the scope of our work. However, a comparison was made with the mercury arc lines emitted by a G. E. "Labarc" when both sources were run at 1 amp. The continuum was 25% as intense as the 2483 and 2652 Å. lines, 7% as intense as the 2894 and 3022 Å. lines and 12% as intense as the 3350 Å. line. These figures should give anyone familiar with this field a satisfactory idea of the performance of the lamp.

The Tube as a Line Spectral Source.—This type of lamp operates when filled with helium, argon, or a mixture of argon and mercury; and presumably when filled with the other rare gases. The argon mercury mixture gave a spectrum from which the far ultraviolet lines, particularly the resonance line, were nearly absent due to the quenching effect of argon while the visible and near ultraviolet lines were very strong.

Acknowledgments.—The author wishes to express his appreciation to Dr. F. T. Gucker, Jr., for his encouragement and assistance in the course of this work and for his assistance in the preparation of the manuscript for publication. It is also a pleasure to acknowledge the helpful advice given by Dr. R. A. Fisher and Dr. W. S. Huxford of the Physics Department of Northwestern University.

Summary

A simple, low voltage hydrogen discharge tube especially designed as an intense source of continuous ultraviolet has been developed. It requires no water cooling, since it produces the same light intensity with only about 5% of the electrical power required by a high voltage hydrogen discharge tube. Details of construction and operation are given.

In addition to being useful as a source of continuous radiation it has been used as a source of the line spectra of mercury and the rare gases.

EVANSTON, ILLINOIS RECEIVED JUNE 22, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Some Thermodynamic Properties of Uni-univalent Halide Mixtures in Aqueous Solution

BY HERBERT S. HARNED

It has been shown experimentally by Güntelberg and by Harned that the logarithm of the activity coefficient of hydrochloric acid in chloride mixtures of constant total ionic strength varies linearly with the molality of the acid. Since these earlier studies, other investigations have confirmed this result.[1]

Recently, from a number of sources, sufficient evidence has been acquired to permit more extended observations of this relation, particularly with respect to concentration and temperature. The results obtained will have a special interest in connection with some recent generalizations made by Åkerlöf[2] regarding the behavior of these mixtures. Of still greater interest will be the limitations which the newer knowledge imposes upon Brönsted's theory of the specific interaction of ions.[3]

For our purposes, the law of the linear variation of the logarithm of the activity coefficient at constant ionic strength may be expressed for the systems of uni-univalent halide acid–halide salt mixtures in the following manner. Thus

$$\begin{array}{l} \log \gamma_1 = \alpha_1 m_1 + \log \gamma_1^0 = \log \gamma_{1(0)} - \alpha_1 m_1 \\ \log \gamma_2 = \alpha_2 m_2 + \log \gamma_2^0 = \log \gamma_{2(0)} - \alpha_2 m_2 \end{array} \quad (1)$$

where the ionic strength, $\mu = m_1 + m_2 =$ constant. The first of these equations refers to the acid (subscript 1) in the mixture, and second to the salt (subscript 2) in the same mixture. γ_1^0 and γ_2^0 are the activity coefficients of the acid at zero concentration in the salt solution and that of the salt at zero concentration in the acid solution, respectively. $\gamma_{1(0)}$ and $\gamma_{2(0)}$ are the activity coefficients of the acid and salt in pure aqueous solution of the acid and salt, respectively. Equation (1) is taken to be valid at any total ionic strength, μ.

The present communication contains measurements of the cells

H_2 (1 atm.) | HCl (0.01), NaCl(m) | AgCl | Ag Type I

which will serve to supplement the available accurate data on this subject. Results have been

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(1) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Harned, THIS JOURNAL, **48**, 326 (1926); see also Harned and Mason, *ibid.*, **53**, 3377 (1931); Hawkins, *ibid.*, **54**, 4480 (1932); Mason and Kellam, *J. Phys. Chem.*, **38**, 689 (1934); Bates and Urmston, THIS JOURNAL, **55**, 4068 (1933); Murdoch and Barton, *ibid.*, **55**, 4074 (1933).

(2) Åkerlöf and Thomas, *ibid.*, **56**, 593 (1934); Åkerlöf, *ibid.*, **56**, 1439 (1934).

(3) Brönsted, *ibid.*, **44**, 877 (1922).

obtained from 0 to 60° at 5° intervals and at salt concentrations which vary from 0 to 3 M. These in combination with the results of Harned and Ehlers, and Harned and Nims[4] make it possible to compute α_1 and α_2 in these mixtures from 0 to 40° and throughout wide ranges of total concentrations. Further data are now available for computing α_1 and α_2 of a number of uni-univalent halide acid–salt mixtures at 25°. The information derivable from these results, namely, the behaviors of α_1 and α_2 as functions of temperature and concentration, is an important addition to the knowledge of such mixtures.

Experimental Results[5]

The measurements of the cells (Type I) were carried out by a technique similar to that employed by Harned and Hamer,[6] and the results were obtained at round concentrations by the method described by them. Measurements at each concentration were made from 0 to 60° at 5° intervals. These were expressed to within ±0.05 mg. by the quadratic equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

The values of E_{25} and the constants a and b are given in Table I.

