

Osmotic and Activity Coefficients for Binary Mixtures of Sodium Chloride, Sodium Sulfate, Magnesium Sulfate, and Magnesium Chloride in Water at 25°.

II. Isopiestic and Electromotive Force Measurements on the Two Systems without Common Ions¹

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Isopiestic measurements are presented for the systems $\text{NaCl-MgSO}_4\text{-H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\text{-MgCl}_2\text{-H}_2\text{O}$. Emf measurements with a Na-sensitive glass electrode *vs.* a Ag-AgCl electrode are presented for the same systems. Parameters obtained from the isopiestic results are used to derive the activity coefficients in the mixtures. The deviations from Harned's rule are less than 2% in the activity coefficient up to an ionic strength of 6. Values of the excess free energy of mixing are given for the binary aqueous mixtures involving NaCl, Na_2SO_4 , MgSO_4 , and MgCl_2 . The cross-square rule, shown to be valid for heats of mixing, is applicable to the free-energy changes for these mixtures.

The purpose of the investigation reported in this series of papers is to explore the free-energy relationships in the six binary salt mixtures made up from NaCl, Na_2SO_4 , MgSO_4 , and MgCl_2 in aqueous solution. In the first paper⁴ we presented the results of isopiestic measurements on the four systems involving a common ion. In this paper we present the results of isopiestic measurements on the systems without a common ion: $\text{NaCl-MgSO}_4\text{-H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\text{-MgCl}_2\text{-H}_2\text{O}$. The results of emf measurements with a Na-sensitive glass electrode on these systems are also given.

The results reported here complete the free-energy measurements for the six binary mixtures noted above. The excess free energies for the six systems are calculated. These calculations indicate that the cross-square relationship first proposed by Young and co-workers⁵ for the heats of mixing of 1:1 electrolytes is also applicable to the excess free energies of mixing for the systems studied here.

Experimental Section

Materials. The stock solutions of the single salts were the same as those used in the previous investigation.⁴ The mixed solutions were prepared by weight from these stock solutions. Distilled water was used in the preparation of all solutions.

Isopiestic Experiments. The apparatus and procedure were the same as described by Rush and Johnson.⁶ For each set of equilibrations, there were two dishes containing the same solution except as noted in the tables. Where there were duplicate dishes, the maximum difference in molality at equilibrium between

the duplicate dishes was 0.2%. The reference solution was NaCl in all cases, and the osmotic coefficients for this salt were taken from Robinson and Stokes.⁷ The temperature was maintained at 25.0°.

Emf Experiments. The apparatus and procedure were similar to those described by Lanier.⁸

The glass electrodes used were Beckman Instruments cationic glass electrodes (39137). Only those which exhibited long stability and quick response were used. In general, the drift was not more than 0.1 mV/hr, and the time to reach equilibrium was less than 15 min.

The Ag-AgCl electrodes were prepared by the method described by Greyson.⁹ A sheet of 1 mm thick AgCl crystal obtained from Harshaw Chemical Co. was cut to approximately 3×5 mm. A piece of No. 18 silver wire 15 cm long was sealed to the AgCl crystal by

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(4) Y. C. Wu, R. M. Rush, and G. Scatchard, *J. Phys. Chem.*, **72**, 4048 (1968).

(5) T. F. Young, Y. C. Wu, and A. A. Krawetz, *Discussions Faraday Soc.*, **24**, 37, 77, 80 (1957).

(6) R. M. Rush and J. S. Johnson, *J. Chem. Eng. Data*, **11**, 590 (1966).

(7) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, revised, Butterworth and Co. Ltd., London, 1965.

(8) R. D. Lanier, *J. Phys. Chem.*, **69**, 3992 (1965).

(9) J. Greyson, *J. Electrochem. Soc.*, **109**, 745 (1962).

heating the wire to red heat and then pressing it into one end of the crystal. The electrode was washed with concentrated NH_4OH , HNO_3 , and water. It was then plated in 0.1 *m* HCl with a Pt anode for a few minutes at about 1 mA. Six electrodes were prepared at one time and were measured against each other. Of those that differed from each other by less than 0.1 mV, one was used in the measurements and the rest were stored in 0.1 *m* HCl.

The emf of a NaCl reference solution was measured both before and after the measurement of the test solution using the same pair of electrodes. The difference was usually 0.2 mV or less. If the change was greater than 0.5 mV, the electrodes were examined and tested and the experiment repeated. The solutions were measured while in a water bath maintained at $25.00 \pm 0.02^\circ$.

