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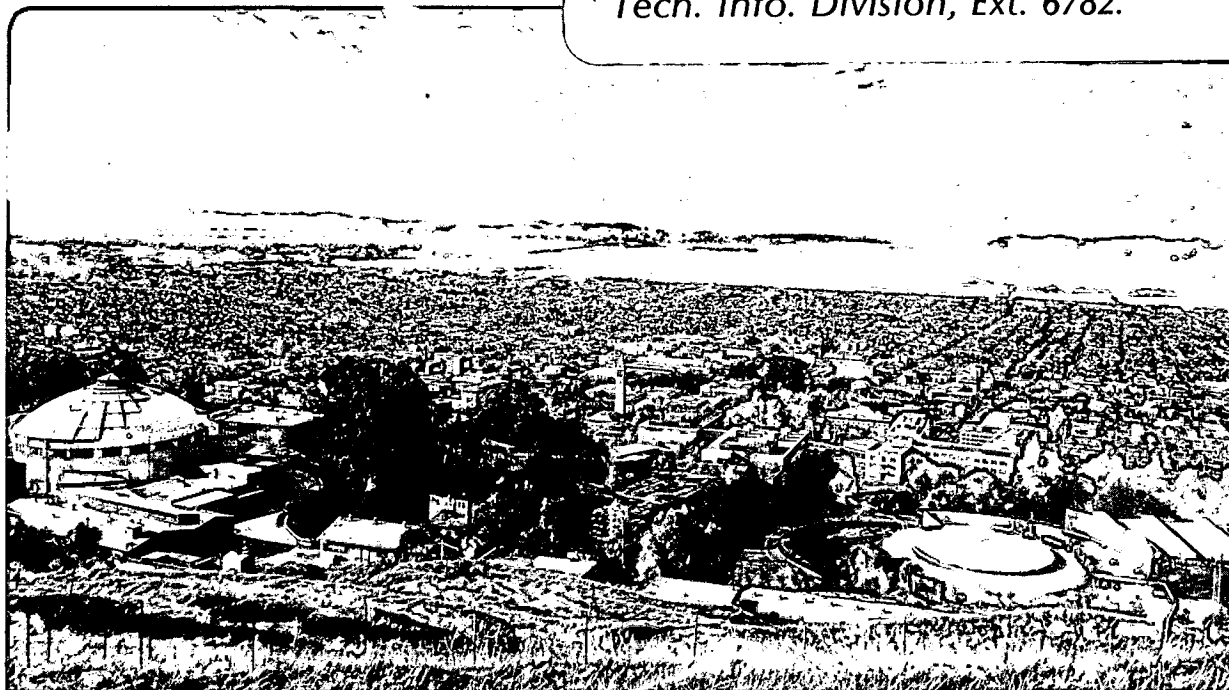
THERMODYNAMICS OF SATURATED ELECTROLYTE MIXTURES
OF NaCl WITH Na₂SO₄ AND WITH MgCl₂

M. Conceição P. de Lima and Kenneth S. Pitzer

December 1, 1982

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Thermodynamics of Saturated Electrolyte Mixtures of
NaCl with Na_2SO_4 and with MgCl_2

M. Conceição P. de Lima¹ and Kenneth S. Pitzer²

Abstract

The ion-interaction equation is used to calculate the mean activity coefficients for the saturated aqueous mixtures, $\text{NaCl} + \text{Na}_2\text{SO}_4$ and $\text{NaCl} + \text{MgCl}_2$. A comparison between these values with those obtained from solubility shows a good agreement over a wide temperature range as well as at high ionic strengths for both mixed systems.

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Introduction

In a previous study⁽¹⁾ dealing with saturated aqueous uni-univalent single and mixed electrolytes, a comparison between the mean activity coefficients obtained from Pitzer's equation with those from solubility has been reported. The present work deals with two mixtures of uni-bivalent electrolytes having one ion in common; NaCl + Na₂SO₄ and NaCl + MgCl₂.

For several reasons these two systems were chosen to be investigated. Apart from being 2-1 charge type electrolyte mixtures for which we wish to test the validity, at high temperatures and ionic strengths, of the recent equations developed for mixed systems,⁽²⁻⁴⁾ Na₂SO₄ and MgCl₂ are the predominant salts in addition to NaCl in many geochemical brines. Also the single electrolytes composing these two mixtures have been studied over a wide range of temperatures providing data to calculate the values of the activity coefficients in both mixed systems.

Data and Equations

For the system NaCl + Na₂SO₄, the solubilities of each component in the mixture from 25 up to 100°C are taken from Seidell⁽⁵⁾ while Shroeder et al.⁽⁶⁾ measured the solubility of Na₂SO₄ from 150 to 350°C.

The ion-interaction model gives the mean activity coefficient of a 1:2 electrolyte, M₂X in a common-ion mixture of a 1:2 (M₂X) and a 1:1 (MY) electrolyte of molalities m₁ and m₂, respectively.

$$\ln \gamma_{\pm}(M_2X) = -2A_{\phi} \left[I^{\frac{1}{2}} / (1 + bI^{\frac{1}{2}}) + (2/b) \ln(1 + bI^{\frac{1}{2}}) \right] \\ + \left(\frac{2}{3} m_2 + 2m_1 \right) [B_{MX} + (m_2 + 2m_1) C_{MX}]$$

$$\begin{aligned}
& + \frac{4}{3} m_2 [B_{MY} + (m_2 + 2m_1) C_{MY} + \frac{1}{2} \theta_{XY}] \\
& + m_1 (m_2 + 2m_1) [2B'_{M_2X} + \frac{4}{3} C_{M_2X}] \\
& + m_2 (m_2 + 2m_1) \{2B'_{MY} + [4C_{MY} + \psi_{MYX}]/3\} \\
& + m_2 m_1 \psi_{MXY}/3
\end{aligned} \tag{1}$$

