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Properties of Aqueous Mixtures of Pure Salts: Thermodynamics of the Ternary System Water-Potassium Chloride-Barium Chloride at 25 °C

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Isopiestic vapor pressure measurements have been made on the system water-potassium chloride-barium chloride. The data have been used to evaluate the activity coefficient of each salt in the presence of the other. Two conditions are considered; in one, the solution is maintained at constant total ionic concentration; in the other, at constant total ionic strength. The excess free energy of mixing is calculated and compared with similar data for the water-hydrochloric acid-barium chloride and water-sodium chloride-barium chloride systems.

1. Introduction

The use of the isopiestic vapor pressure method to determine some thermodynamic properties of the ternary system water-sodium chloride-barium chloride has been described recently [1].[1] This system has several features of simplicity. Thus, the isopiestic ratio (R) of a series of mixed salt solutions is a linear function of the ionic fraction (x); here R is defined as $M_B/(m_B+1.5\ m_c)$ and x as $1.5\ m_c/(m_B+1.5\ m_c)$, where M_B is the molality of the reference solution of sodium chloride and m_B, m_c are the molalities of sodium chloride and barium chloride, respectively, in the mixed solution in isopiestic (vapor-phase) equilibrium with the reference solution.

The ionic fraction, x, defined in this way, is a convenient measure of the solution composition in isopiestic work because, in the limiting case of ideal solutions, all solutions with the same value of $(m_B+1.5\ m_c)$ would have the same aqueous vapor pressure. For example, four solutions, one of 1.5 m sodium chloride only, another of 1.0 m barium chloride only, the third 0.75 m to sodium chloride and 0.5 m to barium chloride, and the fourth 0.3 m to sodium chloride and 0.8 m to barium chloride, would all have the same vapor pressure if they behaved ideally. This would not be true for solutions of the same total ionic strength (m_B+3m_c), even if they were ideal.

The linear relation between isopiestic ratio and ionic fraction for the sodium chloride-barium chloride system enabled us to equate the integral in the McKay-Perring equation [2] to zero and provided a further simplification in the subsequent calculations. Such calculations showed that the equations

$$\log \gamma_B = \log \gamma_B^\circ - \alpha_B m_C \tag{1}$$

$$\log \gamma_c = \log \gamma_c^\circ - \alpha_c m_B \tag{2}$$

described the behavior of the system at constant total ionic concentration, i.e., constant $(m_B+1.5m_c)$; thus the chemical potential of each salt is a linear function of the concentration of the other salt in a system kept at constant total ionic concentration. Similar relations were found to hold for systems of constant total ionic strength (m_B+3m_c), with, of course, different numerical values of the α_B and α_c parameters.

This paper describes similar work on the system water-potassium chloride-barium chloride. The behavior of this system is somewhat more complicated.

2. Definitions

The definitions and symbols of the previous paper [1] will be retained except that D will be used to designate potassium chloride in place of B for sodium chloride. Thus eq (1) becomes

$$\log \gamma_D = \log \gamma_D^\circ - \alpha_D m_c. \tag{3}$$

3. Experimental Procedure

The procedure was as in the previous work [1] except that potassium chloride was used as the reference salt. The potassium chloride was a portion of that used in a study of the system water-potassium chloride-glycine [3].

4. Results

4.1. Isopiestic Data

The experimental results are given in table 1. The second column gives the molality (M_D) of the reference solution of potassium chloride; the third and fourth columns give the molalities of potassium chloride (m_D) and of barium chloride (m_c) in the

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Isopiestic data for the system* H_2O–KCl–$BaCl_2$ *at 25 °C*[a]

Set	M_D	m_D	m_c	x	R	Δ
1	0.7723	0.6309	0.09985	0.1919	0.9892	−0.06
		.4178	.2482	.4712	.9775	−.06
		.1967	.3994	.7528	.9705	+.03
			.5313	1.0	.9691	+.10
	0.7786	0.3099	0.3280	0.6135	0.9709	+0.07
		.2308	.3814	.7125	.9697	−.01
		.1411	.4423	.8246	.9677	+.05
			.5358	1.0	.9688	−.10
	0.7899	0.5789	0.1491	0.2787	0.9842	+0.01
		.4185	.2603	.4827	.9764	+.01
		.2048	.4060	.7483	.9706	+.02
			.5425	1.0	.9706	−.03
	0.7924	0.6644	0.09088	0.1702	0.9864	+0.02
		.5072	.2007	.3725	.9803	+.01
		.3186	.3302	.6086	.9736	−.03
			.5442	1.0	.9707	0
	0.7958	0.7074	0.06345	0.1186	0.9916	+0.13
		.6163	.1269	.2360	.9865	+.04
		.5063	.2028	.3753	.9819	−.07
		.4067	.2712	.5001	.9782	−.10
2	1.0743	0.8081	0.1856	0.2562	0.9889	0
		.5648	.3514	.4827	.9839	+0.07
		.3064	.5228	.7191	.9851	+.04
			.7197	1.0	.9951	−.11
3	1.5519	0.6330	0.6110	0.5915	1.0015	+0.07
		.4063	.7535	.7356	1.0100	+.04
		.2358	.8588	.8453	1.0184	+.04
			.9999	1.0	1.0347	−.13
	1.5837	1.3606	0.1526	0.1440	0.9964	−0.05
		1.1475	.2965	.2786	.9955	−.06
		1.0259	.3772	.3554	.9950	+.05
		0.8270	.5066	.4788	.9978	+.06
4	2.2466	1.9274	0.2142	0.1429	0.9991	−0.01
		1.4671	.5127	.3439	1.0047	+.05
		0.8579	.8894	.6086	1.0249	+.07
		.3443	1.1881	.8381	1.0565	−.09
	2.2611	1.3394	0.6012	0.4024	1.0089	+0.03
		0.6887	.9968	.6846	1.0353	+.07
		.2503	1.2482	.8821	1.0653	−.05
			1.3874	1.0	1.0865	−.05
	2.2788	1.8961	0.2554	0.1681	0.9998	−0.01
		1.1888	.7051	.4708	1.0144	+.01
		0.5955	1.0604	.7276	1.0424	0
			1.3970	1.0	1.0875	−0.01
5	2.4938	1.6329	0.5589	0.3393	1.0091	−0.07
		1.2541	.7931	.4868	1.0205	−.02
		0.3002	1.3455	.8705	1.0756	−.01
			1.5101	1.0	1.1009	+.10
6	2.7188	1.8855	0.5384	0.2999	1.0095	−0.12
		0.5746	1.3145	.7743	1.0677	+.03
		.2539	1.4896	.8980	1.0926	+.04
			1.6244	1.0	1.1159	+.07
	2.7661	2.5365	0.1524	0.0827	1.0004	−0.02
		2.2111	.3630	.1976	1.0038	−.04
		1.7890	.6282	.3450	1.0127	−.01
		1.1054	1.0339	.5850	1.0388	+.06
	2.7763	2.3901	0.2521	0.1366	1.0029	+0.22
		1.5011	.8090	.4470	1.0227	+.06
		0.4287	1.4251	.8330	1.0818	−.09
			1.6547	1.0	1.1185	−.14
	2.8600	2.3016	0.3635	0.1915	1.0046	−0.18
		1.3772	.9332	.5041	1.0299	−.03
		0.9462	1.1832	.6523	1.0511	+.02
			1.6966	1.0	1.1238	+.14

