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Prediction of High-Temperature Thermodynamic Properties of Mixed Electrolyte Solutions Including Solubility Equilibria, Vapor Pressure Depression and Boiling Point Elevation

Roberto T. Pabalan¹ and Kenneth S. Pitzer¹

The Pitzer ion-interaction model, which is theoretically derived but uses empirical parameters evaluated from experimental data on binary and ternary aqueous mixtures, is shown to accurately predict thermodynamic properties of aqueous electrolytes to high temperatures and concentrations and for more complex compositions. Applications of the model include calculations of solubility equilibria, vapor pressures and boiling points of electrolyte mixtures. Examples of these calculations are given below.

1. INTRODUCTION

The thermodynamic properties of aqueous electrolyte mixtures are required to understand various engineering problems in such areas as desalination, steam power generation, and hydrometallurgy, as well as various geochemical processes. Inherent problems associated with experimental work underscore the need for a chemical model capable of predicting thermodynamic properties of electrolyte mixtures over a wide range of temperature, pressure, and solution composition. In this study, the ion-interaction model of Pitzer^{1,2}, which is theoretically derived but uses empirical parameters evaluated from a variety of experimental data on binary and ternary solutions, is shown to accurately predict thermodynamic properties of aqueous electrolytes to high temperatures and concentrations and for more complex compositions. Applications of the model include calculations of solubility equilibria as well as vapor pressure depression and boiling point elevation of electrolyte mixtures. Examples of these calculations to elevated temperatures are given below.

2. REVIEW OF THE ION-INTERACTION MODEL

The ion-interaction or virial coefficient approach of Pitzer^{1,2} starts with a

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virial expansion of the excess free energy of the solution, i.e., the actual free energy of the solution minus the free energy of an ideal solution of the same composition: G^{ex}/RT . The expression for osmotic and activity coefficients follow directly from the equation for G^{ex}/RT through the appropriate derivatives with respect to the number of kilograms of water, n_w , and the molality of the aqueous species, m_i , respectively. Equation 1 shows the expression for the osmotic coefficient, while Eqn. 2 gives the activity coefficient of cation M, with an analogous expression for the activity coefficient of anion X,

$$(\phi-1) = - \frac{\partial G^{ex}/\partial n_w}{RT \sum_i m_i} = (2/\sum_i m_i) \left[-A_\phi I^{3/2}/(1+bI)^{1/2} \right] + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \quad (1)$$

$$+ \sum_{c<c'} \sum_c m_c m_{c'} (\phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a}) + \sum_{a<a'} \sum_a m_a m_{a'} (\phi_{aa'}^\phi + \sum_c m_c \psi_{caa'})$$

and

$$\ln \gamma_M = \frac{1}{RT} \frac{\partial G^{ex}}{\partial m_M} = z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\phi_{Mc} + \sum_a m_a \psi_{Mca}) \quad (2)$$

$$+ \sum_{a<a'} \sum_a m_a m_{a'} \psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca}$$

where c and c' are cations and a and a' are anions. z_M is the charge on cation M, A_ϕ is the Debye-Hückel slope, b is a universal constant with a value $1.2 \text{ kg}^{1/2}/\text{mol}^{1/2}$, and F includes the Debye-Hückel slope and other terms. The double summation indices, $c<c'$ and $a<a'$, denote the sum over all distinguishable pairs of dissimilar cations or anions. The B_{ij} and C_{ijk} terms can be evaluated empirically from data on binary systems, while the terms ϕ_{ij} and ψ_{ijk} arise only for mixed solutions and can best be determined from common ion mixtures. Provided that the temperature and pressure dependencies of these parameters are known, the activity and osmotic coefficients of aqueous electrolyte mixtures at different temperatures and pressures can be calculated.

From standard thermodynamics, various functions can be derived from the equation for excess Gibbs energy, such as the excess enthalpy, entropy and heat capacity, as well as the excess volume. These other functions can be determined experimentally and their evaluation yields accurate data on the temperature- or pressure-dependencies of the ion-interaction coefficients. This means that there is an extensive array of experimental data from which the model parameters and their temperature functions can be evaluated, including:

- 1) freezing point depression
- 2) boiling point elevation
- 3) vapor pressure
- 4) isopiestic concentrations
- 5) E.M.F.

- 6) enthalpy of dilution
- 7) enthalpy of mixing
- 8) enthalpy of solution
- 9) heat capacity
- 10) solubility

Likewise, the evaluation of volumetric data provides the parameters needed to calculate the pressure dependencies of electrolyte activity and thermal properties. Therefore, the ion-interaction model presents a thermodynamically consistent structure for the evaluation and prediction of electrolyte properties. This point is illustrated in Fig. 1, which is a plot of vapor pressures of aqueous KCl solutions at saturation pressure from 200-325°C, showing good agreement between calculated and experimental values. The data used to evaluate the ion-interaction parameters included osmotic coefficient data at saturation pressure to 250°C from Holmes and Mesmer³, but above this temperature the data included only heat capacity values at pressures 179-200 bars and apparent molar volumes from saturation pressure to 500 bars (Pabalan and Pitzer⁴). Thus the equations used to calculate the vapor pressures above 250°C and at saturation pressure are constrained only by the second temperature derivative of the excess Gibbs energy evaluated from the heat capacity data, and by the pressure derivative of the excess Gibbs energy evaluated from volumetric data.

