

# Thermodynamics of Mixed Electrolyte Solutions. VIII. An Isopiestic Study of the Ternary System $\text{KCl-MgCl}_2\text{-H}_2\text{O}$ at $25^\circ\text{C}$

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*The osmotic coefficients of aqueous solutions of mixtures of potassium and magnesium chlorides were derived from isopiestic measurements at  $25^\circ\text{C}$ . The isopiestic data were treated by the methods of both Scatchard and Friedman, and the results obtained agree very well over the ionic strength range of 1–5. Interaction coefficients were obtained from both formalisms. Excess free energies of mixing were calculated and compared with those of similar systems.*

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**KEY WORDS:** Activity coefficients; excess Gibbs free energy of mixing; interaction coefficients; osmotic coefficients; mixed salt solutions; KCl;  $\text{MgCl}_2$ .

## 1. INTRODUCTION

Accurate thermodynamic data on the ternary system  $\text{KCl-MgCl}_2\text{-H}_2\text{O}$  are needed for the interpretation of the quaternary system  $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ .<sup>(1)</sup> Isopiestic measurements reported in the literature<sup>(2)</sup> over an ionic strength range of 3.3 to 6 mole-kg<sup>-1</sup> do not tally with standard data on osmotic coefficients for both pure  $\text{MgCl}_2$ <sup>(3)</sup> and mixed  $\text{KCl-MgCl}_2$  aqueous solutions.<sup>(4)</sup> In order to resolve the discrepancies observed and complete the data needed at lower ionic strengths, an isopiestic study of the ternary system  $\text{KCl-MgCl}_2\text{-H}_2\text{O}$  was initiated to yield the osmotic coefficients and excess Gibbs free energies of mixing at  $25^\circ\text{C}$ .

## 2. EXPERIMENTAL

The isopiestic measurements were made using the apparatus previously described<sup>(5)</sup> and using KCl as the reference electrolyte. Stock solutions of

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**Table I.** Measured and Calculated Osmotic Coefficients  $\phi$  in the KCl-MgCl<sub>2</sub>-H<sub>2</sub>O System at 25°C

$M_r$	$I$	$y_B$	$\phi_{\text{exp}}$	$\phi_{\text{calc}}^a$	$\phi_{\text{calc}}^b$
0.6652 (0.9787)	0.7211	0.1557	0.897	0.898	0.898
	0.7605	0.2510	0.897	0.899	0.899
	0.8889	0.5091	0.901	0.902	0.903
	1.0497	0.7500	0.910	0.909	0.910
	1.2902	1.0	0.925	0.925	0.925
1.0782 (0.9657)	1.2185	0.2510	0.909	0.908	0.908
	1.4091	0.5091	0.922	0.923	0.924
	1.6342	0.7500	0.948	0.947	0.947
	1.9554	1.0	0.990	0.991	0.991
1.8630 (0.9409)	1.9855	0.1557	0.925	0.923	0.923
	2.0699	0.2510	0.936	0.933	0.933
	2.3499	0.5091	0.967	0.970	0.970
	2.6468	0.7500	1.023	1.022	1.022
	3.0409	1.0	1.114	1.114	1.114
2.3132 (0.9263)	2.4661	0.1557	0.935	0.937	0.937
	2.5572	0.2510	0.951	0.950	0.950
	2.8601	0.5091	0.998	0.998	0.997
	3.1954	0.7500	1.064	1.066	1.065
	3.5923	1.0	1.184	1.183	1.183
2.7782 (0.9111)	3.0591	0.2510	0.967	0.969	0.969
	3.3822	0.5102	1.026	1.027	1.027
	3.7211	0.7500	1.112	1.109	1.109
	4.1275	1.0	1.253	1.255	1.255
3.3920 (0.8908)	3.6997	0.2510	0.993	0.994	0.994
	4.0457	0.5102	1.066	1.066	1.066
	4.3952	0.7500	1.169	1.167	1.167
	4.7805	1.0	1.344	1.345	1.345
4.1953 (0.8637)	4.5312	0.2510	1.027	1.027	1.028
	4.8933	0.5102	1.116		
	5.2471	0.7500	1.241		
	5.5890	1.0	1.456		
4.5961 (0.8499)	4.9553	0.2510	1.043		
	5.3002	0.5102	1.144		
	5.6408	0.7500	1.281		
	5.9891	1.0	1.509		

$$^a (1 + y_A)\phi_{\text{calc}} = 2y_A\phi_A^\circ + y_B\phi_B^\circ + y_A y_B(0.0572I - 0.01221I^2).$$

$$^b (1 + y_A)\phi_{\text{calc}} = 2y_A\phi_A^\circ + y_B\phi_B^\circ + y_A y_B(0.09051I - 0.04095I^{3/2}).$$

**Table II.** Measured<sup>a</sup> and Calculated Osmotic Coefficients in the KCl–MgCl<sub>2</sub>–H<sub>2</sub>O System at  $y_B = 0.6$  at 25°C

$I$	$\phi$	$\phi_{\text{calc}}^b$	$\phi_{\text{calc}}^c$
0.50	0.893	0.890	0.890
1.00	0.910	0.907	0.907
1.50	0.931	0.931	0.932
2.50	0.988	0.989	0.989
3.50	1.053	1.053	1.053

<sup>a</sup> Experimental  $\phi$  from ref. 4.