Here B_{MX} , the second virial coefficient, is defined as

$$B_{MX} = \beta_{MX}^{(0)} + (2\beta_{MX}^{(1)}/\alpha^2 I) [1 - (1 + \alpha I)^{\frac{1}{2}} \exp(-\alpha I^{\frac{1}{2}})] \tag{2}$$

C_{M_2X} , the third virial coefficient, is defined as

$$C_{MX} = C_{MX}^{\phi} / 2 |z_M z_X|^{\frac{1}{2}} \tag{3}$$

B'_{MX} , the ionic strength derivative of B_{MX} is given by

$$B'_{MX} = (2\beta_{MX}^{(1)}/\alpha^2 I^2) [1 - 1 + (1 + \alpha I)^{\frac{1}{2}} + \frac{1}{2}\alpha^2 I \exp(-\alpha I^{\frac{1}{2}})] \tag{4}$$

where $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} are specific parameters for the M_2X electrolyte.

Corresponding expressions apply for the MY component. The mixing parameter, θ_{XY} , arises from the differences in short-range interaction between unlike and like pairs of ions of the same sign, and in many cases its effect on the activity coefficient is negligible. Similarly, ψ_{MXY} arises from triple interactions and is also often negligible.

The ionic strength, I , is in this case, of course, equal to $m_2 + 3m_1$.

The empirical parameters α and b have their conventional values, 2.0 and $1.2 \text{ kg}^{\frac{1}{2}}/\text{mole}^{-\frac{1}{2}}$, respectively. The activity coefficient of NaCl in this mixed system is given by a similar equation which is a mere transposition of the equation given below for NaCl in MgCl_2 .

Recently Rogers and Pitzer⁽⁷⁾ measured the heat capacity of aqueous Na_2SO_4 to 200°C and combined their results with literature data at lower temperature to provide equations for the enthalpy and heat capacity as well as for the partial molar heat capacity at zero molality. They also give the temperature-dependent equations for the virial coefficients $\beta^{(0)J}$, $\beta^{(1)J}$ and $C^{\phi J}$ for the heat capacity. The ion-interactions parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} for Na_2SO_4 (have been calculated by integration of these equations, the required integration constants being the values of $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} and their first derivatives with temperature at 25°C. The temperature-dependence equations obtained in this way, which involve parameters $U_5 - U_{15}$ given by Rogers and Pitzer,⁽⁷⁾ follow:

$$\beta^{(0)} = U_5 T^2 + U_6 T + U_7 \log T + \frac{263U_8}{T(T-263)} - \frac{K_1}{T} + K_2 \quad (5)$$

where $K_1 = 2317.94$ and $K_2 = 81.5043$

$$\beta^{(1)} = U_9 T^2 + U_{10} T + U_{11} \log T + \frac{263U_{12}}{T(T-263)} + \frac{680U_{13}}{T(680-T)} - K_3/T + K_4 \quad (6)$$

where $K_3 = 23268.1$ and $K_4 = 1002.77$

$$C^{\phi} = U_{14} T + \frac{263U_{15}}{T(T-263)} - K_5/T + K_6 \quad (7)$$

where $K_5 = -22.6187$ and $K_6 = -0.094327$

The mixing parameters, θ and ψ , in the absence of any literature data at high temperatures, have been assumed to be equal to -0.02 and 0.004, respectively, these values being those at 25°C from Pitzer.⁽³⁾ The ion interaction parameters for pure NaCl have been taken from Silvester and Pitzer.⁽⁸⁾ The values of the activity coefficient of Na_2SO_4 in the mixed system calculated from Pitzer's equation, have

been compared with those obtained from the solubility in combination with properties of the solid and the infinitely dilute solution. The equation for the partial molar heat capacity at zero molality of Na_2SO_4 given by Rogers and Pitzer⁽⁶⁾ was integrated twice to give a temperature dependence equation of $(G_T^\circ - H_{298}^\circ)/T$ for aqueous Na_2SO_4 . For the solid Na_2SO_4 we used the values of $(G_T - H_0)/T$ given by Giauque and Brodale,⁽⁹⁾ together with $(H_{298} - H_0)$, to obtain an equation for $(G_T^\circ - H_{298}^\circ)/T$ as a function of temperature. We then used the equation for the standard free energy of solution

$$\frac{\Delta G^\circ}{T} = \frac{G_T^\circ - H_{298}^\circ}{T} \text{ aq} - \frac{G_T^\circ - H_{298}^\circ}{T} \text{ solid} + \frac{\Delta H_s^\circ(298)}{T} \quad (8)$$

which is related to the mean activity coefficient by

$$\frac{\Delta G^\circ}{T} = -R \ln[(m_2 + 2m_1)^2 m_1 \gamma_{\pm}^3] \quad (9)$$

The values of the activity coefficient for NaCl in the mixed system obtained from solubility data were calculated from the equation of ΔG_s° as a function of temperature derived from pure NaCl by Silvester and Pitzer.⁽⁸⁾

For the system $\text{NaCl} + \text{MgCl}_2$, the solubilities of NaCl in the mixture have been taken from Seidell.⁽⁵⁾ We accepted the values of Achowmow et al.⁽¹⁰⁾ who made solubility measurements from 100 up to 200°C. At each temperature the data corresponding to the presence of very small amounts of NaCl have been discarded. At lower temperatures solubility data from Keitel⁽¹¹⁾ are available, but due to their poor accuracy, they were not included in the present activity coefficient calculations.