[a] D=KCl, C=$BaCl_2$ x is the "ionic fraction" of $BaCl_2$, $1.5m_c/(m_D+1.5m_c)$ R is the isopiestic ratio, $M_D/(m_D+1.5m_c)$.
Δ is the percentage difference between R calculated by eq (4) with the parameters of table 2 and R (obs), the latter being given in column 6.

mixed solution in isopiestic equilibrium with the reference solution of potassium chloride at molality M_D. The fifth column gives values of the ionic fraction, $x=1.5m_c/(m_D+1.5m_c)$ and the sixth column values of the isopiestic ratio, $R=M_D/(m_D+1.5m_c)$.

Figure 1 is a plot of isopiestic ratio versus ionic fraction for some sets of results recorded in table 1. Unlike the plots for sodium chloride-barium chloride mixtures, where R was found to be linear in x, the plots for these potassium chloride-barium chloride mixtures show marked curvature. They can, however, be represented adequately by a quadratic equation

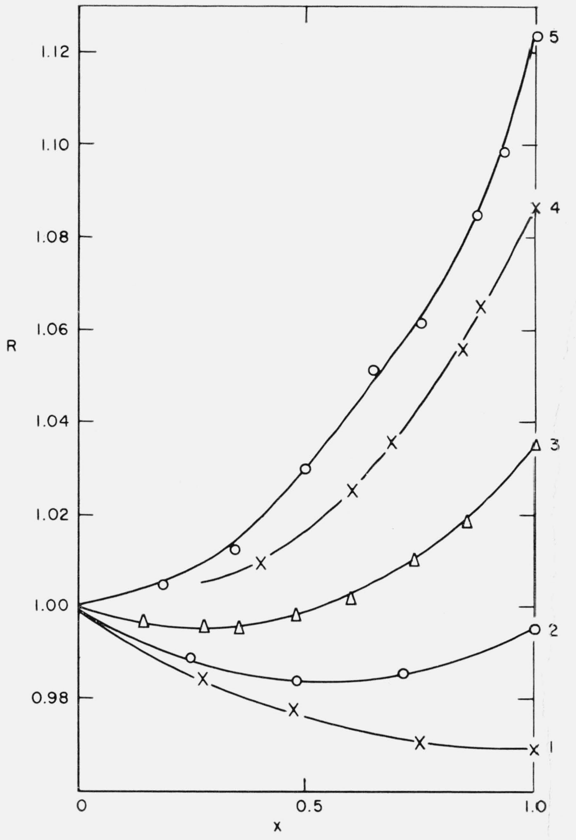

FIGURE 1. *Isopiestic ratio of potassium chloride-barium chloride solutions versus ionic fraction.*

$$R=1-ax-bx^2. \tag{4}$$

The last column of table 1 gives the percentage difference between the observed isopiestic ratios and those calculated by eq (4), using the numerical values of a and b given in table 2.

4.2. Activity Coefficients at Constant Total Ionic Concentration

The McKay-Perring equation [2] can be written

$$\ln \gamma_D=\ln \Gamma_D+\ln R+\int_0^{M_D\varphi} f(m, M_D, x)\,d(M_D\varphi) \tag{5}$$

where

$$f(m, M_D, x)=\frac{1}{m^2}\left(\frac{\partial m}{\partial \ln x}\right)_{a_w}+\frac{1}{m}-\frac{1}{M_D}. \tag{6}$$

TABLE 2. *Parameters of eq (4)* $R = 1 - ax - bx^2$

Set	M_D	a	b
1	0.7723	0.0661	−0.0362
	.7786	.0687	−.0365
	.7899	.0667	−.0370
	.7924	.0665	−.0372
	.7958	.0642	−.0373
2	1.0743	.0563	−.0503
3	1.5519	.0394	−.0728
	1.5837	.0390	−.0743
4	2.2466	.0220	−.1054
	2.2611	.0200	−.1060
	2.2788	.0195	−.1069
5	2.4938	.0151	−.1170
6	2.7188	.0109	−.1275
	2.7661	.0083	−.1297
	2.7763	.0095	−.1302
	2.8600	.0089	−.1341

If the isopiestic ratio is quadratic in x, according to eq (4), then eq (6) becomes

$$f(m, M_D, x) = \frac{bx^2}{M_D} \tag{7}$$

and the integral in eq (5) becomes

$$x^2 \int_0^{M_D\varphi} \frac{b}{M_D} \cdot d(M_D\varphi).$$

In the particular case of potassium chloride-barium chloride mixtures, it so happens that b can be represented as a linear function of M_D,

$$b = -0.0469 M_D \tag{8}$$

and the integral in eq (5) can be evaluated as

$$-0.0469 x^2 M_D \varphi$$

or

$$-0.0204 x^2 M_D \varphi$$

if eq (5) is converted into decadic logarithms.

TABLE 3. *Parameters of eq (3) and eq (2)*

Set	M_D (mean)	α_D	α_c	$(\alpha_D + 1.5\alpha_c)$
1	0.7858	0.0484	0.0029	0.0527
2	1.0743	.0301	.0173	.0561
3	1.5678	.0152	.0304	.0608
4	2.2622	.0053	.0403	.0658
5	2.4938	.0035	.0421	.0667
6	2.7803	.0018	.0440	.0678

The activity coefficients of potassium chloride and barium chloride in the mixed solutions have been calculated by eq (5). Then, assuming that eq (3) and eq (2) were valid for this system, as they were for the sodium chloride-barium chloride system, values of α_D and α_c were calculated. For example, at $M_D = 1.0743$, $-\log \Gamma_D = 0.2217$ [4]; for $m_D = 0.3064$, $m_c = 0.5228$, $x = 0.7191$, it was found that $R = 0.9851$ or $\log R = -0.0065$. Moreover, at this value of M_D, $-0.0204\, M_D\varphi = -0.0196$ so that $-0.0204 x^2 M_D = -0.0101$; this is the contribution of the integral term in eq (5) to $\log \gamma_D$. Thus $\log \gamma_D = -0.2383$. But the total ionic concentration of this mixed solution is $(m_D + 1.5m_c) = 1.0906$ and a solution of potassium chloride only at this concentration has $\log \mathring{\gamma}_D = -0.2225$. Hence $\alpha_D m_c = 0.0158$ and $\alpha_D = 0.0302$. Using all the data in table 1, the values of α_D and α_c given in table 3 were calculated.