<sup>b</sup> Calculated by Scatchard's method.

<sup>c</sup> Calculated by Friedman's method.

the salts and their mixtures were prepared as before and the osmotic coefficients were isopiastically determined over an ionic strength of 0.8 to 6 at 25°C.

### 3. RESULTS

The isopiestic data are given in Table I. The first column gives the molality of the KCl reference solution and the water activity of the set,<sup>(3)</sup> the second column gives  $I$ , the total ionic strength of the mixed salt solution, and the third column gives the ionic strength fraction of the magnesium chloride,  $y_B = I_B/I = 3m_B/(m_A + 3m_B)$ , where  $m_A$  is the molality of KCl and  $m_B$  the molality of MgCl<sub>2</sub>. The quantity  $\phi$  is the observed osmotic coefficient of the solution. The results of Robinson and Stokes<sup>(4)</sup> are listed in Table II.

### 4. THE EXCESS GIBBS FREE ENERGY OF MIXING

The excess Gibbs free energy of mixing  $\Delta G^{\text{ex}}(y, I)$  is usually defined as

$$\Delta G^{\text{ex}}(y, I) = G^{\text{ex}}(y, I) - y_A G^{\text{ex}}(0, I) - y_B G^{\text{ex}}(1, I) \quad (1)$$

where  $G^{\text{ex}}(0, I)$  and  $G^{\text{ex}}(1, I)$  apply to solutions of pure KCl and MgCl<sub>2</sub>, respectively.

The most direct way of calculating  $\Delta G^{\text{ex}}(y, I)$  makes use of Eq. (16.32) from ref. (6) whereby

$$[\partial(\Delta G^{\text{ex}}/I)/\partial(1/I)]_{P,T,y} = \Delta G_w^{\text{ex}}(y, I) \quad (2)$$

$\Delta G_w^{\text{ex}}(y, I)$  is the solvent contribution to the excess free energy of mixing and is obviously defined by

$$\Delta G_w^{\text{ex}}(y, I) \equiv G_w^{\text{ex}}(y, I) = y_A G_w^{\text{ex}}(0, I) - y_B G_w^{\text{ex}}(1, I) \quad (3)$$

The integration of Eq. (2) at constant  $y$  yields<sup>(6)</sup>

$$\Delta G^{\text{ex}}(y, I) = I \int_0^I \Delta G_w^{\text{ex}}(y, I') d(1/I') \quad (4)$$

The solvent contribution  $\Delta G_w^{\text{ex}}(y, I)$  can be derived from the osmotic coefficients since by definition<sup>(6)</sup>

$$G_w^{\text{ex}}(y, I) = -RTm(y, I)[\phi(y, I) - 1] \quad (5)$$

$$G_w^{\text{ex}}(0, I) = -RTm(0, I)[\phi(0, I) - 1] \quad (6)$$

$$G_w^{\text{ex}}(1, I) = -RTm(1, I)[\phi(1, I) - 1] \quad (7)$$

where  $m(y, I)$ ,  $m(0, I)$ , and  $m(1, I)$  represent the molalities of the mixed solution and the pure KCl and  $\text{MgCl}_2$  solutions, respectively, at the same ionic strength  $I$ .

It follows that

$$\begin{aligned} \Delta G_w^{\text{ex}}(y, I) = -RTI \left[ \frac{m(y, I)}{I} \phi(y, I) - y_A \frac{m(0, I)}{I} \phi(0, I) \right. \\ \left. - y_B \frac{m(1, I)}{I} \phi(1, I) \right] \end{aligned} \quad (8)$$

which in the case of an unsymmetrical mixture (KCl– $\text{MgCl}_2$ – $\text{H}_2\text{O}$ ) yields

$$\Delta G_w^{\text{ex}}(y, I) = -RTI[(1 + y_A)\phi(y, I) - 2y_A\phi(0, I) - y_B\phi(1, I)] \quad (9)$$

since according to Friedman's nomenclature<sup>(6)</sup>

$$\begin{aligned} m(y, I)/I &= 1 + y_A \\ m(0, I)/I &= 2 \\ m(1, I)/I &= 1 \end{aligned} \quad (10)$$

or

$$\Delta G_w^{\text{ex}}(y, I) \equiv -RTI\Delta \quad (11)$$

Substituting in Eq. (4) one obtains

$$\begin{aligned} \Delta G^{\text{ex}}(y, I) &= -RTI \int_0^I \Delta d \ln(1/I) = 2RTI \int_0^I \Delta d \ln(\sqrt{I}) \\ &= 2RTI \int_0^I (\Delta/\sqrt{I}) d(\sqrt{I}) \end{aligned} \quad (12)$$