The activity coefficients of NaCl in the mixtures were calculated from the equation

$$\log \gamma_{\pm} = \frac{E - E_R}{118.3} + \log a_{\pm R} - \frac{1}{2} \log m_{\text{Na}} m_{\text{Cl}} \quad (1)$$

where E and E_R are the observed emf's in millivolts of the test and reference solutions, respectively (E_R is the average of the measurements made before and after the measurement of E); $a_{\pm R}$ is the mean activity of the reference solution; and m_{Na} and m_{Cl} are the molalities of the sodium and chloride ions, respectively, in the test solution.

The accuracy of the procedure was tested with a series of standard NaCl solutions in the range 1.0–6.16 *m*. The deviations from the results calculated from the activity coefficients given by Robinson and Stokes⁷ were less than 0.4 mV.

Results

Isopiestic Data. The results of the isopiestic measurements are given in Tables I and II. Here we have tabulated $\nu m\phi$ and the osmotic coefficients for the two- and three-component systems for each of the equilibrations (ν is the number of moles of ions per mole of solute, m is the concentration in moles per kilogram of water, and ϕ is the osmotic coefficient; for the three-component mixtures νm is the sum of the values of νm

Table I: Osmotic Coefficients for the System NaCl– MgSO_4 – H_2O

$\nu m\phi$	MgSO_4				
	0	0.0779	0.1993	0.4249	1
$\nu m\phi$	MgSO_4				
	0	0.2526	0.4990	0.7472	1
7.3064	1.0729	1.0740	1.0739	1.0693	1.0619
4.0910	0.9874	0.9739	0.9517	0.9059	0.7908
2.5410	0.9487	0.9285	0.8955	0.8284	0.6490
1.7464	0.9332	0.9115	0.8735	0.7961	0.5790
1.3186	0.9261	0.9038	0.8636	0.7819	0.5455
1.0203	0.9220	0.8967	0.8552	0.7726	0.5260

Table II: Osmotic Coefficients for the System Na_2SO_4 – MgCl_2 – H_2O ^a

$\nu m\phi$	MgCl_2			ϕ_{NaCl}
	0	0.2438	0.5486	0.7747
7.3064		0.8885		1.2626
4.0910		0.7832		1.0664
2.5410		0.7485		0.9633
1.7464		0.7449		0.9124
1.3186		0.7489		0.8853
1.0203		0.7533		0.8658
3.5602	0.6282		0.9317	0.9738
2.2199	0.6395		0.8686	0.9420
1.4777	0.6691		0.8392	0.9287
1.0851	0.6936		0.8262	0.9227
0.7715	0.7214		0.8203	0.9204

^a Single dish for all measurements except those for pure NaCl and Na_2SO_4 .

for the two salts). The compositions of the mixtures are given as ionic strength fractions $y_A = I_A/I$, where I is the total ionic strength on the molality scale and I_A the ionic strength of component A, and as osmolality fractions $z_A = \nu_A m_A / (\nu_A m_A + \nu_B m_B)$. Where there were duplicate dishes, the results given are averages.

The ranges of ionic strengths for the mixtures reported here are 0.7–7.8 for NaCl– MgSO_4 and 0.9–8.2 for Na_2SO_4 – MgCl_2 . The equations and coefficients presented in this paper should not be used for calculations at ionic strengths higher than those given above with the further restriction that for NaCl– MgSO_4 mixtures calculations should not be carried beyond $I = 6$, the limit for the two-component data for NaCl. Extrapolations to lower values than those given above are less likely to be in error because the equations include a Debye–Hückel term.

The treatment of the experimental data was the same as that used in the previous paper⁴ which utilized the equations developed by Scatchard.¹⁰ These equations are given below. In these equations a_J is the distance-of-closest-approach parameter for component J and $S = -1.17202$ for aqueous solutions at 25° .

$$\phi = 1 + \frac{I}{\nu_A m_A + \nu_B m_B} [\alpha_A + (\alpha_B - \alpha_A)y_B + \beta_{AB}^{(0)}y_B(1 - y_B) + \beta_{AB}^{(1)}y_B(1 - y_B)(1 - 2y_B)] \quad (2)$$

$$\alpha_J = \frac{2S}{a_J^2 I} \left[1 + a_J I^{1/2} - \frac{1}{1 + a_J I^{1/2}} - 2 \ln(1 + a_J I^{1/2}) \right] + a_J^{(1)}I + a_J^{(2)}I^2 + a_J^{(3)}I^3 \quad (3)$$

$$\beta_{AB}^{(0)} = b_{AB}^{(0,1)}I + b_{AB}^{(0,2)}I^2 + b_{AB}^{(0,3)}I^3 \quad (4)$$

$$\beta_{AB}^{(1)} = b_{AB}^{(1,2)}I^2 + b_{AB}^{(1,3)}I^3 \quad (5)$$

(10) G. Scatchard, *J. Amer. Chem. Soc.*, **83**, 2636 (1961).