Pitzer's equation for the mean activity coefficient of NaCl (MX) in NaCl (MX, m_2) + MgCl₂ (NX₂, m_3) mixture is

$$\begin{aligned} \ln \gamma_{MX} = & -A_{\phi} [I^{1/2}/(1+bI^{1/2}) + (2/b) \ln(1+bI^{1/2})] \\ & + (2m_2 + 2m_3) [B_{MX} + (m_2 + 2m_3) C_{MX}] \\ & + m_3 [B_{NX} + (m_2 + 2m_3) C_{NX} + \theta_{MN}] \\ & + (m_2 + 2m_3) [m_2 (B'_{MX} + C_{MX}) + m_3 (B'_{NX_2} + C_{NX_2} + \psi_{MNX}/2)] \\ & + m_2 m_3 \psi_{MNX}/2. \end{aligned} \quad (10)$$

The parameters and quantities here expressed have the same definitions as for the previous mixture. The mixing parameters θ and ψ were assumed to be equal to zero as reported by Pitzer and Kim⁽⁴⁾ for 25°C. The pure NaCl parameters were taken from Silvester and Pitzer⁽⁸⁾ and those for MgCl₂ from the data of Holmes et al.⁽¹²⁾ on their isopiestic measurements of this electrolyte in Water. Their studies covered the molality range from 1 to 6 mol Kg⁻¹, for the NaCl used as standard solution, at the temperatures 382.0, 413.8, 445.4, and 474.0 K. The pure MgCl₂ parameters given at these four temperatures together with those derived at 25°C by Rard and Miller⁽¹³⁾ have been fitted by least-squares to a quadratic expression to obtain values at intermediate temperatures. This is shown in fig. 1; where the curves represent the values from the quadratic equations (eq. 11-13) for the ion-interaction parameters and the points the values from fits to the data at individual temperatures. The for temperature dependent equations obtained/the three parameters and the corresponding standard deviations for the fitting are

$$\beta^{(0)} = 5.93915 \times 10^{-7} T^2 - 9.31654 \times 10^{-4} T + 0.576066 \quad (11)$$

$$\sigma = 0.0019$$

$$\beta^{(1)} = 2.60169 \times 10^{-5} T^2 - 1.09438 \times 10^{-2} T + 2.60135$$

$$\sigma = 0.018$$

$$C^\phi = 3.01823 \times 10^{-7} T^2 - 2.89125 \times 10^{-4} T + 6.57867 \times 10^{-2}$$

$$\sigma = 0.00057$$

Here again the activity coefficients of the NaCl in this mixture were calculated from the ΔG_s° equation given by Silvester and Pitzer⁽⁸⁾ for NaCl in Water.

Results and Discussion

Figures 2 and 3 show the comparison of the activity coefficients from solution and solubility data for the mixture NaCl + Na₂SO₄. Included are points calculated by similar methods for pure Na₂SO₄ by Pitzer and Murdzek.⁽¹⁴⁾ The mean activity coefficients of NaCl at 38°C (the only temperature at which enough data for plotting were available) and of Na₂SO₄ at this same temperature as well as at some high temperatures are plotted against y , the ionic strength fraction of Na₂SO₄. The solid lines represent the predicted values of the activity coefficients from Pitzer's equation and the points those obtained from solubility data. The solid circles correspond to the values of the activity coefficients when both NaCl and Na₂SO₄ are present as solid phase. For NaCl, the agreement between the two sets of results from 25 up to 100°C (the available range of solubility data) is good and at 38°C the activity coefficients seem to be almost invariable with composition for the covered range. The activity coefficients of Na₂SO₄ from the two sources are in general, in good

agreement up to 300°C, which involves an extrapolation of 100°C above the claimed range of validity for data on pure Na_2SO_4 .⁽⁶⁾ At 200°C, for the lower values of $y(\text{Na}_2\text{SO}_4)$, the agreement is only reasonable. As might be expected, above 300°C, the results deviate rapidly, and therefore they have not been plotted. The values of the activity coefficients show a decrease as the temperature increases. At the two highest temperatures, the trend of the activity coefficients with composition seems somewhat different from that shown up to 200°C, where a decrease with increase in y is observed. At 300°C, the activity coefficients seem to increase as y increases, becoming almost independent on composition at high values of ionic strength fraction.

Considering fig. 4, where the values of the activity coefficients for NaCl in the mixture $\text{NaCl} + \text{MgCl}_2$ are plotted against y , the ionic strength fraction of MgCl_2 , at 100, 125, 150, 175, and 200°C, one can say that for all these temperatures the agreement between the two sets of results is excellent. Here again, the solid curves represent the predicted values from solution properties and the points those from solubility data. Figure 4 shows that there is a monotonic decrease in the activity coefficients as the temperature is increased. For all the temperatures the activity coefficients increase with increase of $y(\text{MgCl}_2)$.

At the two highest temperatures, 175 and 200°C, the trend of the activity coefficients of NaCl observed for high values of $y(\text{Na}_2\text{SO}_4)$ where the agreement is still good, seems interesting. To understand this behavior we consider the actual solubility values shown in Table I. The solubility of MgCl_2 increases remarkably rapidly as the molality

of NaCl becomes small. Since B_{MgCl} is substantial, approximately 0.3, the term $m_3 B_{\text{NX}}$ in eq. (10) increases rapidly in this range. This increase in m_3 implies, of course, an increase in ionic strength and in the Debye-Hückel term which is negative and partially compensates the term $m_3 B_{\text{NX}}$. But the effect of further increase in an already high ionic strength is not very large in the Debye-Hückel term especially for a 1-1 electrolyte.