The integrand in Eq. (12) can be written

$$\begin{aligned} \Delta/\sqrt{I} = \{ & (1 + y_A)[\phi(y, I) - I] - 2y_A[\phi(0, I) - 1] \\ & - y_B[\phi(1, I) - 1]\}/\sqrt{I} \end{aligned} \quad (13)$$

and its limiting value can be calculated using the Debye-Hückel limiting law for the osmotic coefficient  $\phi^{(7)}$

$$\phi - 1 = -\frac{4.606A\sqrt{I}}{3} \cdot \frac{I}{\sum m_i} \quad (14)$$

Substitution of Eq. (14) in Eq. (13) yields

$$\lim(\Delta_{I \rightarrow 0}/\sqrt{I}) = (-4.606A/3)(1 - y_A - y_B) \equiv 0 \quad (15)$$

The difficulty caused by the lower limit of the integral in Eq. (4) has thus been overcome. This is generally true and can be shown to hold for any kind of mixture.<sup>(8)</sup> The case of asymmetric mixtures will be considered later.

The activity coefficients can be obtained in a straightforward manner from the excess free energy of mixing. By definition

$$\Delta G^{\text{ex}}(y, I) = \Delta G_w^{\text{ex}} + RTI \left[ 2y_A \ln \frac{\gamma_A(y, I)}{\gamma_A(0, I)} + y_B \ln \frac{\gamma_B(y, I)}{\gamma_B(1, I)} \right] \quad (16)$$

or

$$\frac{\Delta G^{\text{ex}}(y, I) + RTI\Delta}{RTI} = 2y_A \ln \frac{\gamma_A(y, I)}{\gamma_A(0, I)} + y_B \ln \frac{\gamma_B(y, I)}{\gamma_B(1, I)} \quad (17)$$

On the other hand, if  $y = y_B$ ,

$$\begin{aligned} \left[ \frac{\partial \Delta G^{\text{ex}}(y, I)}{\partial y} \right]_I = RTI & \left[ -2 \ln \frac{\gamma_A(y, I)}{\gamma_A(0, I)} + \ln \frac{\gamma_B(y, I)}{\gamma_B(1, I)} \right. \\ & \left. - [2\phi(0, I) - \phi(1, I) - 1] \right] \end{aligned} \quad (18)$$

Friedman<sup>(6)</sup> has extended Mayer's ionic solution theory<sup>(9)</sup> and expressed the excess free energy of mixing as

$$\Delta G^{\text{ex}}(y, I) = RTI^2 y_A y_B [g_0 + g_1(y_A - y_B) + \dots] \quad (19)$$

where the  $g_i$  are interaction parameters depending only on  $I$ . Hence, combining Eqs. (17), (18), and (19), we obtain (when  $g_1 = 0$ )

$$2 \ln \frac{\gamma_A(y, I)}{\gamma_A(0, I)} = \Delta - y[2\phi(0, I) - \phi(1, I) - 1] + y^2 g_0 I \quad (20)$$

$$\ln \frac{\gamma_B(y, I)}{\gamma_B(1, I)} = \Delta + (1 - y)[2\phi(0, I) - \phi(1, I) - 1] + (1 - y)^2 g_0 I \quad (21)$$

## 5. TREATMENT OF RESULTS

The results reported in this paper were analyzed by two methods. The first method used is the neutral electrolyte treatment of mixed salt solutions by Scatchard<sup>(10-12)</sup> which in asymmetrical salt mixtures leads to the following expression for  $\Delta$ :

$$\Delta = \beta_0 y_A y_B + \beta_1 y_A y_B (y_A - y_B) \quad (22)$$

where

$$\beta_0 = b_{01}I + b_{02}I^2 + b_{03}I^3 \quad (23)$$

$$\beta_1 = b_{12}I^2 + b_{13}I^3 \quad (24)$$

The  $b_{ij}$  parameters were evaluated from the measured osmotic coefficients by the least-squares method applied to Eq. (22),  $\beta_0$  and  $\beta_1$  being expressed by Eqs. (23) and (24). Some osmotic coefficients, as noted in Tables I and II, were omitted in these calculations because the ionic strengths of the solutions exceed that of the saturated solutions of the reference salt. It was found that  $\Delta$  could be expressed by only two parameters, as checked with an  $F$  test 95% level. The values of the Scatchard coefficients  $b_{ij}$  which best reproduced the observed osmotic coefficients within a standard deviation of  $\sigma = 0.0019$  are  $b_{01} = 0.0572$  and  $b_{02} = -0.0122$ .