It was shown in the appendix to the previous paper [1] that, if eq (3) and eq (2) do indeed describe the behavior of this system, then $(\alpha_D + 1.5\alpha_c)$ must be constant at all values of M_D. The last column of table 3 gives values of $(\alpha_D + 1.5\alpha_c)$ which are also plotted as the lower curve of figure 2. It is clear that, in the present instance, $(\alpha_D + 1.5\alpha_c)$ increases with M_D. This implies that there are terms in higher powers of m_D and m_c in eq (3) and eq (2) such as

$$\log \gamma_D = \log \mathring{\gamma}_D - \alpha_D m_c - \beta_D m_c^2 \tag{9}$$

$$\log \gamma_c = \log \mathring{\gamma}_c - \alpha_c m_D - \beta_c m_D^2 \tag{10}$$

where the α and β terms must be related by the equation

$$3(\alpha_D + 1.5\alpha_c) = \text{constant} - 2(2\beta_D + 4.5\beta_c)m \tag{11}$$

where $m = (m_D + 1.5m_c)$. From the slope of the plot in figure 3 we calculate

$$(2\beta_D + 4.5\beta_c) = -0.0117$$

or

$$\beta_c = -0.0026$$

if $\beta_D = 0$.

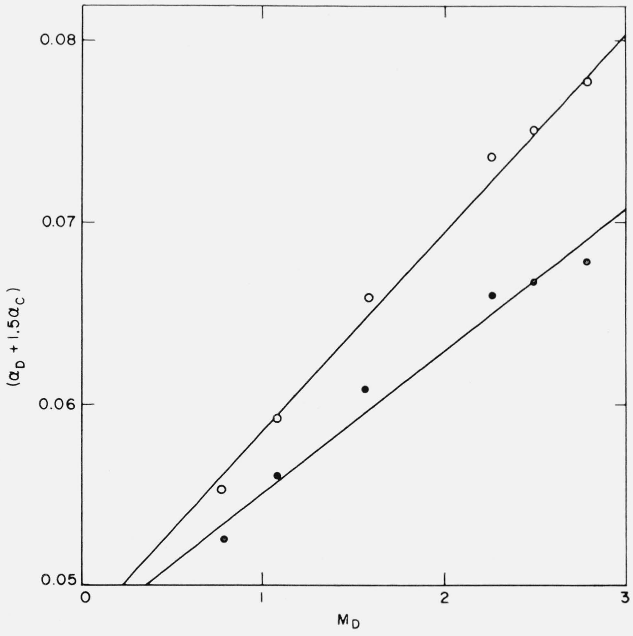

FIGURE 2. $(\alpha_D + 1.5\alpha_c)$ *versus* M_D

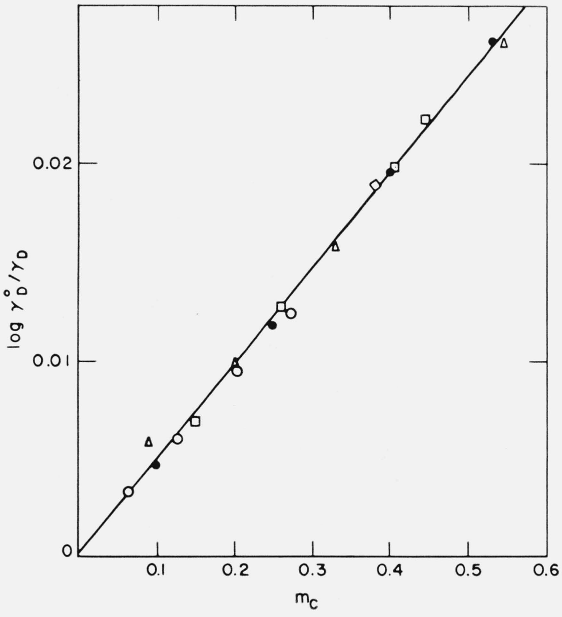

FIGURE 3. *Variation of the activity coefficient of potassium chloride on addition of barium chloride.*

$m \sim 0.8$

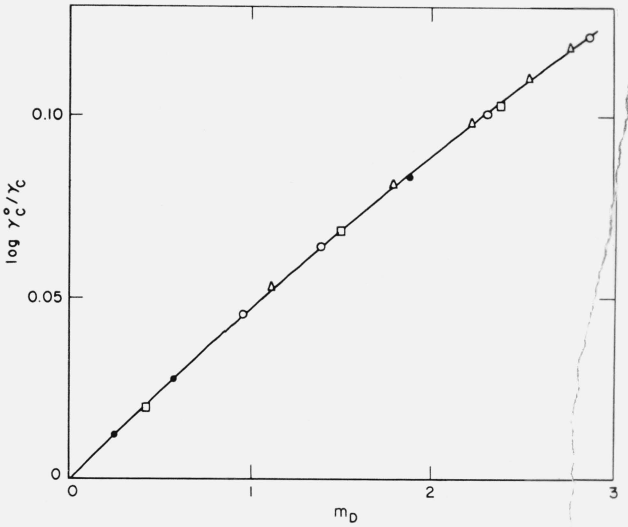

FIGURE 4. *Variation of the activity coefficient of barium chloride on addition of potassium chloride.*

$m \sim 2.8$

We now examine the data for the most concentrated solutions (set 6), because it is here that square terms in eq (9) and eq (10) will be more readily discerned. But in these concentrated solutions, the activity coefficient of potassium chloride is almost constant; log γ_D changes by only 0.0031 at the most and $\alpha_D=0.0018$ gives an adequate description of the change in log γ_D with a change in m_c as demanded by eq (3). It is, therefore, unlikely that there is a significant term in m_c^2 in eq (9).

Moreover, we can use the data for the activity coefficient of potassium chloride derived from the more dilute solutions (set 1); we find that log γ_D changes by a larger amount—as much as 0.0263. These values of log γ_D°/γ_D have been plotted in figure 3; there is no indication of curvature and hence a linear term only is needed as in eq (3).