TABLE I

CONSTANTS OF EQUATION (2)

$m_1 = 0.01 \quad \mu = m_1 + m_2$

	E_{25}	$a \times 10^6$	$b \times 10^6$
0.01	0.46416	175	−3.0
.02	.44815	124	−3.0
.03	.43891	94	−2.95
.06	.42330	50	−2.9
.11	.40996	12	−2.8
.21	.39550	− 35	−2.8
.51	.37422	− 97	−2.65
1.01	.35502	−149	−2.5
2.01	.32949	−210	−2.0
3.01	.30906	−247	−1.5

Method of Computation of α_1 and α_2.—The values of α_1 may be computed directly at a given concentration if the activity coefficient of the acid in pure water and the activity coefficient of the acid in the salt solution are known. The first of these has been derived from measurements of the cells

$$H_2 \mid HX(m) \mid AgX \mid Ag;\ X = Cl : Br \qquad \text{Type II}$$

and the second from cells of Type I, or

$$H_2 \mid HX(m_1).\ MX(m_2) \mid AgX \mid Ag;\ \begin{cases} X = Cl : Br \\ M = Li, Na, K, Cs \end{cases} \qquad \text{Type I}$$

Thus

$$\alpha_1 = (\log \gamma_{1(0)} - \log \gamma_1)/(m - m_1) \qquad (3)$$

where the subscript 1(0) refers to the acid in pure water at a concentration μ.

The computation of α_2 from the values of α_1 and other known data may be made by the use of the Gibbs–Duhem equation in the form.

$$m_H\, d \ln a_H a_X + m_M\, d \ln a_M a_X = -55.5\, d \ln a_W \qquad (4)$$

where a_H, a_M, a_X represent the activities of the ionic species denoted by subscripts and a_W is the activity of water. Since the anion is common in all the mixtures under consideration, $m = m_X = m_H + m_M$ = constant, this equation becomes

$$2m_1\, d \log \gamma_1 + 2m_2\, d \log \gamma_2 = -55.5\, d \log a_w \qquad (5)$$

γ_1 and γ_2 equal the activity coefficients $(\gamma_H\gamma_X)^{1/2}$ and $(\gamma_M\gamma_X)^{1/2}$, respectively. According to equation (1), $d \log \gamma_1 = \alpha_1\, d\, m_1$ and $d \log \gamma_2 = \alpha_2\, d\, m_2$, whence equation (5) becomes

$$2\alpha_1 m_1\, d\, m_1 + 2\alpha_2 m_2 d\, m_2 = -55.5\, d \log a_w \qquad (6)$$

Let $m_1 = mx$; then $m_2 = (1 - x)m$, where x can have any value from 0 to 1. Employing these values in equation (6) and performing the integration, we obtain

$$x^2(\alpha_1 + \alpha_2) - 2\alpha_2 x = -55.5/m^2 \int_0^x d \log a_w \qquad (7)$$

an equation which is fundamental to all subsequent discussion.

Upon integration from x equals 0 to 1 or from the pure salt to pure acid solution, we readily obtain

$$\alpha_2 = \alpha_1 + (55.5/m^2) \log (a_1/a_2) \qquad (8)$$

where a_1 and a_2 are the activities of water of the pure acid and pure salt solutions, respectively. Equation (8) gives us a means of computing α_2 from α_1. Since the thermodynamic data of the halide electrolytes in water have been expressed in terms of activity coefficients, we have evaluated the activity ratio in equation (8) by means of the equation

$$\ln \frac{a_0}{a} = \frac{m}{55.5}\left[\nu + \frac{\nu}{m}\int_1^\gamma d \ln \gamma\right] \qquad (9)$$ [7]

a_0 is the activity of the pure solvent, and ν for the uni-univalent salts in question equals 2. The logarithm of the ratio of the activities of water of

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[4] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933); Harned and Nims, *ibid.*, **54**, 423 (1932).

[5] These results formed part of a Thesis presented by George E. Mannweiler to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Master of Science, June, 1934. The principal part of the work in this Thesis will be published in a subsequent article.

[6] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); **55**, 4496 (1933).

[7] Harned in Taylor, "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, 1931, Chap. XII, Equation 102, Vol. I, p. 779.

TABLE II

THE VALUES OF (α_1) AND ($-\alpha_2$) FOR UNI-UNIVALENT HALIDE SOLUTION AT 25°

					α_1				
m	0.1	0.5	1	1.5	2	3	4	5	6
LiCl[a]	0.007[b]	0.0060	0.0050	0.0054	0.0052	0.0037	−0.0025[c]	....	−0.0086[c]
NaCl[d]	.042[b]	.0035	.0324	....	.0308	.0306	.0296[c]	0.0297[c]	.0287[c]
KCl[e]	.080[b]	.0624	.0563	.0552	.0567	.0625	.0660[c]	.0722[c]	....
CsCl[f]	.140[b]	.1046	.1004	.0992	.0992	.0980	....	....	....
LiBr[g]	....	.0055	.0055	.0054	.0041	....	....	....	....
NaBr[h]	(.050)	.0383	.0375	.0364	.0385	....	....	....	....
KBr[h]	(.098)	.0884	.0800	.0808	.0802	.0860	....	....	....
γ_{HCl}	.796	.757	.809	.896	1.009	1.316	1.762[i]	2.374[i]	3.220[i]
γ_{HBr}	.802	.788	.873	....	1.169	1.671	....	....	....
	[log $\gamma_{0.1}$ + 10]				($-\alpha_2$)				
LiCl	9.8982	0.011	0.012	0.011	0.012	0.013	....	....	....
NaCl	9.8910	.057	.058	....	.058	.058	....	....	....
KCl	9.8842	.074	.072	.069	.064	.054	....	....	....
CaCl	9.8762	.070	.060	.053	.046	.041	....	....	....
LiBr	9.8998	.034	.030	.030	.030	....	....	....	....
NaBr	9.8915	.070	.068	.067	.063	....	....	....	....
KBr	9.8847	.076	.069	.065	.065	....	....	....	....