Henceforth the excess free energy of mixing is given by

$$\Delta G^{\text{ex}}(y, I) = 2RT y_A y_B I \int_0^I (b_{01}I^{1/2} + b_{02}I^{3/2}) d\sqrt{I} \quad (25)$$

or

$$\Delta G^{\text{ex}}(y, I) = RTI^2 y_A y_B (b_{01} + \frac{1}{2}b_{02}I) \quad (26)$$

which leads to

$$g_0 = b_{01} + \frac{1}{2}b_{02}I \quad (27)$$

$$g_1 = 0 \quad (28)$$

The mean activity coefficients of potassium chloride (A) and magnesium chloride (B) in the mixed aqueous solutions are, respectively, given by the following expressions:

$$\ln \frac{\gamma_A(y, I)}{\gamma_A(0, I)} = \frac{y}{2} \{b_{01}I + b_{02}I^2 - [2\phi(0, I) - \phi(1, I) - 1]\} - \frac{b_{02}}{4} y^2 I^2 \quad (29)$$

$$\ln \frac{\gamma_B(y, I)}{\gamma_B(1, I)} = (1 - y)[b_{01}I + b_{02}I^2 + 2\phi(0, I) - \phi(1, I) - 1] - \frac{b_{02}}{2} (1 - y)^2 I^2 \quad (30)$$

which are identical to Scatchard's original equation.<sup>(11)</sup> The calculated values of the activity and osmotic coefficients and the excess Gibbs free energies of mixing at round values of  $I$  and  $y$  are shown in Table III.

The second method is concerned with the least-squares evaluation of the coefficients in

$$\Delta/y_A y_B = \sum_{i=2}^n A_i I^{i/2} + (y_A - y_B) \sum_{i=2}^n B_i I^{i/2} \quad (31)$$

No  $B_i$  coefficients were found to be needed (95% confidence test) and  $A_i$  start from  $i = 2$ , since  $A_1$  is equal to zero, as was shown in Sec. 4. Two  $A_i$  coefficients were found to be sufficient to best reproduce the experimental values of the osmotic coefficients within a standard deviation of  $\sigma = 0.0018$ . Their values are  $A_2 = 0.09051$  and  $A_3 = -0.04095$ . It can easily be shown that

$$\Delta G^{\text{ex}}(y, I) = y_A y_B RT I^2 [A_2 + (2A_3/3)I^{1/2}] \quad (32)$$

leading to

$$\begin{aligned} g_0 &= A_2 + (2A_3/3)I^{1/2} \\ g_1 &= 0 \end{aligned} \quad (33)$$

**Table III.** Calculated Values of Osmotic and Mean Activity Coefficients and Excess Gibbs Free Energy at 25°C (Scatchard's Method)

$I$	$y_B$	$\phi$	$-\log \gamma_A$	$-\log \gamma_B$	$\Delta G^{\text{ex}}/RT$
1.0	0.0	0.897	0.219	0.352	0.0
	0.200	0.902	0.212	0.347	0.008
	0.400	0.905	0.206	0.343	0.012
	0.600	0.907	0.199	0.338	0.012
	0.800	0.906	0.192	0.333	0.008
	1.000	0.901	0.185	0.328	0.0
1.5	0.0	0.902	0.235	0.352	0.0
	0.200	0.913	0.226	0.347	0.017
	0.400	0.922	0.217	0.341	0.026
	0.600	0.931	0.207	0.335	0.026
	0.800	0.940	0.198	0.329	0.017
	1.000	0.947	0.188	0.322	0.0