$$\ln \gamma_{\pm A} = \frac{I_A}{\nu_A m_A} [A_A + \alpha_A + (\alpha_B - \alpha_A)y_B + \beta_{AB}^{(0)} + (B_{AB}^{(0)} - \beta_{AB}^{(0)})y_B^2 + \beta_{AB}^{(1)}y_B + 3(B_{AB}^{(1)} - \beta_{AB}^{(1)})y_B^2 - 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)})y_B^3] \quad (6)$$

$$\ln \gamma_{\pm B} = \frac{I_B}{\nu_B m_B} [A_B + \alpha_B + (\alpha_A - \alpha_B)y_A + \beta_{AB}^{(0)}y_A + (B_{AB}^{(0)} - \beta_{AB}^{(0)})y_A^2 - \beta_{AB}^{(1)}y_A - 3(B_{AB}^{(1)} - \beta_{AB}^{(1)})y_A^2 + 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)})y_A^3] \quad (7)$$

$$A_J + \alpha_J = \frac{2SI^{1/2}}{1 + a_J I^{1/2}} + 2a_J^{(1)}I + \frac{3}{2}a_J^{(2)}I^2 + \frac{4}{3}a_J^{(3)}I^3 \quad (8)$$

$$B_{AB}^{(0)} = b_{AB}^{(0,1)}I + \frac{1}{2}b_{AB}^{(0,2)}I^2 + \frac{1}{3}b_{AB}^{(0,3)}I^3 \quad (9)$$

$$B_{AB}^{(1)} = \frac{1}{2}b_{AB}^{(1,2)}I^2 + \frac{1}{3}b_{AB}^{(1,3)}I^3 \quad (10)$$

For the limiting two-component systems we use the parameters given by Lietzke and Stoughton¹¹ (derived from the data of Robinson and Stokes⁷) and shown in Table III. (It should be noted that the power series coefficients given by Lietzke and Stoughton, B , C , and D , are multiplied by the factor $-2/z_+z_-$ to obtain the coefficients $a_J^{(i)}$.)

The b coefficients of eq 4 and 5 were obtained from the observed osmotic coefficients of the mixtures by the method of least squares. The values thus obtained are given in Table IV along with the standard deviation $\sigma = [\sum d^2/(n - k)]^{1/2}$, where d is the deviation, n the number of observations, k the number of variable parameters, and the summation is over all observations. For both systems, fits were obtained using combinations of

Table III: Parameters for the Two-Component Systems^a

	NaCl	Na ₂ SO ₄	MgSO ₄	MgCl ₂
a	1.45397	1.24072	1.37486	1.60067
$a^{(1)}$	0.04472	-0.06580	-0.02712	0.06633
$a^{(2)}$	0.018616	0.007263	0.004213	0.009003
$a^{(3)}$	-0.0010724	-0.0001945	-0.0000950	-0.0002545

^a Adapted from ref 11.

Table IV: Parameters for the Three-Component Systems

	NaCl (A)- MgSO ₄ (B)	Na ₂ SO ₄ (A)- MgCl ₂ (B)
$b_{AB}^{(0,1)}$
$b_{AB}^{(0,2)}$	-0.00798	-0.00657
$b_{AB}^{(0,3)}$	0.000855	0.000231
σ (in ϕ)	0.0012	0.0022