We return to the data for set 6 and examine the variation of log γ_c with m_D. Figure 4 is a plot of log γ_c°/γ_c against m_D; some curvature is apparent and the best fit to the data is found, by the method least squares, to be log $\gamma_c^\circ/\gamma_c=0.0496\ m_D-0.0025\ m_D^2$. The data for set 4 also show slight curvature when log γ_c°/γ_c is plotted against m_D, the curvature corresponding to $\beta_c=-0.0032$. We now try a value between these two, say $\beta_c=-0.0030$.

Table 4 gives the activity coefficient of barium chloride in the solutions of set 6 calculated from the isopiestic data. The fourth column gives calculated values assuming that eq (2) holds, with only one parameter, $\alpha_c=0.0441$. The last column gives values calculated by the two-parameter equation (10) with $\alpha_c=0.0508$, $\beta_c=-0.0030$. Inspection of the last two columns shows that, in general, the two-parameter equation is superior to the one-parameter equation. The average difference between log γ_D observed and that calculated by the linear equation is 0.0025, between log γ_D observed and that calculated by the quadratic equation is 0.0009. The data for the other five sets of results in table 1 have been recalculated assuming $\beta_c=-0.0030$ throughout. The best values of α_c, together with the α_D values of table 3 and values of $(\alpha_D+1.5\alpha_c)$, are given in table 5. This table also gives average differences between "observed" values of log γ_c and those calculated by the α_c parameters of table 4 and $\beta_c=-0.0030$.

These values of $(\alpha_D+1.5\alpha_c)$ are plotted as the upper line in figure 2. The slope of the line, according to eq (11) corresponds to $\beta_c=-0.0036$ if $\beta_D=0$. This is in reasonable but not very good agreement with the value of $\beta_c=-0.0030$ which we used above.

TABLE 4. *Activity coefficient of barium chloride in potassium chloride solutions*

$m \sim 2.8.$

m_D	m_C	log γ_c°/γ_c		
		obs	calc[a]	calc[b]
0. 2539	1. 4896	0. 0124	0. 0112	0. 0127
. 5746	1. 3145	. 0276	. 0254	. 0282
1. 8855	0. 5384	. 0829	. 0832	. 0851
2. 7188	--------	. 1148	. 1199	. 1159
1. 1054	1. 0389	0. 0532	0. 0487	0. 0524
1. 7890	0. 6282	. 0816	. 0789	. 0813
2. 2111	. 3630	. 0986	. 0975	. 0976
2. 5365	. 1524	. 1104	. 1119	. 1096
2. 7661	--------	. 1189	. 1220	. 1175
0. 4287	1. 4251	0. 0196	0. 0189	0. 0213
1. 5011	0. 8090	. 0680	. 0662	. 0695
2. 3901	. 2521	. 1027	. 1054	. 1043
2. 7763	--------	. 1179	. 1224	. 1179
0. 9462	1. 1832	0. 0456	0. 0417	0. 0454
1. 3772	0. 9332	. 0644	. 0607	. 0643
2. 3016	. 3635	. 1013	. 1015	. 1010
2. 8600	--------	. 1230	. 1261	. 1208

[a] Calculated by eq (2) with $\alpha_c=0.0441$.
[b] Calculated by eq (10) with $\alpha_c=0.0508$ and $\beta_c=-0.0030$.

The discrepancy may be due to a small β_D term which would be difficult to detect; it may also be due to a possible variation of β_c with M_D.

Figure 5 illustrates the variation of activity coefficient at constant total ionic concentration. The plots on the left refer to a total ionic concentration of 1, those on the right to a total ionic concentration of 2.5. The data for NaCl-BaCl$_2$ were taken from the previous paper [1].

TABLE 5. *Parameters of eq (9) and eq (10)*

Set	M_D (mcan)	α_D	α_c	$(\alpha_B+1.5\alpha_c)$	Δ[a]
1	0.7858	0.0484	0.0046	0.0553	0.0006
2	1.0743	.0301	.0194	.0592	.0001
3	1.5678	.0152	.0337	.0658	.0005
4	2.2622	.0053	.0455	.0736	.0004
5	2.4938	.0035	.0477	.0751	.0004
6	2.7803	.0018	.0508	.0777	.0011
$\beta_D=0,\ \beta_c=-0.0030$					

[a] Δ is the average difference between log γ_c (obs.) and that calculated by eq (10), using the recorded values of α_c and $\beta_c=-0.0030$.

At a total ionic concentration of 1 there is not much variation of the activity coefficient of any component when one is replaced by another; for example the top curve at the left shows that $-\log\gamma_{\mathrm{NaCl}}=0.1825$ in a solution containing sodium chloride only and 0.1929 when $x=0.5$, $m_B=0.5$, $m_c=0.333$. In the limiting case where the solution contains no sodium chloride and the barium chloride concentration is 0.667, $-\log\gamma_{\mathrm{NaCl}}=0.2032$.

It will be seen that the addition of barium chloride to a solution of sodium chloride decreases the activity coefficient of sodium chloride; conversely, the addition of sodium chloride to a solution of barium chloride increases the activity coefficient of barium chloride; in other words, on admixture, the activity coefficients of the two solutes come closer together. This occurs so often that it might be termed the "expected" behavior. One of the few exceptions known occurs in the hydrochloric acid-lithium chloride system [5] at high concentrations where the addition of lithium chloride to a solution of hydrochloric acid "unexpectedly" *increases* the activity coefficient of hydrochloric acid.

In the potassium chloride-barium chloride system at a total ionic concentration of 1, neither salt has much influence on the activity coefficient of the other. But each salt decreases the activity coefficient of the other, and here we see an example of unusual salt interaction.

Turning now to a consideration of the systems at a total ionic concentration of 2.5, in the system sodium chloride-barium chloride, the activity coefficient of sodium chloride is raised on admixture with barium chloride but that of barium chloride is lowered on admixture with sodium chloride. The activity coefficients become more separated on admixture but only by a small amount. The separation effect is much more marked in the potassium chloride-barium chloride system. The effect of barium chloride on the activity coefficient is "normal", lowering the activity coefficient of potassium chloride in its own solution at 2.5*m*, $\gamma_{\mathrm{KCl}}=0.569$, to $\gamma_{\mathrm{KCl}}=0.562$ in the limiting case where the solution contains only barium chloride. But the effect of potassium chloride on the activity coefficient of barium chloride is marked. Thus, $\gamma_c=0.446$ for a solution containing barium chloride only at $m=2.5$, $m_c=1.667$. This is decreased further by the addition of potassium chloride and in the limiting case where the solution contains potassium chloride only at a concentration of 2.5 *m*, $\gamma_c=0.354$.