Table III. Continued

$I$	$y_B$	$\phi$	$-\log \gamma_A$	$-\log \gamma_B$	$\Delta G^{\text{ex}}/RT$
2.0	0.0	0.911	0.243	0.340	0.0
	0.200	0.927	0.232	0.334	0.029
	0.400	0.943	0.221	0.328	0.043
	0.600	0.960	0.209	0.320	0.043
	0.800	0.978	0.197	0.312	0.029
	1.000	0.998	0.185	0.303	0.0
2.5	0.0	0.922	0.246	0.322	0.0
	0.200	0.943	0.234	0.315	0.042
	0.400	0.965	0.221	0.308	0.063
	0.600	0.990	0.207	0.299	0.063
	0.800	1.018	0.193	0.289	0.042
	1.000	1.053	0.178	0.277	0.0
3.0	0.0	0.935	0.246	0.299	0.0
	0.200	0.960	0.232	0.292	0.056
	0.400	0.988	0.218	0.283	0.084
	0.600	1.021	0.202	0.272	0.084
	0.800	1.061	0.186	0.260	0.056
	1.000	1.111	0.168	0.245	0.0
3.5	0.0	0.949	0.244	0.274	0.0
	0.200	0.978	0.229	0.266	0.070
	0.400	1.013	0.213	0.256	0.106
	0.600	1.054	0.196	0.243	0.106
	0.800	1.105	0.177	0.227	0.070
	1.000	1.173	0.157	0.209	0.0
4.0	0.0	0.963	0.240	0.247	0.0
	0.200	0.997	0.224	0.238	0.084
	0.400	1.037	0.207	0.226	0.126
	0.600	1.087	0.188	0.210	0.126
	0.800	1.150	0.167	0.192	0.084
	1.000	1.237	0.144	0.169	0.0
4.5	0.0	0.978	0.235	0.219	0.0
	0.200	1.015	0.219	0.209	0.097
	0.400	1.061	0.200	0.195	0.145
	0.600	1.120	0.179	0.176	0.145
	0.800	1.197	0.156	0.153	0.097
	1.000	1.304	0.130	0.126	0.0
5.0	0.0	0.992	0.230	0.191	0.0
	0.200	1.033	0.212	0.180	0.107
	0.400	1.085	0.192	0.163	0.160
	0.600	1.153	0.169	0.141	0.160
	0.800	1.245	0.144	0.113	0.107
	1.000	1.374	0.116	0.080	0.0



The expressions for the activity coefficients of KCl (A) and  $\text{MgCl}_2$  (B) in the mixture are

$$\ln \frac{\gamma_A(y, I)}{\gamma_A(0, I)} = \frac{y}{2} [A_2 I + A_3 I^{3/2} - 2\phi(0, I) - \phi(1, I) + 1] - \left[ \frac{A_3}{3} \right] y^2 I^2 \quad (34)$$

$$\ln \frac{\gamma_B(y, I)}{\gamma_B(1, I)} = (1 - y)[A_2 I + A_3 I^{3/2} + 2\phi(0, I) - \phi(1, I) - 1] - \left[ \frac{A_3}{3} \right] (1 - y)^2 I^2 \quad (35)$$

The calculated values are given in Table IV.

**Table IV.** Calculated Values of Osmotic and Mean Activity Coefficients and Excess Gibbs Free Energy at 25°C (Friedman's Method)

$I$	$y_B$	$\phi$	$-\log \gamma_A$	$-\log \gamma_B$	$\Delta G^{\text{ex}}/RT$
1.0	0.0	0.897	0.219	0.347	0.0
	0.200	0.902	0.212	0.344	0.010
	0.400	0.906	0.205	0.341	0.015
	0.600	0.907	0.198	0.337	0.015
	0.800	0.906	0.190	0.332	0.010
	1.000	0.901	0.183	0.328	0.0
1.5	0.0	0.902	0.235	0.347	0.0
	0.200	0.913	0.226	0.343	0.020
	0.400	0.923	0.216	0.339	0.031
	0.600	0.932	0.206	0.334	0.031
	0.800	0.940	0.196	0.328	0.020
	1.000	0.947	0.186	0.322	0.0
2.0	0.0	0.911	0.243	0.335	0.0
	0.200	0.927	0.232	0.331	0.033
	0.400	0.943	0.220	0.326	0.050
	0.600	0.959	0.208	0.320	0.050
	0.800	0.978	0.196	0.312	0.033
	1.000	0.998	0.182	0.303	0.0
2.5	0.0	0.922	0.246	0.316	0.0
	0.200	0.943	0.233	0.312	0.047
	0.400	0.965	0.220	0.306	0.071
	0.600	0.989	0.206	0.298	0.071
	0.800	1.018	0.191	0.289	0.047
	1.000	1.053	0.175	0.277	0.0