In structural terms this effect is a repulsive increment in the Mg-Cl interaction which raises the activity coefficient of the Cl^- ion and thus affects the mean activity coefficient of NaCl. While this explanation is, undoubtedly, over simplified, it is interesting that the ion-interaction equations for mixtures do reproduce the observed behavior quite accurately even in this region of initially unexpected behavior.

Tables giving details of calculated results for the $\text{NaCl-Na}_2\text{SO}_4$ system are included in the Appendix. The last column gives references to the individual investigators of solubility studies.

Acknowledgment

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TABLE I. Activity Coefficients of NaCl in Saturated Aqueous Mixture NaCl + MgCl₂. Only NaCl is Present as Solid Phase; all Solubility² Values are from ref. 10

| t, °C | m ₂ (NaCl) | m ₃ (MgCl ₂) | γ _± (NaCl) from | |
|-------|-----------------------|-------------------------------------|----------------------------|-----------------|
| | | | Solution Data | Solubility Data |
| 100 | 4.82 ₅ | 1.05 ₀ | 1.063 | 1.059 |
| 100 | 1.81 ₄ | 3.15 ₁ | 1.618 | 1.595 |
| 125 | 5.09 ₉ | 1.05 ₀ | 0.946 | 0.945 |
| 125 | 2.05 ₃ | 3.15 ₁ | 1.380 | 1.382 |
| 150 | 5.33 ₉ | 1.05 ₀ | 0.819 | 0.828 |
| 150 | 2.36 ₁ | 3.15 ₁ | 1.161 | 1.154 |
| 175 | 5.64 ₇ | 1.05 ₀ | 0.693 | 0.700 |
| 175 | 2.66 ₉ | 3.15 ₁ | 0.956 | 0.946 |
| 175 | 0.889 ₈ | 5.25 ₁ | 1.447 | 1.455 |
| 200 | 6.05 ₇ | 1.05 ₀ | 0.573 | 0.568 |
| 200 | 3.01 ₂ | 3.15 ₁ | 0.772 | 0.753 |
| 200 | 1.02 ₇ | 5.25 ₁ | 1.117 | 1.160 |
| 200 | 0.479 ₁ | 7.35 ₁ | 1.652 | 1.479 |

Figure Captions

Figure 1. The ion-interaction parameters for MgCl_2 as a function of temperature.

Figure 2. The activity coefficient of saturated solutions of $\text{NaCl-Na}_2\text{SO}_4$. The points are calculated from solubility while the curves are calculated from the ion-interaction equation. The solid symbol indicates that both solids are present.

Figure 3. The activity coefficient of saturated solutions of $\text{NaCl-Na}_2\text{SO}_4$. Details are the same as in Figure 2.

Figure 4. The activity coefficient of NaCl in saturated solutions with MgCl_2 . Details are the same as in Figure 2.