[a] Harned and Copson, THIS JOURNAL, **55**, 2206 (1933). [b] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Harned, THIS JOURNAL, **48**, 326 (1926). [c] Hawkins, *ibid.*, **54**, 4480 (1932). [d] Present communication, Table I. [e] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933). [f] Harned and Schupp, *ibid.*, **52**, 3892 (1930). [g] Vance, *ibid.*, **55**, 4518 (1933). [h] Harned and Hamer, *ibid.*, **55**, 4496 (1933). [i] Randall and Young, *ibid.*, **50**, 989 (1928).

solutions of two uni-univalent electrolytes at a given concentration, m, is readily found from two of these equations to be

$$\log \frac{a_1}{a_2} = \frac{2}{55.5}\left[\int_1^{\gamma_{2(0)}} m \, d \log \gamma_2 - \int_1^{\gamma_{1(0)}} m \, d \log \gamma_1\right] \qquad (10)$$

whence from equation (8)

$$\alpha_2 = \alpha_1 + \frac{2}{m^2}\left[\int_1^{\gamma_{2(0)}} m \, d \log \gamma_2 - \int_1^{\gamma_{1(0)}} m \, d \log \gamma_1\right] \qquad (11)$$

The subscript (0) refers to activity coefficients of pure aqueous solutions of the acid or the salt. When this subscript is omitted, the activity coefficient of the substance in question in the mixture is under consideration. Since α_1 is known by experiment and since the integrals on the right may be computed, α_2 may be calculated. This equation has been derived upon the assumption that equations (1) are valid. From experimental evidence we know that the first of these relations is true for the variation of log γ_1 with m_1 in the cases of hydrochloric and hydrobromic acids in their corresponding alkali salt solutions. Indeed judging from electromotive force and solubility measurements the law is valid within narrow limits in dilute solutions and also in solutions of potassium chloride or sodium chloride at 5 *M* and 6 *M*, respectively. No direct experimental data confirm the linear law for the logarithm of the activity coefficient of the salt in the acid solution, that is to say, the constancy of α_2. Since so much evidence confirms the validity of the first of the relations given by equation (1), we shall proceed by assuming the second of these relations to be valid.

The Halide Acid–Alkali Salt Mixtures at 25°.—The values of α_1 for hydrochloric acid in lithium, sodium, potassium and cesium chloride solutions and for hydrobromic acid in lithium, sodium, and potassium bromide solutions computed by equation (3) are compiled in Table II. The activity coefficient of hydrochloric acid in pure aqueous solution was obtained from the data of Harned and Ehlers and Randall and Young[8] and is given in the eighth row of the table. The ninth row of the table contains the activity coefficient of hydrobromic acid taken from the data compiled by Harned.[9] The preceding rows contain α_1 of the acids in the halide solutions designated. The sources of the data are given in the references below the table. The accuracy of this determination is difficult to estimate since it depends on the concentration. If we assume errors of ±0.05, ±0.1, ±0.2, and ±0.2 mv., at 0.1, 0.5, 1, and 3 *M*, respectively, then the maximum error in α_1 is ±0.004, ±0.0034, ±0.0034, and ±0.0011 at these concentrations. At 0.1 *M* Güntelberg's results are consistent to within

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[8] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933); Randall and Young, *ibid.*, **50**, 989 (1928).

[9] Ref. 7, Chap. XII, p. 772.

±0.02 mv. and are in agreement with Harned's values. The consistency of the present results as judged from graphs is of the order of ±0.001 at 0.1 *M*, ±0.0006 at 0.5 *M* and 1 *M*, and ±0.0004 at the higher concentrations.

The values of $(-\alpha_2)$ given in the second part of the table were obtained from α_1 and the activity coefficient data by means of equation (11). The values of log γ employed in the graphical integration for the sodium and potassium chloride and bromide solutions were taken from the data of Harned and Robinson and Sinclair, and for the case of cesium chloride from the combined data of Robinson and Sinclair and Schupp.[10] The values of log γ for the lithium chloride solutions were those of Robinson and Sinclair. In some cases, the earlier results were changed slightly to conform with the values of log $\gamma_{0.1}$ given in Table II. Since we have employed data from so many sources, it is difficult to estimate the accuracy of the computation of $(-\alpha_2)$. From 0.5 to 3 *M* the consistency of the data as judged from graphs is of the order of ±0.002 and it appears that on the whole the results may be relied on to this extent.

Hydrochloric Acid–Sodium Chloride Mixtures from 0 to 40°.—For mixtures of hydrochloric acid and sodium chloride, accurate data are available which make possible the computation of α_1 and α_2 from 0 to 40° and from 0.3 to 3 *M*. The integral on the right of equation (11) was computed from activity coefficients of Harned and Ehlers (hydrochloric acid) and Harned and Nims (sodium chloride).[11] The values of α_1 were obtained from the electromotive forces given in Table I of the present communication and the electromotive force data of Harned and Ehlers.[12] The values at 0.1 *M* were obtained from the very careful measurements of Güntelberg (20°) and also those of Harned (25°). From 0.5 *M* to 3 *M*, the results are consistent to within the limit of ±0.0006 in the case of α_1 and ±0.001 in the case of α_2. Table III contains the values of these quantities at 25° and at 10° intervals from 0 to 40°.

TABLE III

THE VALUES OF α_1 AND $(-\alpha_2)$ FOR HYDROCHLORIC ACID–SODIUM CHLORIDE MIXTURES FROM 0 TO 40°

tm	0.1	0.3	0.5	1	2	3
			(α_1)			
0	(0.052)	0.048	0.0444	0.0421	0.0410	0.0406
10	..	.044	.0402	.0381	.0370	.0366
20	.044[a]	.040	.0361	.0341	.0330	.0326
25[c]	.042[b]	.0375	.0341	.0322	.0311	.0306
30	..	.035	.0320	.0302	.0290	.0286
40	(.035)	.030	.0280	.0263	.0251	.0246
			$(-\alpha_2)$			
0		0.081	0.0816	0.0785	0.0724	0.0702
10		.068	.0702	.0685	.0658	.0644
20		.060	.0625	.0619	.0600	.0594
25		.057	.0587	.0577	.0578	.0574
30		.054	.0550	.0549	.0552	...
40		.047	.0474	.0482	.0493	...