Table IV. Continued

$I$	$y_B$	$\phi$	$-\log \gamma_A$	$-\log \gamma_B$	$\Delta G^{\text{ex}}/RT$
3.0	0.0	0.935	0.246	0.294	0.0
	0.200	0.960	0.232	0.289	0.062
	0.400	0.988	0.217	0.282	0.093
	0.600	1.021	0.201	0.272	0.093
	0.800	1.060	0.184	0.260	0.062
	1.000	1.111	0.166	0.245	0.0
3.5	0.0	0.949	0.244	0.268	0.0
	0.200	0.978	0.229	0.263	0.077
	0.400	1.012	0.213	0.254	0.116
	0.600	1.053	0.195	0.242	0.116
	0.800	1.105	0.175	0.227	0.077
	1.000	1.173	0.154	0.209	0.0
4.0	0.0	0.963	0.240	0.242	0.0
	0.200	0.997	0.224	0.235	0.092
	0.400	1.037	0.206	0.224	0.138
	0.600	1.087	0.187	0.210	0.138
	0.800	1.150	0.165	0.191	0.092
	1.000	1.237	0.142	0.169	0.0
4.5	0.0	0.978	0.235	0.214	0.0
	0.200	1.016	0.218	0.205	0.105
	0.400	1.062	0.199	0.192	0.158
	0.600	1.121	0.178	0.175	0.158
	0.800	1.198	0.154	0.153	0.105
	1.000	1.304	0.128	0.126	0.0
5.0	0.0	0.992	0.230	0.186	0.0
	0.200	1.034	0.212	0.176	0.118
	0.400	1.087	0.191	0.160	0.177
	0.600	1.155	0.168	0.139	0.177
	0.800	1.246	0.142	0.112	0.118
	1.000	1.374	0.113	0.080	0.0

## 6. DISCUSSION

The good agreement between the two methods of treating the isopiestic data is illustrated in Table V. Calculated values of the activity coefficients for KCl obtained from the isopiestic measurements are compared at an ionic strength of 1.0 *m* with those determined directly from emf measurements<sup>(13)</sup> in Table VI. The agreement is very good. The average deviation in  $\gamma^{\text{trace}}$  is reasonable and the values of  $g_0$  obtained by both methods are similar, but a deviation trend may be seen which increases toward the lower

**Table V.** Friedman's Pair-Interaction Parameter ( $g_0$ ) and Activity Coefficients  $\gamma_i^{\text{trace}}$  of a Trace Amount of Component  $i$  in the KCl (A)–MgCl<sub>2</sub> (B)–H<sub>2</sub>O System at 25°C

$I$	$g_0(\text{S})$	$g_0(\text{F})$	$\gamma_A^{\text{tr}}(\text{S})^a$	$\gamma_A^{\text{tr}}(\text{F})^b$	$\gamma_B^{\text{tr}}(\text{S})$	$\gamma_B^{\text{tr}}(\text{F})$
1.0	0.051	0.063	0.653	0.660	0.445	0.450
1.5	0.048	0.057	0.649	0.652	0.445	0.451
2.0	0.045	0.052	0.653	0.657	0.457	0.463
2.5	0.042	0.047	0.664	0.668	0.477	0.483
3.0	0.039	0.043	0.679	0.683	0.502	0.509
3.5	0.036	0.039	0.697	0.701	0.532	0.539
4.0	0.033	0.036	0.718	0.722	0.566	0.573
4.5	0.030	0.032	0.741	0.745	0.604	0.611
5.0	0.027	0.029	0.766	0.770	0.644	0.652

<sup>a</sup> (S), calculated by Scatchard's method.

<sup>b</sup> (F), calculated by Friedman's method.

concentrations. The interactions between the two ions which contribute to a charge asymmetric mixture of salts with a common ion have been calculated by Friedman.<sup>(6)</sup> All possible pairs contribute to  $g_0$ , while the effect of triplet interactions is more complicated since they contribute to both  $g_0$  and  $g_1$ . The values of  $g_0$  are all positive and decrease with ionic strength, reflecting the increasing effect of the triplet-formation contribution. Extrapolation of  $g_0$  below the experimental range using Eqs. (27) and (34) would indicate that it tends either to 0.0572 or 0.0905. However, for unsymmetrical

**Table VI.** Activity Coefficients of KCl in the KCl–MgCl<sub>2</sub>–H<sub>2</sub>O System ( $I = 1$ )

$y_B$	$-\log \gamma(\text{G})^a$	$-\log \gamma(\text{S})^b$	$-\log \gamma(\text{F})^c$
0.0	0.2190	0.2190	0.2190
0.1982	0.2129	0.2125	0.2123
0.3308	0.2087	0.2081	0.2076
0.4258	0.2055	0.2049	0.2041
0.5527	0.2013	0.2005	0.1995
0.6977	0.1964	0.1955	0.1940
0.7717	0.1941	0.1929	0.1912
0.8455	0.1917	0.1903	0.1883
0.8833	0.1905	0.1890	0.1870

<sup>a</sup> (G), ref. 13.

<sup>b</sup> (S), calculated by Scatchard's method.