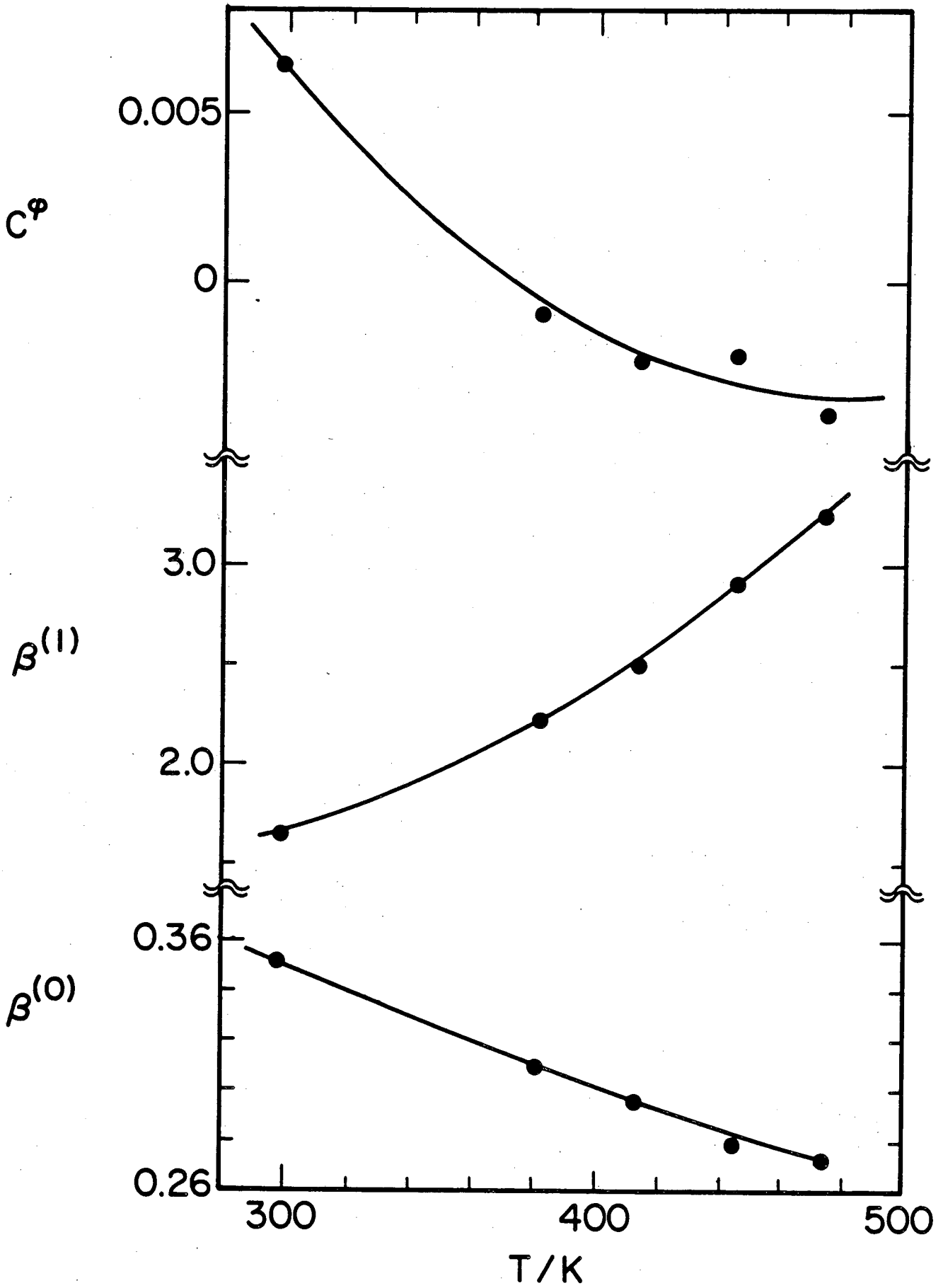


Figure 1

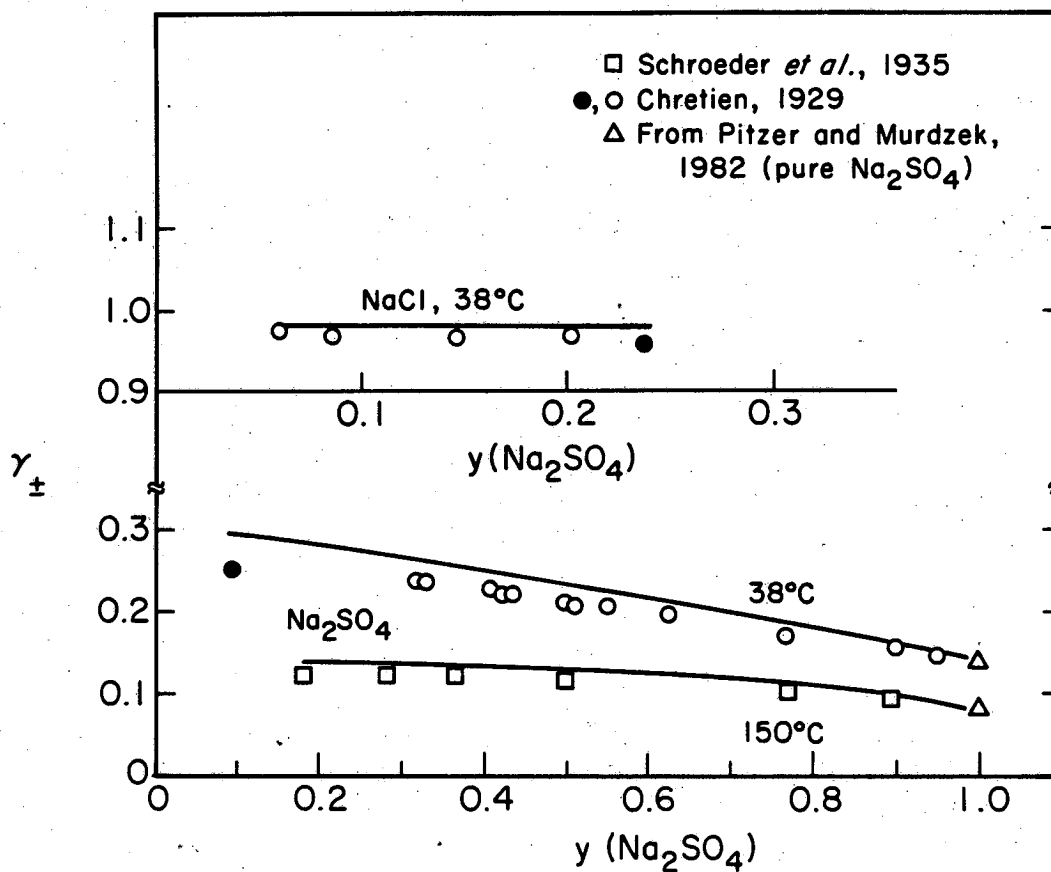


Figure 2. The activity coefficient of saturated solutions of NaCl- Na_2SO_4 . The points are calculated from solubility while the curves are calculated from the ion-interaction equation. The solid symbol indicates that both solids are present.