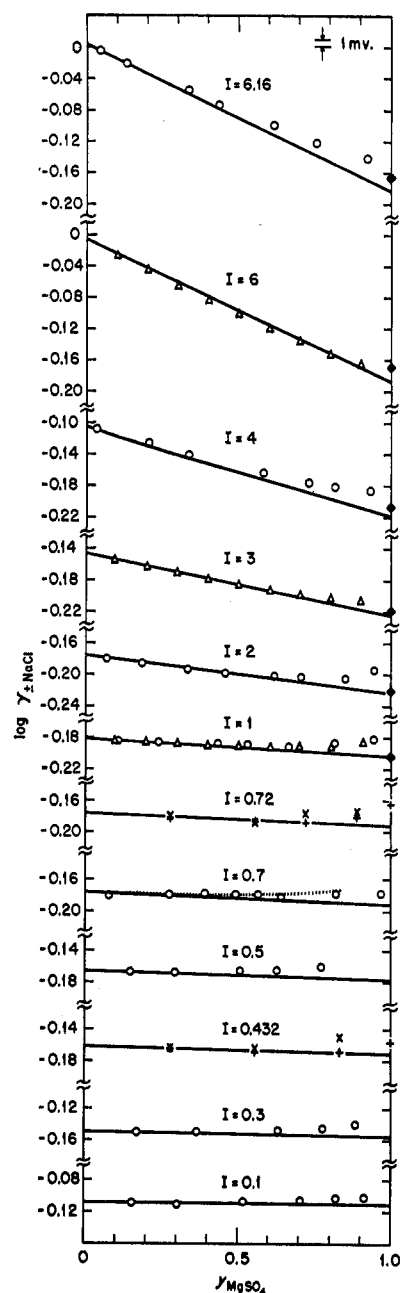


Figure 1. Activity coefficients of NaCl in MgSO₄: —, this work, isopiestic; O, this work, emf; Δ, this work, emf (Lanier); . . . , Gieskes (ref 12); +, Platford, isopiestic (ref 13); ×, Platford, emf (ref 13); ♦, estimate from two-component data.

parameters other than those shown in the table. The sets of parameters given in Table IV are those with the least number of parameters which do not represent a significant increase in the standard deviation (σ). It was not necessary to include the terms $b_{AB}^{(0,1)}$, $b_{AB}^{(1,2)}$, or $b_{AB}^{(1,3)}$ for the systems reported here (these terms were set equal to zero for the determination of the other terms).

(11) M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.*, **66**, 508 (1962).

The experimental values can thus be represented by eq 2 with a parameters of Table III and the b parameters of Table IV. The same parameters may be used to calculate the activity coefficient of either component by eq 6 or 7.

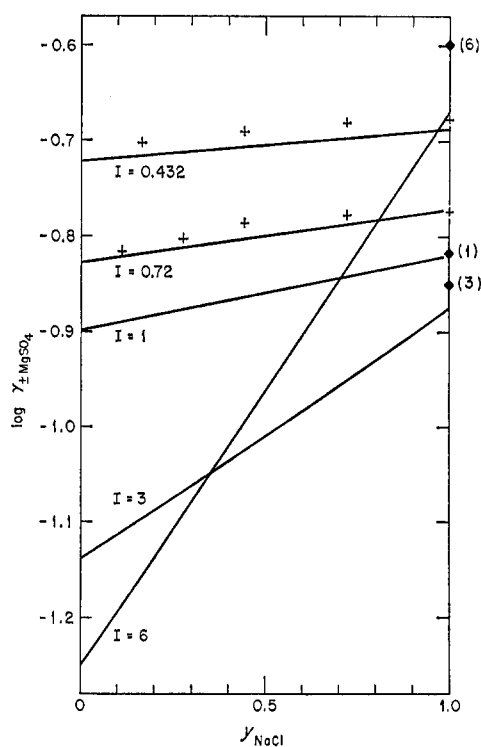


Figure 2. Activity coefficients of MgSO_4 in NaCl : —, this work; +, Platford, isopiestic (ref 13); ◆, estimate from two-component data.

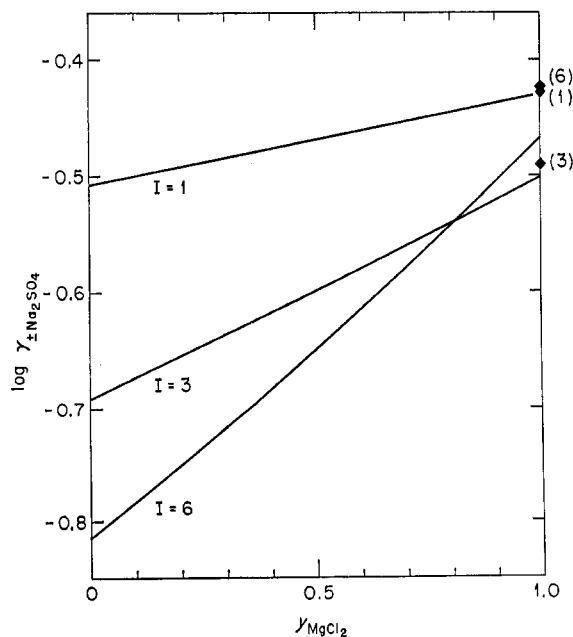


Figure 3. Activity coefficients of Na_2SO_4 in MgCl_2 : ◆, estimate from two-component data.

