bromide electrodes took somewhat longer to equilibrate. For example, cells of the type

$$H_2 \mid HBr \mid AgBr \mid Ag$$

take about four hours to reach a constant and reproducible electromotive force. This remains constant for from four to ten hours and then slowly decreases. In the present investigation the solution and electrode were kept in contact from four to five hours before the first measurement. Removal of the solution and immediate refilling could be carried out without considerably affecting the electromotive force. Consequently, the second and third measurements were carried out within ten to twenty minutes after the first one.

The first column of the table gives the molal salt concentrations, the columns headed "No." contain the number of determinations, the columns *E* contain the mean electromotive forces and those headed Δ (mv.) the total deviations in millivolts. In the case of potassium bromide these results check those obtained by Harned and Douglas well at the lower concentrations. Thus they obtained −0.0324, 0.0746, 0.1068, 0.1266 and 0.1410 at concentrations of 0.05, 0.5, 1, 1.5 and 2 molal, which compare favor-

TABLE III

ELECTROMOTIVE FORCES OF THE CELLS $Ag \mid AgX \mid MX(m) \mid M_xHg \mid MX(0.1) \mid AgX \mid Ag$ CONTAINING POTASSIUM BROMIDE, SODIUM CHLORIDE AND SODIUM BROMIDE. $t = 25°$

	MX = KBr; M = K			MX = NaCl; M = Na			MX = NaBr; M = Na		
m	No.	E	Δ (mv.)	No.	E	Δ (mv.)	No.	E	Δ (mv.)
0.05	9	−0.03232	0.14	.	.....	..	.	.....	..
0.1	.	.00000	..	.	0.00000	..	.	0.00000	..
0.2	6	.03214	.20	8	.03247	0.19	6	.03274	0.12
0.5	6	.07455	.13	6	.07566	.15	6	.07691	.11
1	6	.10687	.09	6	.10957[a]	.14	6	.11183	.11
1.5	3	.12620	.02	10	.13033[a]	.16	6	.13332	.24
2	6	.14045	.17	9	.14621[a]	.20	6	.15070	.21
2.49	3	.15162	.08	.	.....	..	.	.....	..
2.5	3	.15193	.10	3	.15923	.15	6	.16500	.31
3	9	.16143	.31	6	.17037	.07	6	.17756	.22
3.5	5	.17008	.20	3	.18188[b]	.10	6	.18842	.30
4	6	.17784	.26	6	.19079[a]	.08	6	.19877	.23

[a] Three were obtained with Type 3 electrode.

[b] One was obtained with Type 3 electrode.

ably with those given in Table III. In the case of the cells containing sodium bromide, they obtained 0.0773, 0.1123, 0.1345, 0.1508, 0.1659 and 0.1779 at 0.5, 1, 1.5, 2, 2.5 and 3 molal salt concentrations, which agree fairly well with the later results. The total deviations of the results are seen to be within 0.3 millivolt. We regard this as very good since the cell mechanism is complicated, since the conditions of flow of the amalgam were varied in each case and since new silver–silver halide electrodes were made for each run of three or less results. It has been our experience that results of very high consistency may be obtained by performing each operation in exactly the same manner. We do not believe that results thus obtained are necessarily the correct reversible electromotive forces. We have, therefore, preferred to sacrifice consistency by varying the cell mechanism in the ways previously described.

3. Lithium Chloride and Bromide.—In Table IV are given the results obtained with lithium amalgams. Since we were never able to obtain as steady readings with these as with the sodium or potassium amalgams, we regard the results as having approximately an accuracy of ± 0.2 mv. up to 2 molal. In the case of cells containing salt at higher concentrations than this, the accuracy decreases. We obtained 0.1168 and 0.1958 volt with cells containing lithium chloride at 1 and 3 molal concentrations, respectively, which agree fairly well with 0.1165 and 0.1954 previously determined by MacInnes and Beattie. Since all the electrodes were prepared in an entirely different manner from that employed by these investigators, the result is encouraging.