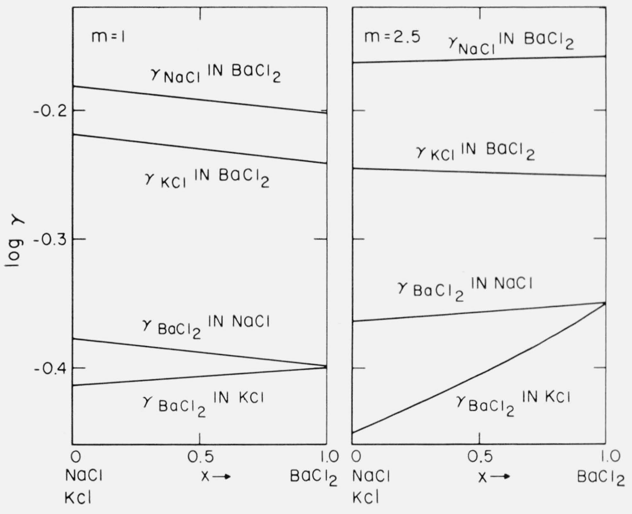

FIGURE 5. *Activity coefficients of the systems* NaCl-BaCl$_2$ *and* KCl-BaCl$_2$.

4.3. Activity Coefficients at Constant Total Ionic Strength

The isopiestic method used in this work is well adapted for a study of systems at constant total ionic concentration and not so suitable for systems at constant total ionic strength. Nevertheless, it is of interest to obtain some description, if only approximate, of such systems. The procedure is as follows. By definition,

$$I=m_D+3m_c \tag{12}$$

and we have defined *m* as

$$m=m_D+1.5m_c, \tag{13}$$

hence

$$I=m+1.5m_c=m(1+x)$$

$$=\frac{M_D}{R}(1+x)=M_D\frac{1+x}{1-ax-bx^2} \tag{14}$$

or

$$bIx^2+(aI+M_D)x-(I-M_D)=0. \tag{15}$$

Then, for any value of M_D corresponding to an entry in table 1 and for any selected value of *I*, *x* can be calculated using the values of a and b given in table 2. For example, if $M_D=2.4938$, $a=0.0151$, $b=-0.1170$, then the solution of eq (15) for $I=3.5$ is $x=0.4241$. By eq (4), $R=1.0147$ and so $m=2.4577$, $m_D=1.4154$, $m_c=0.6949$. For this value of M_D the integral term of eq (7) is $-0.0204x^2M_D\varphi=-0.0085$. At $M_D=2.4938$, $\log \Gamma_D=-0.2448$ [4] and $\log R=0.0063$ so that, by eq (5), $\log \gamma_D=-0.2470$. But at this total ionic strength, $\log \gamma_D^{\circ}=-0.2427$ and if the equations

$$\log \gamma_D=\log \gamma_D^{\circ}-\alpha_D I_c \qquad (16)$$

$$\log \gamma_c=\log \gamma_c^{\circ}-\alpha_c I_B \qquad (17)$$

hold, then $\alpha_D=0.0021$. Note that, in order not to introduce too many symbols, α_D has been used with different meanings in eq (3) and eq (16) and also α_c in eq (2) and eq (17).

In this way, values of α_D and α_c at various values of I have been evaluated and are given in table 6 along with values of $(2\alpha_D+\alpha_c)$. As was shown before [1], if eq (16) and eq (17) hold, which means that there are no terms such as $\beta_D I_c^2$, then $(2\alpha_D+\alpha_c)$ must be independent of I. It is clear from figure 6 that this quantity is not independent of I. The dependence of $(2\alpha_D+\alpha_c)$ on I is given by

$$(2\alpha_D+\alpha_c)=\text{constant}-2(2\beta_D+\beta_c). \qquad (18)$$

TABLE 6. *Parameters of eq (16) and eq (17)*

I	α_D	α_c	$(2\alpha_D+\alpha_c)$
1.0	−0.008	0.033	0.017
1.5	−.003	.025	.019
2.0	−.002	.022	.018
2.5	0	.021	.021
3.0	+0.001	.021	.023
3.5	.002	.020	.024
4.0	.003	.021	.027

The variation of $(2\,\alpha_D+\alpha_c)$ with I (fig. 6) suggests that $(2\,\beta_D+\beta_c)$ is about 0.0033. This would be consistent with both β_D and β_c having values about 0.001 but in the absence of more extensive data it is not possible to assign an accurate value to $(2\beta_D+\beta_c)$ or to say how it is divided between β_D and β_c.

The data in figure 6 suggest that α_c may have very large values in dilute solution and α_D large, negative values. This cannot be stated with certitude until more data are available in dilute solutions, but it would not be inconsistent with the behavior found in other systems, for example, hydrochloric acid-cesium chloride [6].

The α_D and α_c parameters are small compared with those found for the hydrochloric acid-barium chloride system [7], but comparable with those for the sodium chloride-barium chloride system [1]. There is one remarkable difference, however, in that α_c has positive values at all values of I accessible to calculation. This means that potassium chloride decreases the activity coefficient of barium chloride in systems at constant total ionic strength.

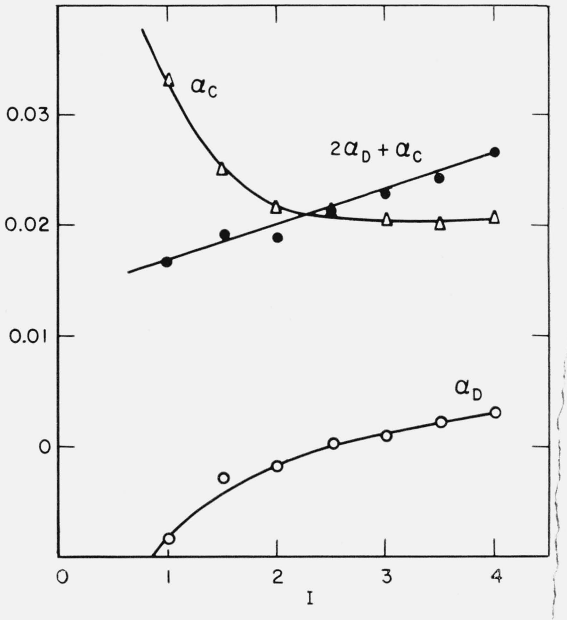

FIGURE 6. *Parameters of eq (16) and eq (17).*

Shonhorn and Gregor [8] have made measurements of the potassium chloride-barium chloride system using as one electrode multilayer membranes of barium stearate. They found $\alpha_D=-0.044$, $\alpha_c=-0.072$ at $I=0.6$ and $\alpha_D=-0.058$, $\alpha_c=-0.081$ at $I=1.5$. These are very different to the values we have found; at this stage we can do little more than note the difference; we might perhaps say that the reversibility of this electrode to barium ions could be questioned and suggest that measurements on this system with a potassium glass electrode would be useful.