The variation of activity coefficients with composition at several ionic strengths for the systems studied is shown in Figures 1-4. The lines representing our

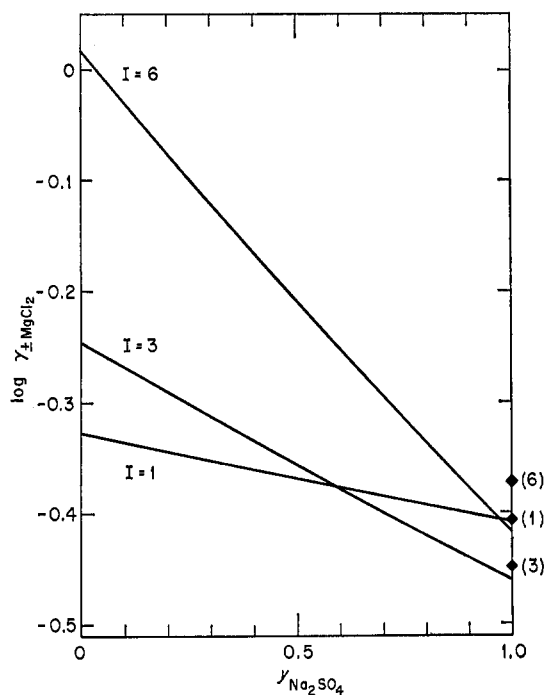


Figure 4. Activity coefficients of MgCl_2 in Na_2SO_4 : ◆, estimate from two-component data.

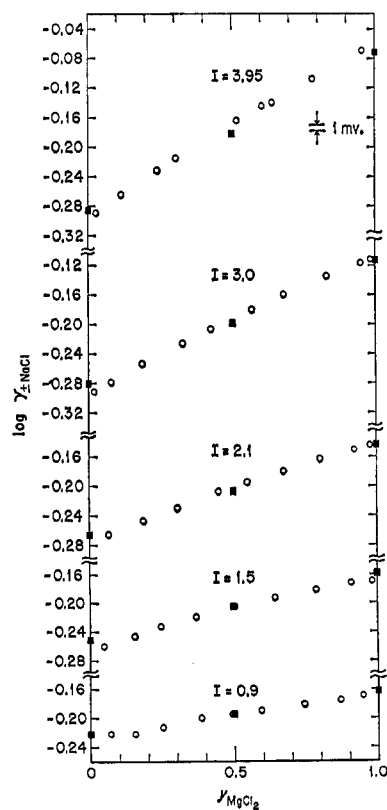


Figure 5. Activity coefficients of NaCl in the system Na_2SO_4 - MgCl_2 - H_2O : ■, values from other three-component data.

isopiestic results were calculated using eq 6 and 7 and the parameters given in Tables III and IV. Where available, the results of other investigators are also shown (where necessary, these results were adjusted to correspond to the values we used for $\log \gamma_{\pm}$ for the pure salt).

Emf. The results of the emf measurements are shown in Figures 1 and 5. Values of $\log \gamma_{\pm}$ were calculated from the observed emf's using eq 1. These values were adjusted so that the values for the pure NaCl solutions are consistent with the parameters of Table III.

Discussion

The values of $\log \gamma_{\pm \text{NaCl}}$ from our isopiestic and emf results for the system $\text{NaCl-MgSO}_4\text{-H}_2\text{O}$ are compared in Figure 1. The results of several other investigators are included in this figure. Gieskes¹² used a Na-sensitive glass electrode *vs.* a Ag-AgCl electrode and reported results at an ionic strength of 0.7 (the approximate concentration of sea water). The values shown in Figure 1 are the uncorrected (stoichiometric) values (labeled "MgSO₄") taken from Figure 5 of Gieskes' paper. Platford¹³ reported results at ionic strengths of 0.72 and 0.432. He presented results using both the isopiestic technique and emf measurements using a sodium amalgam electrode *vs.* a Ag-AgCl electrode.

The emf measurements are, in general, in good agreement with the isopiestic results. However, at low NaCl fractions, the emf results at all concentrations show an upward curvature that is not observed in the results derived from our isopiestic measurements. The deviations are of the order of several millivolts and appear to be real and reproducible. Lanier³ observed this same upward curvature in mixtures of NaCl with various other salts. He suggested as explanations for this effect the sensitivity of the glass electrode to the divalent ion in cases where the second salt contained a divalent ion and to difficulties with the Ag-AgCl electrode in cases where the second salt was not a chloride. For the NaCl-MgSO_4 mixtures both of these effects could appear and seem to be the most likely explanations for the observed deviations.