[a] Güntelberg, *loc. cit.* [b] Harned, *loc. cit.* [c] The results at 25° differ slightly from those in Table II. This is due to the fact that the values in this table were smoothed against *T*.

Limitations of Empirical Rules of Åkerlöf and Thomas.—We shall first consider two empirical relations which Åkerlöf and Thomas have employed[2] for computing solubility data in concentrated solutions.

The first of these rules is expressed by

$$\log (\gamma_{1(0)}/\gamma_{2(0)}) = Bm \qquad (12)$$

where *B* is a constant. If this relation be employed in conjunction with equation (11), it is found that at constant temperature

$$(\alpha_1 - \alpha_2) = B \neq f(m) \qquad (13)$$

Further, if both this and equations (1) are valid, in other words if all these relations are linear, then

$$\left.\begin{aligned} (\alpha_1 - \alpha_2)\, m &= \log (\gamma_{1(0)}/\gamma_{2(0)}) \\ \log \gamma_1{}^0 &= \log \gamma_2{}^0 \end{aligned}\right\} \qquad (14)$$

and according to equation (11)

$$\log \frac{\gamma_{1(0)}}{\gamma_{2(0)}} = -\frac{2}{m}\left[\int_1^{\gamma_{2(0)}} m \, \mathrm{d} \log \gamma_2 - \int_1^{\gamma_{1(0)}} m \, \mathrm{d} \log \gamma_1\right] \qquad (15)$$

We may readily test these relations by means of the above data. From the activity coefficients of the acids and the pure salts at various concentrations, the left side of equation (12) was computed, and the value of *B* at each concentration was determined. For example in the case of the chlorides $\gamma_{1(0)}$ is the activity coefficient of hydrochloric acid and $\gamma_{2(0)}$ that of the designated chloride at a concentration, *m*. The results are given in Table IV.

It is to be noticed that when *B* is small, the variation of *B* with concentration is small, but that in general *B* decreases with increasing concentration. Where *B* is larger, the actual and

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(10) Harned, THIS JOURNAL, **51**, 416 (1929); Harned and Schupp, *ibid.*, **52**, 3886 (1930); Robinson and Sinclair, *ibid.*, **56**, 1830 (1934).

(11) The activity coefficients of Harned and Nims were recomputed from the electromotive forces. The values of $(-\log \gamma)$ at 0.1 *M* were found to be 0.1070, 0.1070, 0.1080, 0.1090, 0.1100 and 0.1109 at 0, 10, 20, 25, 30 and 40°, respectively. All other values of γ were adjusted to these values.

(12) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933); Harned and Nims, *ibid.*, **54**, 423 (1932).

TABLE IV

VALUES OF B AT DIFFERENT CONCENTRATIONS

m	0.5	1	2	3
LiCl	0.020	0.017	0.018	0.018
NaCl	.096	.091	.089	.084
KCl	.140	.132	.124	.121
CsCl	.200	.175	.156	.150
LiBr	.036	.035	.034	
NaBr	.112	.104	.102	
KBr	.168	.155	.149	

percentage deviation of B with concentration is greater. In Fig. 1, B is plotted against m and the variation of B with m is represented by the crosses and dashed lines. The solid lines in the figure represent the values of $(\alpha_1 - \alpha_2)$ obtained from Table II. In the cases of the lithium chloride–hydrochloric acid and lithium bromide–hydrobromic acid mixtures B does not vary appreciably with m and therefore $(\alpha_1 - \alpha_2) = B$ according to equation (13). This equality may not be exact but it is within the experimental error. In the case of the sodium salt mixtures B is slightly different from $(\alpha_1 - \alpha_2)$ and a similar but greater difference occurs with the potassium salt mixtures and finally a still greater difference with the cesium salt mixture. This is in accord with the character of equation (11) and the nature of the variation of B with m as well as the linear variations represented by equations (1).