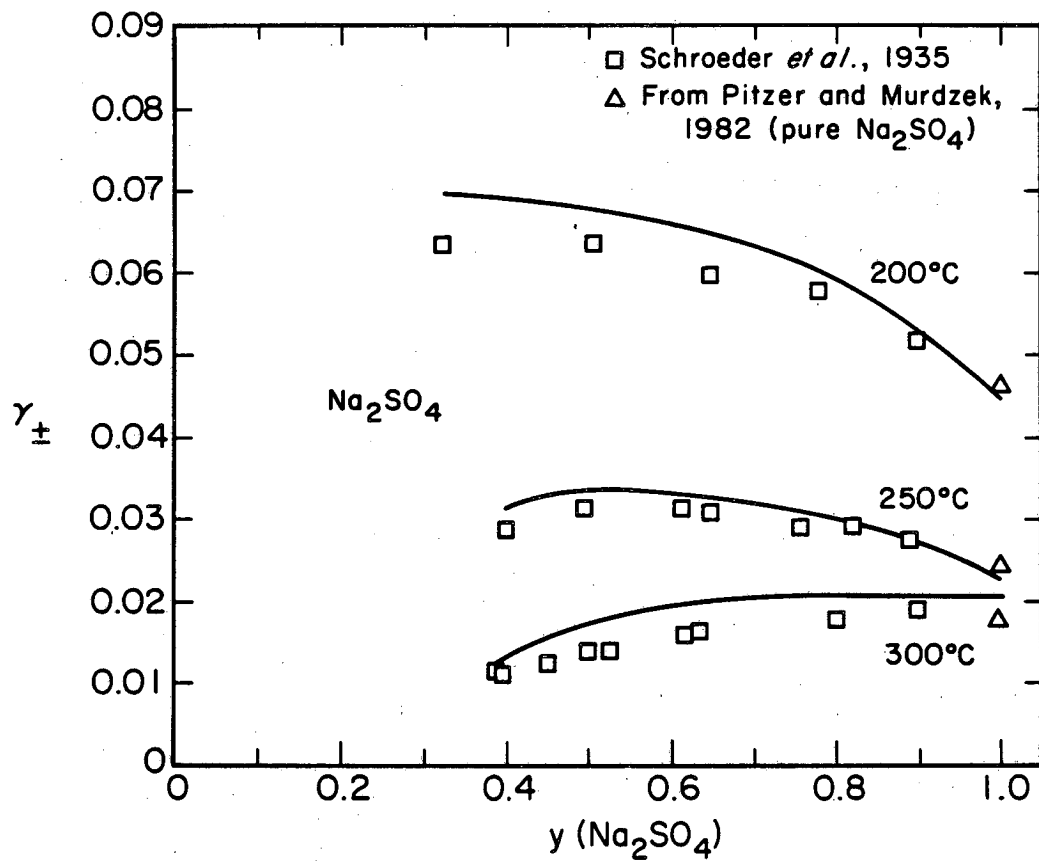


Figure 3. The activity coefficient of saturated solutions of $\text{NaCl-Na}_2\text{SO}_4$. Details are the same as in Figure 2.

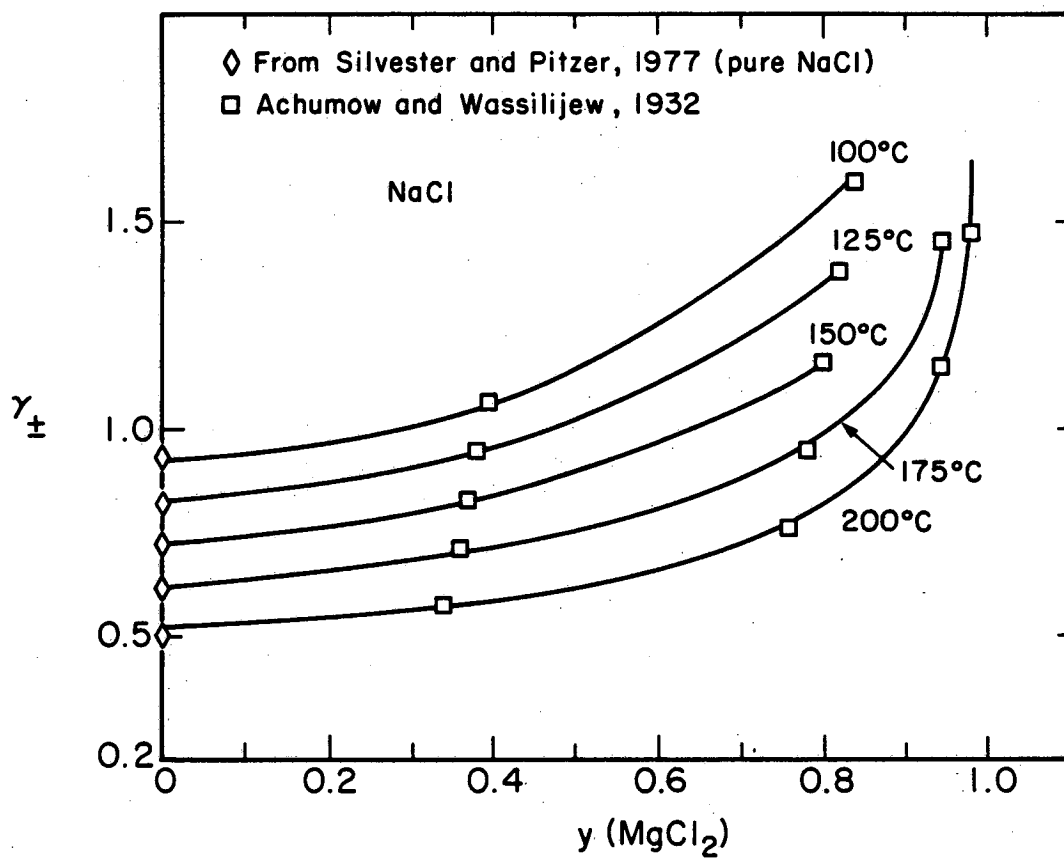


Figure 4. The activity coefficient of NaCl in saturated solutions with MgCl_2 . Details are the same as in Figure 2.