Comparison of the isopiestic and emf results for the system $\text{Na}_2\text{SO}_4\text{-MgCl}_2\text{-H}_2\text{O}$ is more difficult since the emf measurements give the quantity $\log \gamma_{\pm \text{NaCl}}$. With NaCl as a component the system becomes a four-component one except at the two ends and the midpoint. It is possible to calculate from the isopiestic results values of $\log \gamma_{\pm \text{NaCl}}$ at these three points, and these values are shown in Figure 5 with square symbols. The values at $y_{\text{MgCl}_2} = 0$ were calculated from the $\text{NaCl-Na}_2\text{SO}_4\text{-H}_2\text{O}$ parameters with $y_{\text{NaCl}} = 0$; for $y_{\text{MgCl}_2} = 1$, the values were calculated from the parameters for $\text{MgCl}_2\text{-NaCl-H}_2\text{O}$ with $y_{\text{NaCl}} = 0$; and for $y_{\text{MgCl}_2} = 0.5$ the parameters for $\text{NaCl-MgSO}_4\text{-H}_2\text{O}$ were used with $y_{\text{MgSO}_4} = 0.6667$. The results of these cal-

Table V: Values of the Parameters Q_{AB} and Q_{BA}

<i>I</i>	Q_{AB}	Q_{BA}
NaCl (A)-MgSO₄ (B)		
1	-0.022	0.080
2	-0.024	0.083
3	-0.026	0.088
4	-0.028	0.092
5	-0.029	0.095
6	-0.030	0.097
Na₂SO₄ (A)-MgCl₂ (B)		
1	0.078	-0.080
2	0.068	-0.073
3	0.064	-0.072
4	0.061	-0.072
5	0.059	-0.072
6	0.058	-0.073

culations are in good agreement with the observed (emf) values. (One observed point is not shown in Figure 5. It deviated from the trend of the other points at the same concentration by about 10 mV and was discarded as a wild point.)

Equations 6 and 7 provide a means of estimating the activity coefficients in mixtures from the data on the limiting two-component systems. The A and α terms are derived from the two-component systems and limiting the equations to these terms (*i.e.*, with all b coefficients equal to zero) provides such an estimate. Such estimates for the systems studied in this investigation are shown in Figures 1-4. At $I = 1$, the error introduced by these estimates is less than 1% in γ_{\pm} ; at $I = 6$, the error varies from 4 to 18%.

In general, the systems investigated here follow closely the linear relationship between $\log \gamma_{\pm A}$ and y_B as expressed in Harned's rule.¹⁴ In Table V values are given for the quantities

$$Q_{AB} = [\log (\gamma_{\pm A(B)} / \gamma_{\pm A(A)})] / I$$

and

$$Q_{BA} = [\log (\gamma_{\pm B(A)} / \gamma_{\pm B(B)})] / I$$

where $\gamma_{\pm A(B)}$ is the activity coefficient of component A in a pure solution of component B ($y_B = 1$) and $\gamma_{\pm A(A)}$ is the activity coefficient of component A in a pure solution of component A ($y_B = 0$) with analogous definitions for the quantities involved in Q_{BA} . These quantities thus represent a straight-line approximation for the variation of $\log \gamma_{\pm}$ with y using the end points to define the straight line. The deviations from the straight line are 2% or less in γ_{\pm} in all cases.

(12) J. M. T. M. Gieskes, *Z. Phys. Chem.* (Frankfurt am Main), **50**, 78 (1966).

(13) R. F. Platford, *Can. J. Chem.*, **45**, 821 (1967).

(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 14.

Further Results for the System NaCl-Na₂SO₄-H₂O

Recently Synnott and Butler¹⁵ published activity coefficients of Na₂SO₄ in the system NaCl-Na₂SO₄-H₂O at $I = 1$. These measurements were made with a lead amalgam-lead sulfate electrode *vs.* a Na-sensitive glass electrode. Their results are in good agreement with our values obtained by the isopiestic method,⁴ the maximum deviation being equivalent to about 0.5 mV. Their results confirm our conclusion that Harned's rule is closely followed for Na₂SO₄ under these conditions. Recent isopiestic measurements of Platford,¹⁶ analyzed by the procedure used here, give activity coefficients of NaCl and Na₂SO₄ in very good agreement with values obtained from isopiestic results reported in our previous paper;⁴ the maximum differences between $\log \gamma_{\pm}$ of either NaCl or Na₂SO₄ between the two sets, found for trace concentrations of the electrolyte in question, is 0.002 for $I = 1$, 0.005 for $I = 3$, and 0.012 for $I = 6$.