5. Excess Free Energy of Mixing

By this we mean the excess free energy when a solution of potassium chloride and another solution of barium chloride are mixed under specified conditions.[2] We are particularly interested in the condition of constant total ionic concentration. This results if a solution of y_D kg of water containing potassium chloride sufficient to give a molality m is mixed with a solution of y_c kg of water containing barium chloride sufficient to give a molality $m/1.5$, $(y_D+y_c=1)$. This gives a solution containing 1 kg of water, y_D m moles of potassium chloride and y_c $m/1.5$ moles of barium chloride. For example, a solution containing 0.5 kg of water and 0.75 mole of potassium chloride (molality 1.5, total ionic concentration 1.5) might be mixed with a solution containing 0.5 kg of water and 0.5 moles of barium chloride (molality 1.0, total ionic concentration 1.5). The result would be a solution containing 1 kg of water, 0.75 m to potassium chloride, 0.5 m to barium chloride, of total ionic concentration 1.50.

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[2] The *total* free energy of mixing contains a term which, for 1:1-electrolytes, is $2RT\ m\ [y_B \ln y_B+y_c \ln y_c]$. This is ignored in calculating the *excess* free energy of mixing (see appendix).

The general equations for the excess free energy of mixing are developed in the appendix to this paper. For the case where potassium chloride and barium chloride solutions are mixed without change in total ionic concentration and the final molalities are such that $m_D=1.5m_c$ and $\beta_D=0$ in eq (9),

$$\frac{\Delta G^E}{2.303RT}=-m_D m_c(\alpha_D+1.5\alpha_c)-4.5m_D m_c^2\beta_c$$

$$=-\frac{m^2}{6}(\alpha_D+1.5\alpha_c)-\frac{m^3}{4}\beta_c.$$

Using values of $(\alpha_D+1.5\alpha_c)$ interpolated at round values of m from table 5, values of $\triangle G^E$ have been calculated. These are given in table 7. They are remarkable in being comparatively large (and negative). In this respect they contrast with corresponding data for the mixture of solutions of sodium chloride and barium chloride where no free energy of mixing exceeding 1 cal mol^{-1} is found. This is a consequence of the comparatively large values of $(\alpha_D+1.5\alpha_c)$ for the potassium chloride-barium chloride system and the almost negligible values of $(\alpha_D+1.5\alpha_c)$ for the sodium chloride-barium chloride system.

TABLE 7. *Excess free energy of mixing* [a]

Constant total ionic concentration		Constant total ionic strength			
m	KCl-BaCl$_2$	I	KCl-BaCl$_2$	NaCl-BaCl$_2$	HCl-BaCl$_2$
	ΔG^E		ΔG^E	ΔG^E	ΔG^E
0.75	−7	1.0	−3	−2	−10
1.0	−12	1.5	−7	−4	----------
1.5	−30	2.0	−12	−7	−33
2.0	−55	2.5	−22	−11	----------
2.5	−93	3.0	−35	−17	−72
3.0	−134	3.5	−50	−26	----------
		4.0	−73	−35	----------

[a] In calories per kg of water, 1 calorie=4.1840 J.

It is also shown in the appendix that for a system with $\beta_D=\beta_c=0$, the excess free energy of mixing at constant total ionic strength with $I/2=I_D=I_c$, is

$$\frac{\Delta G^E}{2.303RT}=-\frac{I^2}{8}(2\alpha_D+\alpha_c).$$

Values of ΔG^E have been calculated using $(2\alpha_D+\alpha_c)$ values from table 6. The results are given in table 7 along with values of ΔG^E for the hydrochloric acid-barium chloride [7] and sodium chloride-barium chloride [1] systems. It will be noted that in the potassium chloride-barium chloride system, the decrease in free energy on mixing is much larger at constant total ionic concentration than at constant total ionic strength. At constant total ionic strength, the values are greatest in the hydrochloric acid-barium chloride system and least in the sodium chloride-barium chloride system. This suggests that, with increasing atomic number of the univalent cation, there is a minimum in the free energy decrease at the sodium chloride-barium system.

These excess free energies of mixing, the one at constant total ionic concentration, the other at constant total ionic strength, are not independent. This can be shown by the following example. Consider an admixture process represented schematically by:

1 | 0.5 kg H_2O
1.333 moles of D

+

2 | 0.5 kg H_2O
0.889 moles of C

$\longrightarrow$ 1 kg H_2O
1.333 moles of D
0.889 moles of C

Each of the single salt solutions has a total ionic concentration of $m=2.667$ and so has the solution formed after mixing. The excess free energy of mixing, interpolated from table 7, is −107 cal per kg water.

The same mixed solution could, however, be made by a process at constant total ionic strength:

3 | 0.333 kg H_2O
1.333 moles of D

+

4 | 0.667 kg H_2O
0.889 moles of C

$\longrightarrow$ 1 kg H_2O
1.333 moles of D
0.889 moles of C

Each of the single salt solutions has a total ionic strength $I=4$ and so has the solution formed after mixing. The free energy of mixing at $I=4$ is recorded in table 7 as −73 cal per kg of water. This, however, refers to mixing which produces a solution in which potassium chloride and barium chloride are present at equal ionic strength, the concentration of potassium chloride being $2m$ and that of barium chloride $0.667m$. We are now discussing the position when $I_D=m_D=1.333$, $m_c=0.889$, $I_c=2.667$. It is shown in the appendix to this paper that the excess free energy of mixing (if $\beta_D=\beta_c=0$) is given by:

$$\frac{\Delta G^E}{2.303RT}=-\frac{1}{2}I_D I_c(2\alpha_D+\alpha_c)$$

or, using the values of α_D and α_c given in table 6 at $I=4$,

$$\Delta G^E=-65 \text{ cal per kg of water.}$$

The excess free energy of the solutions in boxes 3 and 4 above over that of the solutions in boxes 1 and 2 is given by:

$$\frac{\Delta G}{RT}=\frac{1}{3}[-2m_3\varphi_3+2m_3\ln\gamma_3]+\frac{2}{3}[-3m_4\varphi_4+3m_4\ln\gamma_4]$$

$$-\frac{1}{2}[-2m_1\varphi_1+2m_1\ln\gamma_1]-\frac{1}{2}[-3m_2\varphi_2+2m_2\ln\gamma_2]$$

where the subscripts refer to the values of m, φ, and γ appropriate to the solutions represented by each of the four boxes. Substituting these values of m, φ, and γ [1, 4], we find $\Delta G=-47$ cal per kg of water. Thus we could produce the mixed solution by two routes. The solutions represented by boxes 1 and 2 could be mixed without change in total ionic concentration and with a decrease of free energy of 107 cal per kg of water. Alternatively, they could be converted into the solutions represented by boxes 3 and 4 and then mixed without change in total ionic strength. The decrease in free energy would be $65+47=112$ cal per kg of water. The decrease in free energy should be the same by either route. Exact agreement cannot be expected because of errors due to interpolation and because of the possibility of a β term in eq (17) which would affect the value of -65 cal per kg of water for the free energy of mixing at constant total ionic strength. The agreement is good enough, however, to show that there is internal consistency between the results at constant total ionic strength and those at constant total ionic concentration.