<sup>c</sup> (F), calculated by Friedman's method.

mixtures of the type  $\text{KCl-MgCl}_2$ , Friedman<sup>(6)</sup> has shown that the cluster theory predicts that as  $I \rightarrow 0$ ,  $g_0$  goes to  $-\infty$  as  $\ln I$ . It is possible that expansions of  $\Delta$  in Eqs. (27) and (34) are inappropriate and may lead to errors in the calculation of  $\Delta G^{\text{ex}}(y, I)$  and activity coefficients from vapor-pressure measurements. Recent measurements of the mean activity coefficients of  $\text{LaCl}_3$ <sup>(14)</sup> and  $\text{CaCl}_2\text{-CaSO}_4$ <sup>(15)</sup> in aqueous solutions seem to present the first quantitative evidence which confirms the existence of a higher-order limiting law.<sup>(6)</sup>

The expression for the excess Gibbs free energy of unsymmetrical electrolytes given by Eq. (17.8) of ref. 6,

$$\frac{G^{\text{ex}} - \text{DHLL}}{RT} = -\frac{1}{3V} \left[ \frac{n_3}{n_2} \right]^2 A^2 I^2 \ln I + O(I^2) \quad (36)$$

where DHLL is the Debye-Hückel limiting law,  $n_i$  is the  $i$ th reduced moment of the concentration of charge types, and  $V$  is the specific volume of the solvent, leads to the following expression for the osmotic coefficient [Eq. (17.10) of ref. 6]:

$$\phi - \text{DHLL} = -\frac{n_3^2}{6Vn_2} A^2 I \ln I + O(I) \quad (37)$$

Using Eq. (37) for an asymmetric mixture of electrolytes ( $\text{KCl-MgCl}_2\text{-H}_2\text{O}$ ) we obtain

$$\begin{aligned} \Delta = & (1 + y_A)[\phi(y, I) - \text{DHLL}(y, I)] - 2y_A[\phi(0, I) - \text{DHLL}(0, I)] \\ & - y_B[\phi(1, I) - \text{DHLL}(1, I)] \end{aligned} \quad (38)$$

From Eq. (14) it can easily be shown that

$$(1 + y_A)\text{DHLL}(y, I) - 2y_A\text{DHLL}(0, I) - y_B\text{DHLL}(1, I) \equiv 0 \quad (39)$$

Noting that for solutions of symmetrical electrolytes the third moment vanishes, the higher-order limiting law gives

$$(1 + y_A)[\phi(y, I) - \text{DHLL}(y, I)] = -0.456y_B^2 I \ln I + O(I) \quad (40)$$

$$2y_A[\phi(0, I) - \text{DHLL}(0, I)] = O(I) \quad (41)$$

$$y_B[\phi(1, I) - \text{DHLL}(1, I)] = -0.456y_B I \ln I + O(I) \quad (42)$$

which yields the limiting law for  $\Delta/\sqrt{I}$ ,

$$\Delta/\sqrt{I} = y_A y_B \sqrt{I} \log I + O(I) = 0.912 y_A y_B \sqrt{I} \ln \sqrt{I} + O(I) \quad (43)$$

and tends to 0 as  $I \rightarrow 0$ . This corresponds to the limiting law for  $\Delta G^{\text{ex}}(y, I)$

$$\Delta G^{\text{ex}}(y, I) = 0.456 y_A y_B R T I^2 \ln I + O(I^2) \quad (44)$$

If we assume that a two-structure model<sup>(16)</sup> may represent an asymmetric mixture of electrolytes at both very low and very high ionic strengths, a stochastic description of the model may be given by

$$P(I) = P(0)f(I) + P(\infty)[1 - f(I)] \quad (45)$$

where  $P(I)$  is the value of a given property of the solution at a given ionic strength  $I$ ,  $P(0)$  and  $P(\infty)$  are given by a Mayer cluster-approach<sup>(9)</sup> description of that property at low and high ionic strength, respectively, and  $f(I)$  satisfies the conditions

$$f(0) = 1, \quad f(\infty) = 0 \quad (46)$$

The property considered in this paper is the excess Gibbs free energy of mixing  $\Delta G^{\text{ex}}(y, I)$ . The use of Eqs. (44) and (32) leads to

$$P(0) = 0.456RTI^2 y_A y_B \ln I \quad (47)$$

$$P(\infty) = RTI^2 y_A y_B [A_2 + \frac{2}{3}A_3 I^{1/2}] \quad (48)$$

while  $f(I)$  is given by

$$f(I) = \exp(-10I^2) \quad (49)$$

as shown by Pitzer<sup>(17)</sup> in his treatment of higher electrostatic terms on the thermodynamics of electrolytes. Substitution of expressions (47), (48), and (49) in Eq. (45) leads to the following expression for  $\Delta G^{\text{ex}}(y, I)$ :

$$\begin{aligned} \Delta G^{\text{ex}}(y, I) = RTI^2 y_A y_B [ & (0.456 \ln I - A_2 - \frac{2}{3}A_3 I^{1/2}) \exp(-10I^2) \\ & + A_2 + \frac{2}{3}A_3 I^{1/2} ] \end{aligned} \quad (50)$$