From the slope of $\log \gamma_{\pm \text{Na}_2\text{SO}_4}$ *vs.* $y_{\text{Na}_2\text{SO}_4}$ Synnott and Butler derived -0.035 for Harned's α_{21} . Earlier,¹⁷ from measurements of $\gamma_{\pm \text{NaCl}}$ in NaCl-Na₂SO₄ solutions and literature values of $\phi_{\text{Na}_2\text{SO}_4}$, they obtained $\alpha_{21} = -0.043$ at $I = 1$; Lanier⁸ by the same procedure, obtained -0.014 . If Harned's rule is obeyed by Na₂SO₄ in NaCl-Na₂SO₄ solutions, $\alpha_{21} = -Q_{\text{BA}}$; the value of α_{21} implied by the isopiestic results is thus -0.041 (Table VII, ref 4).

These values appear quite different. The scatter, however, perhaps reflects the severe strain in the data involved in the procedure of calculating α_{21} from $\gamma_{\pm \text{NaCl}}$ more than inaccuracy of the data; the agreement of $\gamma_{\pm \text{NaCl}}$ for NaCl-Na₂SO₄ solutions in ref 8 with the isopiestic results is not as good as for NaCl-MgCl₂, reported in ref 4, nor as good as for NaCl-MgSO₄, reported in this paper; but it is nevertheless fairly good. (It is of interest that values of $\log \gamma_{\pm \text{NaCl}}$ reported by Platford,¹⁶ which were calculated by the MacKay-Perring technique, appear to agree better with Lanier's values⁸ than with the activity coefficients computed by the techniques of this paper.) Computation of α_{21} from α_{12} magnifies apparent errors greatly when α_{21} , as here, is not greatly different from zero. An error of 0.013 (corresponding to about 1.5 mV) in $\log \gamma_{\pm \text{NaCl}}$ between $y = 0$ and $y = 1$ would, for example, account for the difference between α_{21} of -0.014 and -0.035 .

Excess Free Energy

The osmotic and activity coefficients are measures of the excess free energy of the systems studied. It is thus appropriate to look at the free energy relationships among the three-component systems studied in the present investigation. The systems reported in this and the previous paper⁴ consist of the six binary salt mixtures of NaCl, Na₂SO₄, MgSO₄, and MgCl₂ in aqueous solution. To our knowledge, this is the first such investigation involving mixtures of salts of differ-

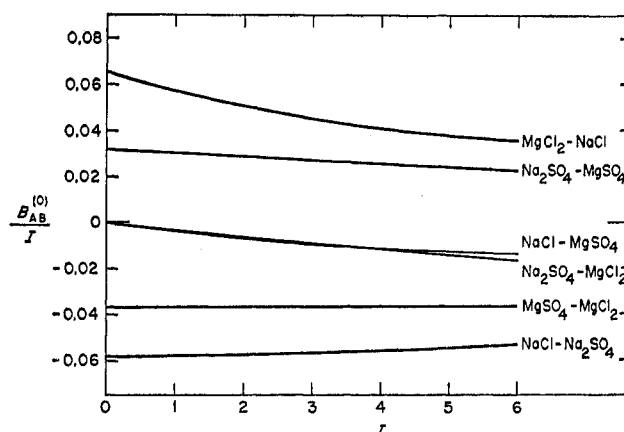


Figure 6. Variation of the parameter $B_{AB}^{(0)}/I$ as a function of I .

ent valence types, except for that of Yoest¹⁸ on mixtures of NaCl, NaClO₄, CuCl₂, and Cu(ClO₄)₂. Some years ago Scatchard and Prentiss¹⁹ studied binary mixtures of KNO₃, KCl, LiCl, and LiNO₃ in aqueous solution. They measured the freezing point depression in these mixtures and gave parameters for the calculation of the osmotic coefficients and the excess free energies. They showed that the osmotic coefficients of the two mixtures without a common ion could be calculated from measurements on the single salts and on mixtures with a common ion. They thus established the validity of the cross-square rule (see below) for the excess free energies of mixing for mixtures of these 1:1 electrolytes. Recently, Covington, Lilley, and Robinson²⁰ have shown the validity of the cross-square rule for the excess free energies of mixing for pairs involving NaCl, KCl, NaBr, and KBr in aqueous solutions.