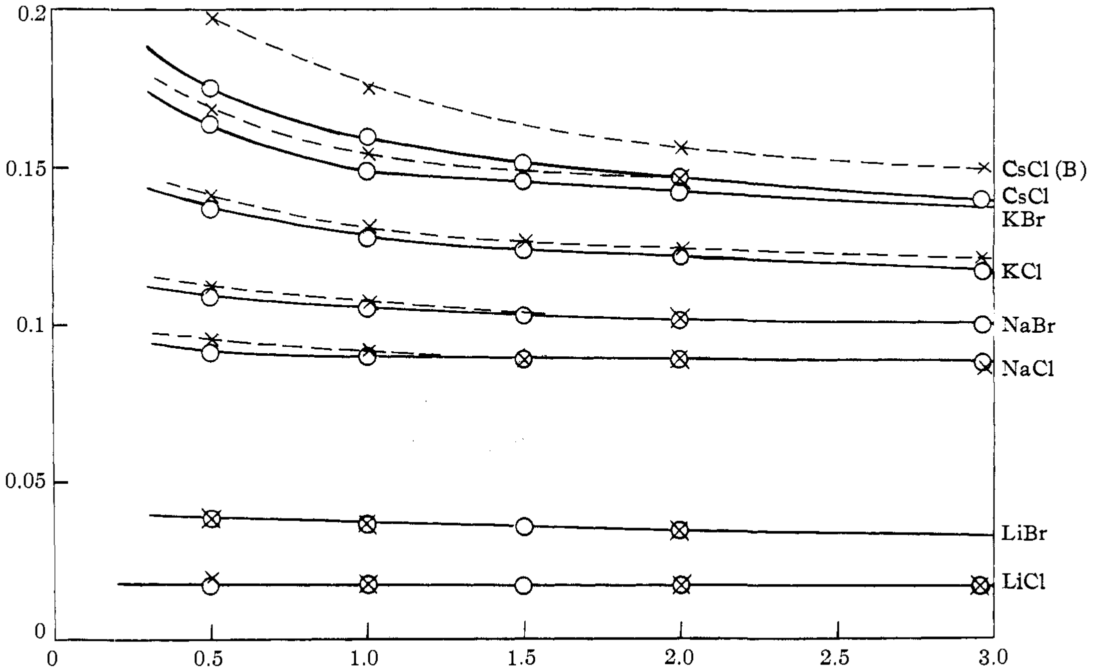

Fig. 1.—Plots of B and $\alpha_1 - \alpha_2$ vs. m for uni-univalent halide solutions: ×, B; ○, $\alpha_1 - \alpha_2$.

The variation of B with m conforms with the contentions of Robinson, and Scatchard and Prentiss,[13] who concluded from heat of dilution data and freezing point data, respectively, that B is not constant and is $f(m)$ in dilute solutions. Even in concentrated solutions care must be employed in the use of these relations while in dilute solutions it is obvious that it is not valid.

The second rule postulated by Åkerlöf and Thomas states that α_1 and α_2 are constants which do not vary with m. In dilute solutions, reference to Tables II and III and Figs. 2 and 3 shows that this is not the case. Since their observations refer particularly to concentrated solutions, we note that there is a general tendency for α_1 and α_2 to vary less as the concentration increases. But even in very concentrated solutions, these quantities still appear to be a function of m. For example, in the case of sodium chloride–hydrochloric acid mixtures α_1 tends to decrease somewhat up to 6 M while for the potassium chloride mixtures it passes through a minimum at about 1.5 M and then increases. We must conclude therefore that at constant temperature α_1 and α_2 are not characteristic constants of a given pair of electrolytes.

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[13] Robinson, THIS JOURNAL, **56**, 2312 (1934); Scatchard and Prentiss, *ibid.*, **56**, 2320 (1934).

Further Discussion of the Derived Parameters, α_1 and α_2.—The curves in Fig. 2 which represent the values of α_1 and $-\alpha_2$ for hydrochloric acid–chloride mixtures are typical of all the results in Table II. In fact, the bromide mixtures exhibit behaviors which parallel those of the chloride mixtures. At higher concentrations, α_1 does not equal $(-\alpha_2)$. As the concentration decreases, there seems to be a tendency in some cases (*e. g.*, CsCl, NaCl, NaBr) for the values to approach each other somewhat. Potassium chloride and bromide mixtures exhibit a more complex behavior since the curves representing the variation of these constants with concentration cross. In some cases, $(-\alpha_2) > \alpha_1$ (*e. g.*, NaCl, LiCl) while in others (*e. g.*, CsCl) $\alpha_1 > (-\alpha_2)$.

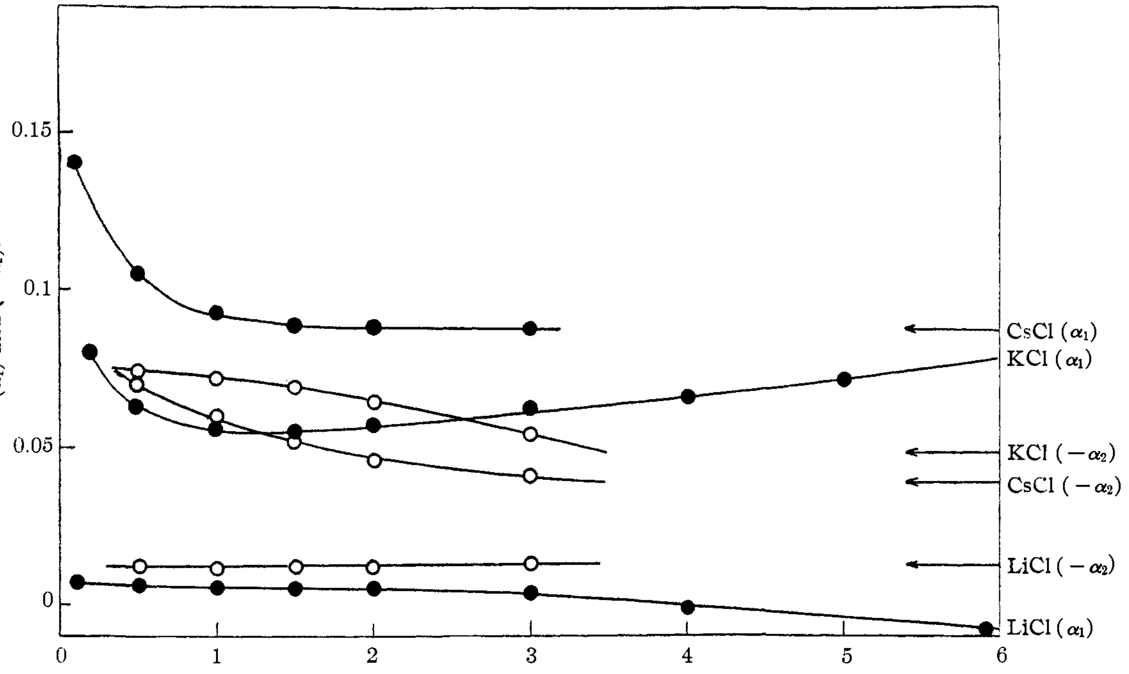

Fig. 2.—Plots of α_1 and $-\alpha_2$ *vs.* m for uni-univalent chloride–hydrochloric acid mixtures.