One possible source of error which is independent of the mechanism and operation of these cells remains to be discussed. In concentrated

TABLE IV

ELECTROMOTIVE FORCES OF THE CELLS Ag | AgX | MX(m) | M_4Hg | MX(0.1) | AgX | Ag CONTAINING LITHIUM CHLORIDE AND LITHIUM BROMIDE. $t = 25°$

	MX = LiCl; M = Li			MX = LiBr; M = Li		
m	No.	*E*	Δ (mv.)	No.	*E*	Δ (mv.)
0.1	.	0.0000	0.0	4	0.0000	0.0
.2	5	.0336	.1	4	.0340	.2
.5	3	.0790	.2	3	.0803	.3
1	3	.1168	.2	3	.1191	.1
1.5	1	(.1417)	...	3	.1444	.6
2	3	.1624	.4	3	.1657	.2
2.5	1	(.1802)	...	3	.1845	.3
3	3	.1958	.5	3	.1998	1.0
3.5	1	(.2112)	...	3	.2160	1.0
4	3	.2250	.2	3	.2324	1.3

In the lithium chloride series the results in parentheses were found with Type 2 silver–silver chloride electrodes. All others were made with Type 1 electrodes. All lithium bromide results were obtained with Type 2 electrodes.

salt solutions the solubility of the silver halides increases rapidly with the salt concentration. The solubility of silver chloride in potassium, sodium and lithium chlorides is not sufficient to cause any error greater than the experimental error of these measurements. On the other hand, the solubility of silver bromide in the corresponding salt solutions is sufficient to cause an error in the solutions of 2 *M* salt concentration and higher. Thus, from the data of Hellwig,[8] we find that in a 3 *M* potassium bromide solution enough silver bromide will be dissolved to cause a maximum error of 0.3 mv. either by reason of its adding bromide ion to the solution or removing bromide ion due to complex formation. This error will be greater in the cases of sodium and lithium bromides. We do not believe that the amalgam electrodes were affected by any silver which may have diffused into the amalgam compartment of the cells. This was shown by the fact that the solution could be removed from the cell, a fresh one introduced and the same result obtained from a measurement taken before diffusion could have taken place. The effect of the solubility of silver iodide in the iodide solutions upon the electromotive force of such cells was pointed out by Harned and Douglas to be of such a magnitude as to render the result uncertain when the iodide solutions were more concentrated than 1 molal.

A Discussion of the Electromotive Forces of Halide Solutions.—In Table V, Part I, the electromotive forces of concentration cells without liquid junction containing the electrolyte at 0.1 *M* and 1 *M* concentrations in the two compartments are compiled.

As a first attempt to consider these results, MacInnes[9] and Harned[10]

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[8] Hellwig, *Z. anorg. Chem.*, **25**, 183 (1900).

[9] MacInnes, THIS JOURNAL, **41**, 1086 (1919).

[10] Harned, *ibid.*, **42**, 1808 (1920).

TABLE V

PART I. ELECTROMOTIVE FORCES OF THE CELLS

$\mathrm{Ag} \mid \mathrm{AgX} \mid \mathrm{MX(1)} \mid \mathrm{M_xHg} \mid \mathrm{MX(0.1)} \mid \mathrm{AgX} \mid \mathrm{Ag}$

$\mathrm{Ag} \mid \mathrm{AgX} \mid \mathrm{HX(1)} \mid \mathrm{H_2} \mid \mathrm{HX(0.1)} \mid \mathrm{AgX} \mid \mathrm{Ag}$

M = Li, Na or K X = Cl, Br or I

Electrolyte	KCl	NaCl	LiCl	HCl	KBr
E	0.10565	0.10957	0.1168	0.1195[a]	0.10687
Electrolyte	NaBr	LiBr	HBr[b]	KI[c]	NaI[c]
E	0.11183	0.1191	0.1227	0.1092	0.1147

[a] Scatchard, THIS JOURNAL, **47**, 2098 (1925); Harned, *ibid.*, **48**, 326 (1926).

[b] Unpublished measurements obtained with air-free HBr solutions by Dr. Geoffrey M. James.

[c] Harned and Douglas, ref. 1e.

PART II. DIFFERENCES IN MILLIVOLTS OF ABOVE CELLS

$\Delta = E_{\mathrm{KBr}} - E_{\mathrm{KCl}}, E_{\mathrm{NaCl}} - E_{\mathrm{KCl}}$, etc.