6. Appendix

Equations for the excess free energy of a solution of two electrolytes are derived as follows [6, 9, 10, 11].

Consider a solution of electrolyte B (giving ν_B ions) at molality m_B, and electrolyte C (giving ν_c ions) at molality m_c. Let ζ be a linear combination of the form

$$\zeta=k_Bm_B+k_cm_c$$

and let y_B, y_c be defined by

$$y_B=k_Bm_B/\zeta,\ y_c=k_cm_c/\zeta,\ y_B+y_c=1.$$

Let the activity coefficients of B and C be given by

$$\ln\gamma_B=\ln\gamma_B^0+A_Bm_c+B_Bm_c^2$$

$$\ln\gamma_c=\ln\gamma_c^0+A_cm_B+B_cm_B^2$$

subject to the condition that ζ is constant; here A_B, A_c are functions of ζ but not of m_B, m_c independently and B_B, B_c are parameters independent of ζ, m_B, and m_c. If both electrolytes are of the 1:1 type, $\nu_B=\nu_c=2$, it is convenient to put $k_B=k_c=1$ and $\zeta=m=m_B+m_c$. The change in free energy on mixing is that for a process which can be represented schematically:

$$\begin{array}{c}\boxed{\begin{array}{c}y_B\text{ kg }H_2O\\ y_Bm\text{ moles of }B\end{array}}\\ +\\ \boxed{\begin{array}{c}y_c\text{ kg }H_2O\\ y_cm\text{ moles of }C\end{array}}\end{array}\longrightarrow\boxed{\begin{array}{c}1\text{ kg }H_2O\\ y_Bm\text{ moles of }B\\ y_cm\text{ moles of }C\end{array}}$$

With respect to B the increment in free energy is $2RTm_B\ln(m_B\gamma_B/m\gamma_B^\circ)$ and with respect to m_c it is $2RTm_c\ln(m_c\gamma_c/m\gamma_c^\circ)$. Thus the increment due to B and C can be written

$$2RTm[y_B\ln y_B+y_c\ln y_c]$$

$$+2RT[m_B\ln\gamma_B/\gamma_B^\circ+m_c\ln\gamma_c/\gamma_c^\circ].$$

The first of these terms will occur in the expression for the free energy increment on mixing even ideal solutions and is not considered part of the *excess* free energy of mixing. An analogous term is found in the expression for the *total* entropy of mixing but not in the expression for the enthalpy of mixing.

The second term,

$$2RT[m_B\ln\gamma_B/\gamma_B^\circ+m_c\ln\gamma_c/\gamma_c^\circ]$$

$$=2RT[m_B(A_Bm_c+B_Bm_c^2)+m_c(A_cm_B+B_cm_B^2)],$$

is part of the free energy change resulting from departures from ideality. This, together with changes in the solvent free energy, constitutes the *excess* free energy of mixing.

In the more complicated case of two electrolytes of different valence type, we can represent the mixing process as:

$$\begin{array}{c}\boxed{\begin{array}{l}y_B\text{ kg }H_2O\\ y_B\zeta/k_B\text{ moles of }B\end{array}}\\ +\\ \boxed{\begin{array}{l}y_c\text{ kg }H_2O\\ y_c\zeta/k_c\text{ moles of }C\end{array}}\end{array}\longrightarrow\boxed{\begin{array}{l}1\text{ kg }H_2O\\ y_B\zeta/k_B\text{ moles of }B\\ y_c\zeta/k_c\text{ moles of }C\end{array}}$$

where all three solutions have the same value of ζ. With respect to B the excess free energy is

$$\nu_BRTm_B\ln\gamma_B/\gamma_B^0=\nu_BRTm_B(A_Bm_c+B_Bm_c^2)$$

and with respect to C the excess free energy is

$$\nu_cRTm_c\ln\gamma_c/\gamma_c^0=\nu_cRTm_c(A_cm_B+B_cm_B^2).$$

As before, the free energy increment of the solvent remains to be computed.

The solvent effect can be evaluated as follows.

The Gibbs-Duhem equation can be written:

$$-55.51d\ln a_w=\nu_B m_B d\ln m_B+\nu_c m_c d\ln m_c+\nu_B m_B d\ln\gamma_B+\nu_c m_c d\ln\gamma_c.$$

The first two terms on the right can be written

$$\zeta\left(\frac{\nu_B}{k_B}-\frac{\nu_c}{k_c}\right)dy_B.$$

The third term is

$$-\frac{\nu_B y_B}{k_B k_c}\zeta^2\left(A_B+\frac{2B_B y_c}{k_c}\zeta\right)dy_B$$

and the fourth term

$$\frac{\nu_c y_c}{k_B k_c}\zeta^2\left(A_c+\frac{2B_c y_B}{k_B}\zeta\right)dy_B.$$

Consequently

$$-55.51d\ln a_w=\zeta\left(\frac{\nu_B}{k_B}-\frac{\nu_c}{k_c}+\frac{\nu_c\zeta}{k_B k_c}A_c\right)dy_B-\frac{\zeta^2}{k_B k_c}(\nu_B A_B+\nu_c A_c)y_B dy_B-\frac{2\zeta^3}{k_B k_c}\left(\frac{\nu_B B_B}{k_c}-\frac{\nu_c B_c}{k_B}\right)y_B y_c dy_B.$$

On integration from $y_B=0$ to y_B,

$$-55.51\ln\frac{a_w}{a_{w(c)}}=\zeta\left(\frac{\nu_B}{k_B}-\frac{\nu_c}{k_c}+\frac{\nu_c\zeta}{k_B k_c}A_c\right)y_B-\frac{\zeta^2}{2k_B k_c}(\nu_B A_B+\nu_c A_c)y_B^2-\frac{\zeta^3}{k_B k_c}\left(\frac{\nu_B B_B}{k_c}-\frac{\nu_c B_c}{k_B}\right)\left(y_B^2-\frac{2y_B^3}{3}\right)$$

where a_w is the water activity of the mixed solution and $a_{w(c)}$ that of the solution containing C only. On integration from $y_B=1$ to y_B,

$$-55.51\ln\frac{a_w}{a_{w(B)}}=\zeta\left(\frac{\nu_c}{k_c}-\frac{\nu_B}{k_B}+\frac{\nu_B}{k_B k_C}\zeta A_B\right)y_c-\frac{\zeta^2}{2k_B k_c}(\nu_B A_B+\nu_c A_c)y_c^2+\frac{\zeta^3}{k_B k_c}\left(\frac{\nu_B B_B}{k_c}-\frac{\nu_c B_c}{k_B}\right)\left(y_c^2-\frac{2y_c^3}{3}\right)$$

where $a_{w(B)}$ is the water activity of the solution containing B only.