The best illustration of these behaviors is given by the sodium chloride mixtures and is shown by Fig. 3 in which the parameters, α_1 and $(-\alpha_2)$ are plotted against m at 0, 25 and 40°. As the concentration decreases, there is a tendency for the corresponding curves of α_1 and $-\alpha_2$ to approach each other somewhat but the evidence indicates that they do not meet even in the dilute solutions.

It is important to note that the values reported for α_1 and $-\alpha_2$ have been derived from electromotive force measurements which have been checked by measurements from various sources. The mixture data have been tested in a number of ways. For example, from mixture data by purely formal methods,[14] Harned was able to compute the activity coefficients of some single electrolytes. Another test of these data consists in computing dissociation constants and total heats of ionization of water in the salt solutions. Agreement was obtained with the best calorimetric data by Harned and Hamer for potassium chloride solutions. The values of α_1 for the chloride solutions at 0.1 M were obtained from the closely agreeing values of Güntelberg and Harned.[14] All the data of the activity coefficients of single electrolytes have been checked in a number of ways. The activity coefficients of hydrochloric acid agree with colorimetric data as shown by Harned and Ehlers. Those of the salt solutions at 25° have been found to be in agreement with the vapor pressure data of Robinson and Sinclair and Robinson.[15] At 0.5 M sodium chloride $(-\alpha_2)$ was found to be 0.0820 from the electromotive force data of Harned and Nims and 0.0814 from the freezing point data of Scatchard and Prentiss.[16] Further the reference value of γ in 0.1 M sodium chloride employed, namely, 0.778, agrees very

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(14) Harned, This Journal, **48**, 326 (1926); Harned and Hamer, *ibid.*, **55**, 4496 (1933); Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

(15) Robinson, This Journal, **57**, 1161 (1935).

(16) Scatchard and Prentiss, *ibid.*, **55**, 4355 (1933).

closely with 0.7784 recently obtained by Brown and MacInnes.[17] In view of these facts, we believe the results are within the limits of accuracy previously discussed.

for all values of x between 0 and 1. Consequently

$$\begin{aligned} \alpha_1 &= -\alpha_2 \\ \alpha_2 &= -(\nu/2)B' = -B' \text{ (1-1 Electrolytes)} \end{aligned} \qquad (20)$$

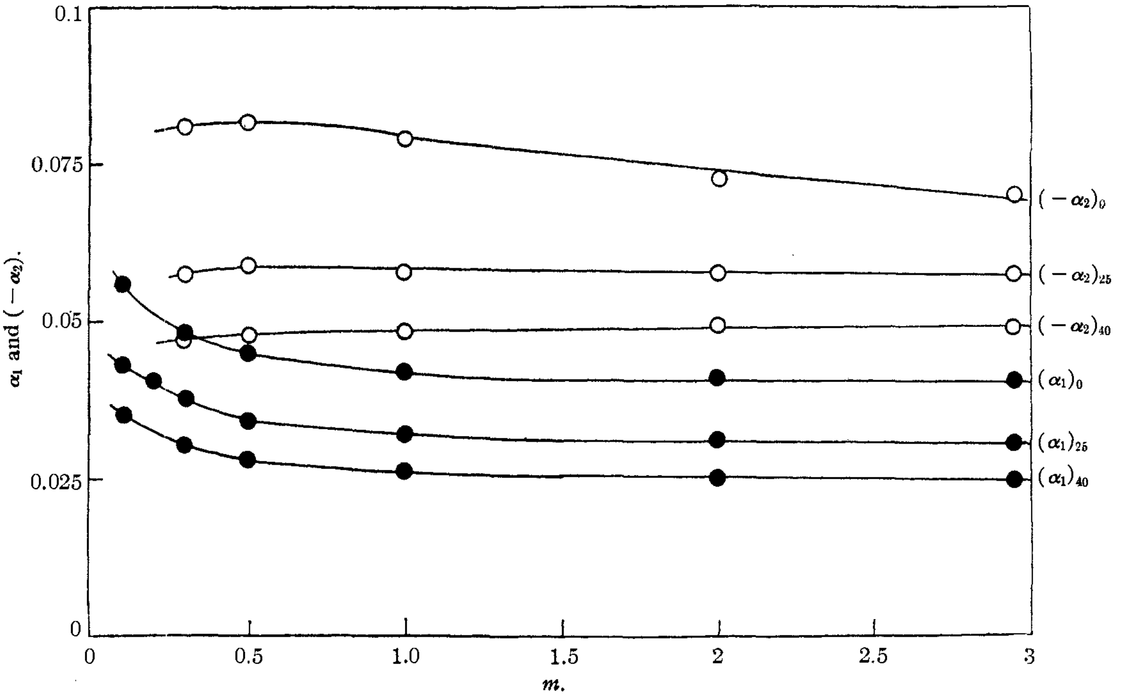

Fig. 3.—Plots of α_1 and $-\alpha_2$ *vs.* m for sodium chloride–hydrochloric acid mixtures at 0, 25 and 40°.