		Δ		Δ	
	KCl	1.3	KBr	2.3	KI
Δ	4.0		5.0		5.5
	NaCl	2.2	NaBr	2.9	NaI
Δ	7.2		7.3		
	LiCl	2.3	LiBr		...
Δ	2.7		3.6		
	HCl	3.2	HBr		...

PART III. SIMILAR DIFFERENCES FOR CELLS CONTAINING 0.1 *M* AND 2 *M* SALT CONCNS.

KCl	1.7	KBr	4.2	KI
7.4		10.3		
NaCl	4.5	NaBr		...
16.2		14.4		
LiCl	3.3	LiBr		...
3.9		8.2		
HCl	7.0	HBr		...

proposed a tentative postulate which was the equivalent of the assumption that the electromotive forces of the cells under discussion referred to a given concentration should be additive. We are now able to show that this postulate is only a rough approximation, and point out the character of the departure from this postulate. In Part II of Table V are given the differences in millivolts of the cells containing the different salts. Although the differences between bromides and chlorides, sodium and potassium salts, etc., are of the same order of magnitude, there appears to be a uniform deviation from a strict additive relationship.

On the other hand, the deviation is not uniform in the cases of the more concentrated solutions, if we can rely on the results obtained for the cells containing lithium salts. This is illustrated by Part III of the table. Thus it is seen that the difference between lithium and sodium chlorides is greater than that between the corresponding bromides.

The Activity Coefficients of Halides.—In order to obtain the activity coefficients of potassium and sodium chlorides and bromides from the results in Tables II and III we have made use of the method of extrapolation employed by Hückel.[11] By means of the equation

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[11] (a) Hückel, *Physik. Z.*, **26**, 93 (1925); (b) Scatchard, THIS JOURNAL, **47**, 2098 (1925); (c) Harned, *ibid.*, **48**, 326 (1926); (d) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

$$\log \gamma = -\frac{0.356\sqrt{2c}}{1 + A\sqrt{2c}} + B \times 2c - \log (1 + 0.036\, m) \qquad (1)$$

where c is the concentration in normality, m the molal concentration and A and B are constants, it is possible to extrapolate to infinite dilution the data at higher concentrations with a considerable degree of certainty. Having evaluated the constants A and B, the activity coefficients, γ, obtained by Equation 1 may be compared with those obtained from the electromotive force data according to the thermodynamic equation of the cells. Since the results were all obtained by the use of the 0.1 M reference solution, this latter equation is

$$E = 0.1183 \log \frac{\gamma m}{\gamma_{0.1} \times 0.1} \qquad (2)$$

where $\gamma_{0.1}$ is the activity coefficient in 0.1 M solution. The results obtained by the use of these two methods are compiled in Table VI. The values, $\gamma_{\text{obs.}}$, are the activity coefficients computed directly from the electromotive force data by Equation 2, employing the reference values in parenthesis at 0.1 M, and $\gamma_{\text{calcd.}}$ are those computed by Equation 1. The values of A and B employed are given in the lower part of the table.