The total excess free energy is

$$\frac{\Delta G^E}{RT}=\nu_B m_B\ln\frac{\gamma_B}{\gamma_B^0}+\nu_c m_c\ln\frac{\gamma_c}{\gamma_0^c}+55.51y_B\ln\frac{a_w}{a_{w(B)}}+55.51y_c\ln\frac{a_w}{a_{w(c)}}$$

which reduces to

$$\frac{\Delta G^E}{RT}=\frac{\zeta^2}{2k_B k_c}y_B y_c(\nu_B A_B+\nu_c A_c)+\frac{\zeta^3}{k_B k_c}y_B y_c\left\{\left(\frac{\nu_B}{k_c}y_B B_B+\frac{\nu_c}{k_B}y_c B_c\right)-\frac{2}{3}\left(\frac{\nu_B B_B}{k_c}-\frac{\nu_c B_c}{k_B}\right)(y_B-y_c)\right\}.$$

Putting $\nu_B=\nu_c=2$, $k_B=k_c=1$,

$$\zeta=m_B+m_c,$$

$$\frac{\Delta G^E}{RT}=m_B m_c\left[(A_B+A_c)+2\left\{(m_B B_B+m_c B_c)-\frac{2}{3}(B_B-B_c)(m_B-m_c)\right\}\right]$$

and when $y_B=y_c=0.5$, $A_B=-2.303\alpha_B$, $A_c=-2.303\alpha_c$, $B_B=-2.303\beta_B$, $B_c=-2.303\beta_c$,

$$\log\gamma_B=\log\gamma_B^0-\alpha_B m_c-\beta_B m_c^2$$

$$\log\gamma_c=\log\gamma_c^0-\alpha_c m_B-\beta_c m_B^2$$

$$\frac{\Delta G^E}{2.303RT}=-\frac{m^2}{4}[(\alpha_B+\alpha_c)+m(\beta_B+\beta_c)].$$

For a mixture of sodium chloride and barium chloride at constant total ionic strength, we put $\nu_B=2$, $\nu_c=3$, $k_B=1$, $k_c=3$, $A_B=-3\times2.303\alpha_B$, $A_c=-2.303\alpha_c$, $B_B=-9\times2.303\beta_B$, $B_c=-2.303\beta_c$, $\zeta=I=I_B+I_c=m_B+3m_c$,

$$\log\gamma_B=\log\gamma_B^0-\alpha_B I_c-\beta_B I_c^2$$

$$\log\gamma_c=\log\gamma_c^0-\alpha_c I_B-\beta_c I_B^2$$

$$\frac{\Delta G^E}{2.303RT}=-\frac{1}{2}I_B I_c(2\alpha_B+\alpha_c)-I_B I_c\left\{2\beta_B I_B+\beta_c I_c-\frac{2}{3}(2\beta_B-\beta_c)(I_B-I_c)\right\}$$

and when $I_B=I_c$, $I/2=I_B=I_c$,

$$\frac{\Delta G^E}{2.303RT}=-\frac{I^2}{8}\{(2\alpha_B+\alpha_c)+I(2\beta_B+\beta_c)\}$$

and when $\beta_B=\beta_c=0$

$$\frac{\Delta G^E}{RT}=-\frac{I^2}{8}(2\alpha_B+\alpha_c).$$

For the condition of constant total ionic concentration, we put $\nu_B=2$, $\nu_c=3$, $k_B=1$, $k_c=1.5$,

$$\zeta = m_B + 1.5m_c = m,$$

$$A_B = -2.303\alpha_B,\ A_c = -2.303\alpha_c,$$

$$B_B = -2.303\beta_B,\ B_c = -2.303\beta_c,$$

$$\log \gamma_B = \log \gamma_B^0 - \alpha_B m_c - \beta_B m_c^2$$

$$\log \gamma_c = \log \gamma_c^0 - \alpha_c m_B - \beta_c m_B^2$$

$$\frac{\Delta G^E}{2.303RT} = -m_B m_c(\alpha_B + 1.5\alpha_c) - m_B m_c \left\{ \frac{2}{1.5} m_B\beta_B + 4.5m_c\beta_c - \frac{2}{3}\left(\frac{2\beta_B}{1.5} - 3\beta_c\right)(m_B - 1.5m_c) \right\}$$

and if $m_B = 1.5m_c$, $m = 2m_B = 3m_c$, $\beta_B = 0$,

$$\frac{\Delta G^E}{2.303RT} = -\frac{m^2}{6}(\alpha_B + 1.5\alpha_c) - \frac{m^3}{4}\beta_c.$$

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7. References

[1] R. A. Robinson and V. E. Bower, J. Res. NBS 69A (Phys. and Chem.) No. 1, 19 (1965).

[2] H. A. C. McKay and J. K. Perring, Trans. Faraday Soc. **49,** 163 (1953).

[3] V. E. Bower and R. A. Robinson, J. Res. NBS 69A (Phys. and Chem.) p. 131 (1965).

[4] R. A. Robinson and R. H. Stokes, Electrolyte solutions, Appendix 8.3, 2d. ed., (Butterworths Scientific Publications, London, 1959).

[5] J. E. Hawkins, J. Am. Chem. Soc. **54,** 4480 (1932).

[6] H. S. Harned and B. B. Owen, The physical chemistry of electrolytic solutions, ch. 14, 3d. ed. p. 610, (Reinhold Publ. Corp., New York, N.Y., (1958).

[7] H. S. Harned and R. Gary, J. Am. Chem. Soc. **76,** 5924 (1954).

[8] H. Schonhorn and H. P. Gregor, J. Am. Chem. Soc. **83,** 3576 (1961).

[9] H. S. Harned, J. Phys. Chem. **63,** 1299 (1959).

[10] H. S. Harned, J. Phys. Chem. **64,** 112 (1960).

[11] H. A. C. McKay, Disc. Faraday Soc. **24,** 76 (1957).

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