Theory of Specific Ionic Interaction

Since these results are of interest in relation to Brönsted's theory of specific ionic interaction, we shall introduce a few of the consequences of this theory.[18] The osmotic coefficient, ϕ, may be introduced into equation (7) by means of the relation

$$-\partial \log a_v = (\nu m/55.5 \times 2.303)\, \partial\phi \qquad (16)$$

and the equation for the variation of the osmotic coefficient in mixtures at constant total molality, m, may be obtained. Thus

$$x^2(\alpha_1 + \alpha_2) - 2\alpha_2 x = \frac{1}{m^2}\int_0^x \frac{\nu m}{2.303}\, \partial\phi \qquad (17)$$

As pointed by Güntelberg, the left side of this equation is quadratic. Brönsted's theory of specific ionic interaction applied to these mixtures leads to the conclusion that both the osmotic coefficient and the logarithm of the activity coefficient vary linearly with the composition. Thus

$$2.303B'm\partial x = \partial\phi \qquad (18)$$

where B' is a constant. Combining this equation with equation (17) and integrating, we find that

$$x(\alpha_1 + \alpha_2) - 2\alpha_2 = \nu B' \qquad (19)$$

The theory of specific ionic interaction as originally formulated requires: (1) the linear variation of log γ at constant total molality (Eq. 1); (2) the linear variation of ϕ (Eq. 18); (3) that $\alpha_1 = -\alpha_2$. These results follow from the assumption that ions of like sign uniformly influence each other in a dilute salt solution. According to this formulation of the theory the factor $(\alpha_1 + \alpha_2)$ is a measure of the deviation from the theory, caused by specific interaction between ions of like sign. Upon the basis of the validity of (1) (Eq. 1), we have computed the factor $(\alpha_1 + \alpha_2)$ and found that at high concentrations it is finite. In this connection, we note that the thermodynamic result given by equation (17) does not require the equality, $\alpha_1 = -\alpha_2$, at any concentration including $m = 0$. Since this depends on the hypothesis of ionic interaction, we have not extended the curves in the figures to lower concentrations where the uncertainty becomes large. This consideration raises the interesting question as to whether $(\alpha_1 + \alpha_2)$ vanishes at any concentration. In Fig. 4, we have plotted the values of this factor against m. The dots and

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(17) Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

(18) Brönsted, *ibid.*, **44**, 877 (1922); **45**, 2898 (1923).

the solid lines represent the results of this investigation. It is apparent that at higher concentrations, 0.3 M and above, $(\alpha_1 + \alpha_2)$ is finite and there is no definite indication that this quantity approaches zero as the concentration decreases. Since Brönsted's theory was never intended to apply to concentrations greater than 0.1 M, these results do not seriously contradict the theory although they definitely show that it is not valid at the higher concentrations.

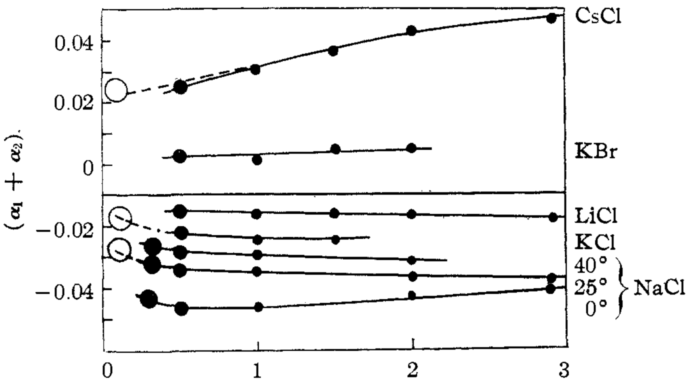

Fig. 4.—Plots of $(\alpha_1 + \alpha_2)$ *vs.* m.

It is apparent (Fig. 4) that the values of $(\alpha_1 + \alpha_2)$ of cesium chloride and sodium chloride mixtures differ considerably. The most recent results for activity coefficients at 0.1 M determined since these calculations were made conform to this distribution. According to our earlier discussion $\log \gamma_{1(0)} - \log \gamma_{2(0)} = \alpha_1 - \alpha_2$ if we neglect the small difference between $(\alpha_1 - \alpha_2)$ and B. Harned and Ehlers obtained −0.0989, and Randall and Young[19] obtained −0.0993 for $\log \gamma_{0.1}$ for hydrochloric acid at 25°. If we employ the mean of these results, and Brown and MacInnes' value of −0.1088 for $\log \gamma_{0.1}$ of sodium chloride, then $(\alpha_1 - \alpha_2) = 0.0097$. From Güntelberg's value of α_1 at 20°, we obtain 0.040 at 25°. Hence, $-\alpha_2 = 0.057$ and $(\alpha_1 + \alpha_2) = -0.017$. For cesium chloride, we use Robinson and Sinclair's value of 0.1238 for $-\log \gamma_{0.1}$. Güntelberg obtained 0.146 for α_1 at 20°. From the temperature coefficient of this quantity, we find that $\alpha_1 = 0.143$ at 25°. Therefore $-\alpha_2 = 0.1040$, and $(\alpha_1 + \alpha_2) = 0.0039$. If we introduce a correction due to the fact that $B > (\alpha_1 - \alpha_2)$, then the value of $(\alpha_1 + \alpha_2)$ is even higher. In the same manner by employing the values of $\log \gamma$ and α_1 given in Table II, we obtain 0.013 and −0.007 for $(\alpha_1 + \alpha_2)$ of the lithium and potassium chloride mixtures, respectively, which appear to lie between the values obtained for the other two salts. The circles in Fig. 4 represent these values with the exception of that of the lithium chloride mixtures, and the dashed lines a prolongation of the plots obtained from our data. Since a computation at this concentration is very sensitive, care must be exercised in drawing conclusions from the results. However, we believe that the spread and distribution of the results are significant. In the case of sodium chloride $(\alpha_1 + \alpha_2)$ seems to tend toward zero but it is too early to draw any conclusion regarding this matter.