The excess free energy, G^e , is the total free energy of the solution less that of the components in their standard state and less the ideal free energy represented by the concentration terms. In the treatment used here the equation for the excess free energy is (ref 10, eq 13)

$$G^e/RT = (n_A^* + n_B^*)[A_{AA}y_A + A_{BB}y_B + B_{AB}^{(0)}y_Ay_B + B_{AB}^{(1)}y_Ay_B(y_A - y_B)] \quad (11)$$

where R is the gas constant, T the temperature in degrees absolute, and $n_J^* = n_J(1/2 \sum_i \nu_{iJ} z_i^2)$ (n_J is the number of moles of solute J , ν_{iJ} is the number of moles of ion i in 1 mol of component J , and z_i is the valence of ion i).

It is convenient to consider the change in excess free energy per kilogram of water on forming a three-

(15) J. C. Synnott and J. N. Butler, *J. Phys. Chem.*, **72**, 2474 (1968).

(16) R. F. Platford, *J. Chem. Eng. Data*, **13**, 46 (1968).

(17) J. N. Butler, P. T. Hsu, and J. C. Synnott, *J. Phys. Chem.*, **71**, 910 (1967).

(18) R. L. Yoest, Ph.D. Thesis, Massachusetts Institute of Technology, 1964.

(19) G. Scatchard and S. S. Prentiss, *J. Amer. Chem. Soc.*, **56**, 2320 (1934).

(20) A. K. Covington, T. H. Lilley, and R. A. Robinson, *J. Phys. Chem.*, **72**, 2759 (1968).

Table VI: Excess Free Energies of Mixing, Calories per Kilogram of Water, at $y_A = y_B = 0.5$

	1	2	3	4	5	6
NaCl-Na ₂ SO ₄	-9	-34	-76	-132	-202	-282
MgCl ₂ -MgSO ₄	-5	-22	-49	-87	-136	-196
Na ₂ SO ₄ -MgSO ₄	4	17	36	61	89	121
NaCl-MgCl ₂	8	30	60	96	138	190
$\Sigma \square$	-2	-9	-29	-62	-111	-167
NaCl-MgSO ₄	-1	-4	-12	-27	-48	-73
Na ₂ SO ₄ -MgCl ₂	-1	-4	-12	-28	-54	-90
$\Sigma \times$	-2	-8	-24	-55	-102	-163
$\Sigma \square - \Sigma \times$	0	-1	-5	-7	-9	-4

component mixture from the limiting two-component solutions at the same ionic strength.

$$\Delta_m G^e = RTI[B_{AB}^{(0)}y_A y_B + B_{AB}^{(1)}y_A y_B(y_A - y_B)] \quad (12)$$

It should be noted that $B_{AB}^{(0)}/I$ and $B_{AB}^{(1)}/I$ correspond to the terms g_0 and $-g_1$ in the treatment given by Friedman.²¹

Values of $\Delta_m G^e$ for mixtures containing equal ionic strength fractions ($y_A = y_B = 0.5$) of the two solutes are given in Table VI. These values were calculated from eq 12 and the b coefficients of Table IV and of Table VI of the previous paper.⁴ Values of the quantity $B_{AB}^{(0)}/I$ for the same systems are shown in Figure 6.

The extensive investigations of Young and coworkers^{5,22} and Wood and coworkers^{23,24} have indicated two general relationships for the heats of mixing of aqueous electrolyte solutions: (1) for two electrolytes with a common ion, the heat of mixing is independent of the common ion; (2) for a system of reciprocal salt pairs, the sum of the heats of mixing for the four pairs with common ions equals the sum for the two pairs without a common ion (cross-square rule). For the excess free energies of mixing for the six salt pairs of the present investigation (involving mixtures of 1:1, 1:2,

and 2:2 electrolytes), the results in Table VI indicate that relationship 1 is only qualitatively true and that the cross-square rule (relationship 2) is obeyed.

It is possible to calculate the excess free energy, osmotic coefficient, and mean activity coefficient of any electrolyte in any mixture of ions approximately from the parameters for the two-component mixtures, and more exactly from these plus the parameters for the three-component mixtures with a common ion, by the ion-component treatment of Scatchard.²⁵ We plan to illustrate this for the four-ion system investigated here and for sea water solutions in the third paper of this series.

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(21) H. L. Friedman, *J. Chem. Phys.*, **32**, 1351 (1960).

(22) Y. C. Wu, M. B. Smith, and T. F. Young, *J. Phys. Chem.*, **69**, 1868, 1873 (1965).

(23) R. H. Wood and R. W. Smith, *ibid.*, **69**, 2974 (1965).

(24) R. H. Wood and H. L. Anderson, *ibid.*, **70**, 992, 1877 (1966).

(25) G. Scatchard, *J. Amer. Chem. Soc.*, **90**, 3124 (1968).