From Eq. (50) the corresponding expression for  $\Delta$  can be derived by application of Eq. (2):

$$\begin{aligned} \Delta = & 0.456I(\ln I + 1 - 20I^2 \ln I) \exp(-10I^2) \\ & + A_2 I[1 - \exp(-10I^2) + 20I^2 \exp(-10I^2)] \\ & + A_3 I^{3/2}[1 - \exp(-10I^2) + 20I^2 \exp(-10I^2)] + \dots \end{aligned} \quad (51)$$

The  $A_i$  parameters were evaluated from the experimental values of  $\Delta$  by the least-squares method applied to Eq. (51). Two parameters only were found to be sufficient to best reproduce the experimental values of the osmotic coefficients within a standard deviation of  $\sigma = 0.0018$ . The values obtained were found to be very similar to those obtained earlier, which will be used for internal consistency.<sup>3</sup>

From Eq. (50) it can easily be shown that  $g_0$  can be expressed at very low ionic strength by

$$g_0 = 0.456 \ln I \quad (52)$$

<sup>3</sup> A study based on literature data is in progress with a view to determining the most appropriate form of the function which should appear in the exponential as well as the effect of valence upon it.

**Table VII.** Calculated Values of  $g_0$  and  $\gamma^{\text{trace}}$  for KCl and  $\text{MgCl}_2$  in the KCl- $\text{MgCl}_2$ - $\text{H}_2\text{O}$  System at  $25^\circ\text{C}$

$I$	$g_0$	$\gamma_A^{\text{tr}}$	$\gamma_B^{\text{tr}}$
1.0	0.063	0.657	0.450
0.9	0.065	0.660	0.453
0.8	0.066	0.664	0.456
0.7	0.066	0.668	0.461
0.6	0.061	0.673	0.466
0.5	0.039	0.678	0.471
0.4	-0.026	0.682	0.474
0.3	-0.178	0.684	0.476
0.2	-0.466	0.697	0.491
0.1	-0.942	0.742	0.553

which agrees with Friedman's new derivation<sup>(18)</sup> of the higher limiting law in a mixture of A (1,1 charge type) with B (1,2 or 2,1 charge type). It is possible to evaluate the activity coefficients of the electrolytes in the mixture by using Eqs. (20) and (21) in conjunction with Eqs. (51) and (52). However, the values obtained are practically identical with those obtained from Eqs. (34) and (35) and will not be listed.

Calculated values of  $g_0$  and  $\gamma^{\text{trace}}$  of KCl and  $\text{MgCl}_2$  over the ionic strength range of 0.1 to 1  $m$  are given in Table VII. These could possibly be checked with future potentiometric measurements as in the KCl- $\text{MgSO}_4$  system.<sup>(19)</sup>

Finally, the values of the excess Gibbs free energy of mixing calculated from the  $b_{ij}$  coefficients of Scatchard are compared with those for the KCl- $\text{CaCl}_2$ - $\text{H}_2\text{O}$ ,<sup>(20)</sup> KCl- $\text{SrCl}_2$ - $\text{H}_2\text{O}$ ,<sup>(21)</sup> and KCl- $\text{BaCl}_2$ - $\text{H}_2\text{O}$ <sup>(22)</sup> systems in Table VIII. There seems to be a trend toward an increase in the magnitude

**Table VIII.** Excess Gibbs Free Energy ( $\text{J}\cdot\text{kg}^{-1}$ ) at  $y_B = 0.5$  for Aqueous Mixtures of Potassium and Alkaline Earth Chlorides

Systems	$I, \text{ moles}\cdot\text{kg}^{-1}$				
	1	2	3	4	4.8
KCl- $\text{MgCl}_2$ - $\text{H}_2\text{O}$	31	111	217	326	398
KCl- $\text{CaCl}_2$ - $\text{H}_2\text{O}$	17	57	99	125	121
KCl- $\text{SrCl}_2$ - $\text{H}_2\text{O}$	6	12	2	-41	-111
KCl- $\text{BaCl}_2$ - $\text{H}_2\text{O}$	4	-9	-61	-151	-235

of  $\Delta G^{\text{ex}}$  with increase in the ionic strength, while for a given ionic strength there is a trend toward negative values with increase in the atomic number of the alkaline earths. Similar effects have been reported<sup>(23)</sup> in mixtures of sodium sulfate with alkali chlorides.

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