TABLE A-1. Activity Coefficients of Na_2SO_4 and NaCl in Saturated Aqueous Mixture $\text{NaCl}+\text{Na}_2\text{SO}_4$. Both Electrolytes are Present as Solid Phase

| t, °C | $m_2(\text{NaCl})$ | $m_3(\text{Na}_2\text{SO}_4)$ | $\gamma_{\pm}(\text{Na}_2\text{SO}_4)$ from | | $\gamma_{\pm}(\text{NaCl})$ from | | Ref. |
|-------|--------------------|-------------------------------|---|-------------|----------------------------------|-------------|---------|
| | | | Soln. Data | Solub. Data | Soln. Data | Solub. Data | |
| 25 | 5.53 ₀ | 0.707 ₆ | 0.264 | 0.242 | 1.001 | 1.000 | (15,16) |
| 25 | 5.47 ₂ | 0.595 ₂ | 0.265 | 0.263 | 0.979 | 1.026 | (17) |
| 25 | 5.60 ₀ | 0.681 ₈ | 0.266 | 0.244 | 1.008 | 0.992 | (18,19) |
| 25 | 5.64 ₆ | 0.692 ₉ | 0.267 | 0.241 | 1.016 | 0.983 | (20) |
| 25 | 5.71 ₄ | 0.728 ₆ | 0.268 | 0.234 | 1.031 | 0.968 | (21) |
| 25 | 5.56 ₅ | 0.690 ₄ | 0.265 | 0.244 | 1.004 | 0.996 | (22) |
| 30 | 5.59 ₇ | 0.668 ₈ | 0.270 | 0.245 | 1.008 | 1.006 | (15,16) |
| 30 | 5.63 ₃ | 0.645 ₂ | 0.271 | 0.248 | 1.010 | 1.004 | (22) |
| 38 | 5.73 ₃ | 0.596 ₈ | 0.287 | 0.250 | 1.035 | 1.008 | (21) |
| 50 | 5.86 ₁ | 0.554 ₃ | 0.277 | 0.246 | 1.015 | 1.005 | (15,16) |
| 75 | 6.20 ₇ | 0.499 ₆ | 0.259 | 0.222 | 0.982 | 0.953 | (15,16) |
| 100 | 6.36 ₉ | 0.456 ₃ | 0.223 | 0.196 | 0.896 | 0.899 | (15,16) |
| 109.1 | 6.58 ₆ | 0.514 ₂ | 0.205 | 0.172 | 0.871 | 0.846 | (15,16) |

TABLE A-2. Activity Coefficients of Na_2SO_4 in Saturated Aqueous Mixture $\text{NaCl}+\text{Na}_2\text{SO}_4$.
Only Na_2SO_4 is Present as Solid Phase

| t, °C | $m_2(\text{NaCl})$ | $m_3(\text{Na}_2\text{SO}_4)$ | $\gamma_{\pm}(\text{Na}_2\text{SO}_4)$ from | | Ref. |
|-------|--------------------|-------------------------------|---|-----------------|---------|
| | | | Solution Data | Solubility Data | |
| 25 | 4.42 ₂ | 1.02 ₈ | 0.235 | 0.223 | (15,16) |
| 30 | 2.91 ₆ | 1.59 ₃ | 0.201 | 0.200 | (15,16) |
| 30 | 4.26 ₀ | 0.944 ₅ | 0.237 | 0.249 | (15,16) |
| 38 | 0.479 ₀ | 3.13 ₃ | 0.151 | 0.146 | (21) |
| 38 | 0.925 ₀ | 2.84 ₀ | 0.159 | 0.153 | (21) |
| 38 | 1.99 ₈ | 2.17 ₆ | 0.182 | 0.172 | (21) |
| 38 | 2.94 ₅ | 1.62 ₂ | 0.204 | 0.193 | (21) |
| 38 | 3.42 ₃ | 1.38 ₆ | 0.216 | 0.203 | (21) |
| 38 | 3.69 ₁ | 1.29 ₀ | 0.223 | 0.207 | (21) |
| 38 | 3.74 ₇ | 1.23 ₇ | 0.225 | 0.211 | (21) |
| 38 | 4.18 ₅ | 1.07 ₂ | 0.236 | 0.219 | (21) |
| 38 | 4.29 ₀ | 1.05 ₅ | 0.238 | 0.218 | (21) |
| 38 | 4.34 ₂ | 1.00 ₅ | 0.240 | 0.223 | (21) |
| 38 | 4.95 ₈ | 0.804 ₀ | 0.256 | 0.235 | (21) |
| 38 | 5.03 ₃ | 0.788 ₀ | 0.258 | 0.235 | (21) |
| 50 | 1.88 ₃ | 2.05 ₂ | 0.182 | 0.176 | (15,16) |
| 50 | 3.79 ₅ | 1.09 ₆ | 0.229 | 0.217 | (15,16) |
| 75 | 1.83 ₁ | 1.91 ₂ | 0.174 | 0.167 | (15,16) |
| 75 | 3.85 ₂ | 0.979 ₇ | 0.219 | 0.205 | (15,16) |
| 100 | 1.78 ₀ | 1.77 ₆ | 0.157 | 0.153 | (15,16) |
| 100 | 4.32 ₂ | 0.845 ₆ | 0.199 | 0.181 | (15,16) |
| 150 | 0.821 ₃ | 2.36 ₆ | 0.0937 | 0.0917 | (6) |
| 150 | 1.66 ₀ | 1.87 ₃ | 0.105 | 0.101 | (6) |
| 150 | 3.42 ₂ | 1.14 ₈ | 0.123 | 0.114 | (6) |