TABLE VI

CALCULATION OF ACTIVITY COEFFICIENTS OF POTASSIUM AND SODIUM CHLORIDES AND BROMIDES BY HÜCKEL'S EQUATION

m	$\gamma_{\text{obs.}}$(KCl)	$\gamma_{\text{calcd.}}$(KCl)	$\gamma_{\text{obs.}}$(KBr)	$\gamma_{\text{calcd.}}$(KBr)	$\gamma_{\text{obs.}}$(NaCl)	$\gamma_{\text{calcd.}}$(NaCl)	$\gamma_{\text{obs.}}$(NaBr)	$\gamma_{\text{calcd.}}$(NaBr)
0.001	0.965	0.965	...	...	0.966	0.965	....	...
.005	.926	.927	...	...	.928	.928	....	...
.01	.899	.901	...	...	.903	.903	....	...
.05	.815	.815	0.816	0.815	.821	.819	0.824[a]	0.822
.1	(.764)	.764	(.765)	.766	(.778)	.775	(.779)	.780
.2	.712	.7115	.715	.715	.732	.729	.737	.737
.5	.644	.643	.653	.651	.678	.678	.696	.694
1	.597	.598	.612	.612	.656	.658	.687	.689
1.5	.576	.579	.595	.597	.658	.662	.696	.699
2	.569	.569	.589	.591	.670	.674	.732	.732
2.5	.568	(.564)	.589	.589	.690	.692	.773	(.752)
3	.571	(.561)	.590	(.587)	.714	.715	.823	(.785)
3.5	.571	(.561)	.599	(.594)	.749	(.739)	.871	...
4	.581	(.574)	.609	(.598)	.779	(.764)	.933	...
	A = 0.76		A = 0.78		A = 0.84		A = 0.88	
	B = 0.0171		B = 0.0204		B = 0.032		B = 0.0383	

[a] Harned and Douglas, ref. 1e.

In our previous computations these constants were obtained from the electromotive forces of the cells at 0.1, 1 and 3 molal concentrations. This elaborate calculation has not been repeated. The B constants of the previous calculations have been changed somewhat to meet the requirements of the new experiments in the concentration range from 0.1 to 2 molal. The values for potassium and sodium chloride at 0.001, 0.005 and 0.01 molal taken from the compilation of Scatchard were obtained by him from freezing point data.[12]

Up to a concentration of 2 *M* the agreement between the observed and calculated values is extraordinarily good. The difference between the values obtained is rarely over two in the third place of activity coefficient, which corresponds to a deviation of a little over 0.1 mv. At concentrations above 2 *M* the values obtained by Hückel's equation are all somewhat less than the observed values and this difference increases with increasing salt concentration.

In the cases of the less accurate results with lithium chloride and bromide, we have made no further calculation by Equation 1 but have simply computed γ by Equation 2. To this end we employed the reference values at 0.1 *M* indicated by parenthesis in Table VII. Some of them had been previously obtained by extrapolation by Equation 1.[11a,d] In the case of the less accurate results with the iodides, suitable values were chosen at 0.1 *M* concentration. In this table we have also included the activity coefficients of hydrochloric acid as recently computed by Randall and Young,[13] hydrobromic acid computed from the results of James[14] and potassium and sodium iodides obtained from the data of Harned and Douglas.[1e]

TABLE VII

THE ACTIVITY COEFFICIENTS OF HALIDES IN CONCENTRATED SOLUTIONS

m	γ_{LiCl}	γ_{LiBr}	γ_{HCl}	γ_{HBr}	γ_{KI}	γ_{NaI}
0.01	0.901	...	0.904	0.906	...	...
.05	.819	...	.829	.831	.820	...
.1	(.779)	(0.794)	(.796)	(.802)	(.775)	(0.788)
.2	.756	.769	.766	.779	.730	.754
.5	.725	.758	.757	.788	.678	.721
1	.757	.806	.810	.873	.649	.734
1.5	.819	.890	.903	...	.646	...
2	.919	.999	1.019	1.169	.646	...
2.5	1.040	1.152	1.151	...	...	...
3	1.174	1.293	1.320	1.671	...	...
3.5	1.358	1.519	1.520	...	...	...
4	1.554	1.829	1.762	...	...	...

The character and distribution of the results are shown in Fig. 2, where γ is plotted against $\mu^{1/2}$.

Comparison of Activity Coefficients Obtained from Electromotive Force and Vapor Pressure Data.—It is a matter of considerable impor-

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[12] Scatchard, THIS JOURNAL, **47**, 648 (1925).

[13] Randall and Young, *ibid.*, **50**, 989 (1928).