These observations lead to some interesting alternative propositions. (1) If $\log \gamma$ varies exactly linearly with m at constant total molality (Eq. 1), then ϕ does not and specific effects between ions of like sign may occur. If this is the case, $(\alpha_1 + \alpha_2)$ may be finite when $m = 0$. (2) If $\log \gamma$ does not vary linearly with m at constant total molality, then the present results require that ϕ does not. Since $\log \gamma_1$ has been shown to obey the linear relationship within very narrow limits, we conclude that in the case of these mixtures any departure from a linear variation is greater for ϕ than for $\log \gamma$.

All our results depend upon the assumption that α_2 is constant, or that the second of the relations in equation (1) is valid. If this is not true, then the above indications of specific effects between ions of like sign may be subject to another interpretation. For instance, Scatchard and Prentiss have extended the theory of specific ionic interaction to terms including higher powers of the concentration. Without abandoning the fundamental postulate of the theory, they arrive at the conclusion that "neither $\log \gamma$ or ϕ need vary linearly except in very dilute solutions, and that α_1 need equal $-\alpha_2$ only at zero concentration."[20,21] It is possible that such an extended theory will account for the deviation from the original theory and exclude specific interaction between ions of like sign.

Summary

1. Measurements of the cells $H_2 \mid HCl(0.01), NaCl(m) \mid AgCl \mid Ag$ from 0 to 60° have been reported.

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[19] Randall and Young, THIS JOURNAL, **50**, 989 (1928).

[20] Quoted from a private communication from Prof. George Scatchard.

[21] Scatchard and Prentiss, THIS JOURNAL, **56**, 2320 (1934).

2. From these and other suitable data, the values of α_1 and α_2 defined by equation (1) have been computed for a number of halide acid–halide mixtures.

3. It has been shown that the empirical rules of Åkerlöf and Thomas that (1) B is a constant and does not vary with the concentration, (2) α_1 and α_2 are not functions of m, are not valid. Neither B, α_1 or α_2 can be regarded as constants characteristic of a given pair of electrolytes.

4. The results have been discussed in relation to the original and extended theory of specific ionic interaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Ionized Water in Sodium Chloride Solutions

BY HERBERT S. HARNED AND GEORGE E. MANNWEILER[1]

From measurements of the cells

$$H_2 \mid MOH(m_0), MX(m) \mid AgX \mid Ag, \text{ and} \qquad (A)$$

$$H_2 \mid HX(m_0), MX(m) \mid AgX \mid Ag \qquad (B)$$

$$M = \text{Li, Na, K}\ X = Cl^-, Br^-$$

the thermodynamic properties of the ions of water in potassium and lithium chloride solutions, and potassium and sodium bromide solutions, have been studied over wide temperature and concentration ranges.[2] The only determination of the activity coefficient and dissociation of water in sodium chloride solutions is contained in the contribution by Harned where the method of determining these quantities from cells without liquid junction was first developed.[3] Since these results were obtained from scattered data at 25° only, they have been redetermined from measurements of the above cells by employing a consistent and more accurate technique. Further, the results have been extended to cover a temperature range from 0 to 60°. From these results we have computed: (1) the ionization constant of water; (2) the ionic activity coefficient product of water in sodium chloride solutions; (3) the ionization of water in sodium chloride solutions; and (4) the heat of ionization of water and the partial molal heat of ionization of water in sodium chloride solutions.

Experimental Results

The electromotive forces of cells of types (A) and (B) may be expressed as functions of the temperature by means of the quadratic equations

$$E_A = E_{A(25)} + c\,(t - 25) + d\,(t - 25)^2 \qquad (1)$$

$$E_B = E_{B(25)} + a\,(t - 25) + b\,(t - 25)^2 \qquad (2)$$

The values of $E_{B(25)}$, a, and b are given in Table I of an earlier investigation[4] and the values of $E_{A(25)}$, c, and d are contained in Table I of this communication. Measurements were made by a technique similar to that employed by Harned and Hamer[2] and Harned and Copson.[2] The experimental results were the mean of three cells which were measured at the concentrations specified from 0 to 60° at 5° intervals. The deviations from the mean were ±0.04 mv. and the experimental results smoothed to round concentrations agree with those computed by equation (2) to within approximately this limit.

TABLE I

$E_{A(25)}$ AND CONSTANTS OF EQUATION (1), $m_0 = 0.01$

μ	$E_{A(25)}$	$c \times 10^6$	$d \times 10^6$
0.02	1.05027	167.4	0.28
.03	1.03244	109.25	.25
.05	1.00887	34.65	.13
.11	0.99098	− 27.40	.12
.21	.97303	− 87.45	.11
.51	.94905	−162.00	.0
1.01	.93055	−225.35	− .07
2.01	.91132	−279.5	− .35
3.01	.89950	−309.1	− .62

The Ionization Constant of Water, the Ionic Activity Coefficient and Dissociation of Water in Sodium Chloride Solutions.—The ionization constant of water was determined from these results by the two methods developed by Harned and Hamer. The equation for the cells of type A may be written in the form

$$E_A - E_0 + \frac{RT}{NF}\ln\frac{m}{m_0} = \frac{RT}{NF}\ln\frac{\gamma_H\gamma_{OH}}{a_{H_2O}} - \frac{RT}{NF}\ln\gamma_H\gamma_{Cl} - \frac{RT}{NF}\ln K \qquad (3)$$

which corresponds to equation (4) of Harned and Hamer. By employing the values of molal po-

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[1] The present communication contains material from a thesis presented by George E. Mannweiler to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Master of Science, June, 1934.

[2] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); (b) **55**, 4496 (1933); Harned and Copson, *ibid.*, **55**, 2206 (1933).

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

[4] Harned, *ibid.*, **57**, 1865 (1935).