TABLE A-2 (continued)

| t, °C | m ₂ (NaCl) | m ₃ (Na ₂ SO ₄) | $\gamma_{\pm}(\text{Na}_2\text{SO}_4)$ from | | Ref. |
|-------|-----------------------|---|---|-----------------|------|
| | | | Solution Data | Solubility Data | |
| 150 | 4.46 ₆ | 0.859 ₀ | 0.131 | 0.120 | (6) |
| 150 | 5.51 ₀ | 0.725 ₀ | 0.133 | 0.117 | (6) |
| 150 | 6.98 ₁ | 0.507 ₀ | 0.136 | 0.120 | (6) |
| 200 | 0.855 ₆ | 2.53 ₄ | 0.0524 | 0.0511 | (6) |
| 200 | 1.67 ₇ | 1.99 ₉ | 0.0594 | 0.0569 | (6) |
| 200 | 2.65 ₂ | 1.63 ₃ | 0.0637 | 0.0592 | (6) |
| 200 | 3.62 ₈ | 1.26 ₇ | 0.0684 | 0.0627 | (6) |
| 200 | 3.76 ₅ | 1.32 ₄ | 0.0667 | 0.0602 | (6) |
| 200 | 5.57 ₈ | 0.894 ₁ | 0.0698 | 0.0625 | (6) |
| 250 | 0.906 ₉ | 2.40 ₁ | 0.0272 | 0.0270 | (6) |
| 250 | 1.38 ₆ | 2.11 ₂ | 0.0292 | 0.0286 | (6) |
| 250 | 1.88 ₂ | 1.97 ₈ | 0.0295 | 0.0284 | (6) |
| 250 | 2.85 ₈ | 1.53 ₅ | 0.0324 | 0.0306 | (6) |
| 250 | 3.88 ₄ | 1.27 ₄ | 0.0331 | 0.0308 | (6) |
| 250 | 2.58 ₄ | 1.61 ₂ | 0.0321 | 0.0305 | (6) |
| 250 | 5.25 ₃ | 1.62 ₂ | 0.0308 | 0.0285 | (6) |
| 300 | 0.530 ₅ | 1.44 ₃ | 0.0210 | 0.0183 | (6) |
| 300 | 1.02 ₇ | 1.35 ₉ | 0.0205 | 0.0176 | (6) |
| 300 | 1.04 ₄ | 1.40 ₈ | 0.0198 | 0.0170 | (6) |
| 300 | 2.08 ₈ | 1.21 ₁ | 0.0192 | 0.0161 | (6) |
| 300 | 2.31 ₀ | 1.23 ₉ | 0.0184 | 0.0154 | (6) |
| 300 | 3.33 ₇ | 1.23 ₂ | 0.0163 | 0.0135 | (6) |
| 300 | 3.57 ₆ | 1.19 ₀ | 0.0162 | 0.0135 | (6) |
| 300 | 4.50 ₀ | 1.23 ₉ | 0.0142 | 0.0195 | (6) |

TABLE A-2 (continued)

| t, °C | m ₂ (NaCl) | m ₃ (Na ₂ SO ₄) | $\gamma_{\pm}(\text{Na}_2\text{SO}_4)$ from | | Ref. |
|-------|-----------------------|---|---|-----------------|------|
| | | | Solution Data | Solubility Data | |
| 300 | 5.57 ₈ | 1.18 ₃ | 0.0129 | 0.0111 | (6) |
| 300 | 5.73 ₂ | 1.24 ₆ | 0.0123 | 0.0107 | (6) |
| 350 | 0.239 ₆ | 0.218 ₂ | 0.0809 | 0.0341 | (6) |
| 350 | 0.633 ₁ | 0.274 ₆ | 0.0571 | 0.0217 | (6) |
| 350 | 0.667 ₃ | 0.366 ₁ | 0.0473 | 0.0177 | (6) |
| 350 | 1.33 ₅ | 0.422 ₄ | 0.0331 | 0.0125 | (6) |
| 350 | 1.38 ₆ | 0.450 ₆ | 0.0310 | 0.0119 | (6) |
| 350 | 1.72 ₈ | 0.506 ₉ | 0.0256 | 0.0101 | (6) |
| 350 | 2.24 ₂ | 0.654 ₇ | 0.0181 | 0.00782 | (6) |
| 350 | 4.22 ₇ | 1.04 ₂ | 0.00797 | 0.00457 | (6) |
| 350 | 5.90 ₃ | 1.35 ₂ | 0.00457 | 0.00340 | (6) |

TABLE A-3. Activity Coefficients of NaCl in Saturated Aqueous Mixture NaCl+Na₂SO₄.
Only NaCl is Present as Solid Phase

| t, °C | m ₂ (NaCl) | m ₃ (Na ₂ SO ₄) | γ _± (NaCl) from | | Ref. |
|-------|-----------------------|---|----------------------------|-----------------|---------|
| | | | Solution Data | Solubility Data | |
| 25 | 5.84 ₂ | 0.327 ₃ | 1.000 | 1.006 | (15,16) |
| 38 | 5.77 ₂ | 0.488 ₂ | 1.029 | 1.018 | (21) |
| 38 | 5.92 ₆ | 0.340 ₇ | 1.034 | 1.016 | (21) |
| 38 | 6.04 ₅ | 0.191 ₅ | 1.036 | 1.019 | (21) |
| 38 | 6.07 ₅ | 0.129 ₆ | 1.034 | 1.025 | (21) |
| 75 | 6.32 ₂ | 0.210 ₈ | 0.980 | 0.976 | (15,16) |
| 100 | 6.55 ₉ | 0.182 ₅ | 0.907 | 0.908 | (15,16) |

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