[14] James, unpublished results.

tance to verify the above method for determining activity coefficients by comparing the values thus obtained with values computed by another method which involves a different experimental mechanism. To this end, the vapor pressure measurements of Lovelace, Frazer and Sease[15] of solutions of potassium chloride at 20° are suitable. Since the vapor pressure measures the activity of the solvent, it is possible to compute the activity of the solute by the equation

$$\partial \ln a_2 = -\frac{N_1}{N_2}\partial \ln a_1 \qquad (3)$$

where a_1, N_1 and a_2, N_2 are the activities and mole fractions of the solvent and solute, respectively. If the vapor pressure of the solvent is not great, the gas laws will hold for the vapor, and the vapor pressure, p_1, may be taken as proportional to α_1. Consequently, by substituting p_1 for α_1 and forming a definite integral, we obtain

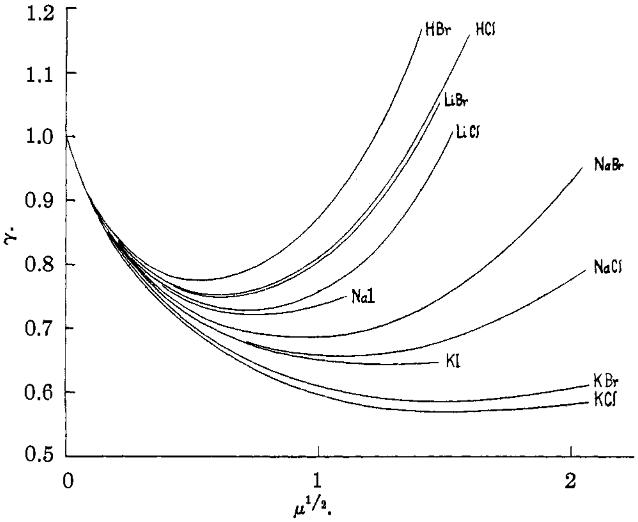

Fig. 2.

$$\int_{\alpha_2'}^{\alpha_2''}\partial \ln \alpha_2 = -\int_{p_1'}^{p_1''}\frac{N_1}{N_2}\partial \ln p_1 \qquad (4)$$

By plotting N_1/N_2 against $\ln p_1$ and evaluating the integral on the right graphically, $\ln \alpha_2''/\alpha_1'$ or $\ln \gamma_2 m_2/\gamma_1 m_1$ may be obtained. From this γ relative to a given concentration may be computed. A similar computation has been made by Scatchard.[16] In Table VIII the result of this calculation is given. The values at 1 *M* were taken to be identical at the two temperatures. The agreement at 0.2 and 0.5 molal is excellent but

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[15] Lovelace, Frazer and Sease, THIS JOURNAL, **43**, 102 (1921).

[16] Scatchard, *ibid.*, **47**, 654 (1925).

TABLE VIII

COMPARISON OF ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE FROM ELECTROMOTIVE FORCE AND VAPOR PRESSURE DATA

m	0.1	0.2	0.5	1	2	3	4
γ (E.m.f.) 25°	0.764	0.712	0.644	(0.597)	0.569	0.571	0.581
γ (V. P.) 20°	(0.780)	0.713	0.643	(0.597)	0.566	0.562	0.565

at 0.1 molal the result is not good. This is probably due to an error in the vapor pressure method. At 2, 3 and 4 molal the values at 20° become increasingly less than those at 25°. This is to be expected since the partial molal heat of dilution is negative. The magnitude of the difference is of the correct order.[17] We regard this agreement in the concentration range of from 0.2 to 4 molal as excellent confirmation of the method employed.

I take this opportunity to express my appreciation to Dr. Geoffrey M. James and Mr. Robert Robinson for the valuable assistance rendered by them at the time of these measurements.

Summary

1. Measurements at 25° of high accuracy of cells of the type

$$\text{Ag} \mid \text{AgX} \mid \text{MX(m)} \mid \text{M}_x\text{Hg} \mid \text{MX(0.1)} \mid \text{AgX} \mid \text{Ag}$$

containing sodium and potassium chlorides and bromides have been made.

2. Similar but less accurate measurements have been made with similar cells containing lithium chloride and bromide.

3. The electromotive forces of halides have been discussed and considerable departure from additivity is observable.

4. The activity coefficients of sodium and potassium chlorides and bromides have been calculated from the results of the electromotive force measurements and compared with those calculated by Hückel's equation.

5. The activity coefficients of ten halides have been calculated and discussed.

6. The activity coefficients of potassium chloride derived from the electromotive force measurements have been compared with those computed from vapor pressure measurements.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

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[17] See Harned, THIS JOURNAL, **44**, 252 (1922).