Ion-interaction coefficients necessary to calculate osmotic and activity coefficients at 25°C are available for a wide variety of binary mixtures (cf., Pitzer¹, Pitzer and Mayorga⁵). Recent experimental measurements of the thermodynamic properties of electrolyte solutions have extended our knowledge of these parameters to higher temperatures. Table 1 shows the binary 1:1, 1:2 or 2:1, and 2:2 electrolyte systems for which high temperature data are available. For ternary mixtures, the mixing terms ϕ_{ij} and ψ_{ijk} required for calculating osmotic and activity coefficients are available at 25°C for a large number of systems and have been reported by various investigators (cf., Pitzer and Kim¹⁴, Pitzer¹⁵, Downes and Pitzer¹⁶, Harvie and Weare¹⁷, Harvie et al.¹⁸). Both these quantities undoubtedly vary with temperature, but they are both small and we found that it was an adequate approximation to hold ϕ_{ij} at its 25°C value and to assume a simple temperature dependence for ψ_{ijk} (Pabalan and Pitzer¹⁹).

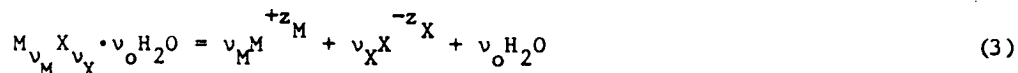
3. APPLICATIONS

Solubility calculations

The calculation of solid solubilities in electrolyte solutions is a rigorous test of models for predicting activity and osmotic coefficients, particularly for complex mixtures where the solubilities are strongly dependent on the solution composition. Even for binary systems solubility calculations frequently represent extrapolations of activity or osmotic coefficients outside the range of other

experiments. In addition, because of the iterative nature of the computations, calculated solubilities are sensitive, not only to the absolute value of the activity or osmotic coefficient at saturation concentration, but also on the dependence of activity or osmotic coefficients on molality.

Solubility calculations involve several steps, but the basic theory is well-known. For a hydrated solid, $M_{v_M} X_{v_X} \cdot v_o H_2O$, having v_M cations, M, of charge z_M , and v_X anions, X, of charge z_X , as well as v_o molecules of water, the equilibrium constant at a fixed temperature and pressure for the dissolution reaction



is given by

$$\ln K = -(v_M \mu_M^o + v_X \mu_X^o + v_o \mu_{H_2O}^o) / RT + \mu_s^o / RT \quad (4)$$

where the μ_i^o 's represent the standard state chemical potential of the solid, of water, or of the aqueous ions.

The equilibrium constant can be calculated provided the chemical potential values are available at the temperature and pressure of interest. At constant pressure, the temperature dependence of the standard state chemical potential of component i is given by

$$\mu_{i,T_f}^o - \mu_{i,T_r}^o = -S_{i,T_r}^o (T_f - T_r) + \int_{T_r}^{T_f} C_{p_i}^o dT - T \int_{T_r}^{T_f} (C_{p_i}^o / T) dT \quad (5)$$

where S_i^o represents the standard entropy of component i , and $C_{p_i}^o$ is the standard state heat capacity (at constant pressure) which itself is a function of temperature. T_r and T_f are the reference temperature and temperature of interest, respectively.

In the case of water, the chemical potential at T and P can be conveniently calculated from the equation of state of Haar et al.²⁰. For the solids, although there are some inaccuracies or lack of data at high temperatures, their data base is well organized and given in the compilations of Kelley²¹, Stull and Prophet²², Robie et al.²³, and Wagman et al.²⁴. In the case of aqueous ions, additivity rules allow us to use standard state heat capacities of neutral electrolytes in calculating equilibrium constants for dissolution reactions. An extensive array of data extending upward in temperature is now available for the most important aqueous solutes, as shown in Table 1.

In terms of activities or molalities, the equilibrium constant for the solubility reaction is given by

$$\ln K = v_M \ln(m_M \gamma_M) + v_X \ln(m_X \gamma_X) + v_o \ln(a_{H_2O}) \quad (6)$$

where m_i and γ_i represent the molality and activity coefficient of the aqueous ions, respectively.

The activity of water is related to the osmotic coefficient, ϕ , by

$$\ln a_w = -\phi(M_w/1000) \sum_i m_i \quad (7)$$

where M_w is the molecular mass of water and the sum covers all solute species.

The following figures show the results for some of the systems we have looked at (Pabalan and Pitzer¹⁹). An example of solubility calculations for a 1:1 electrolyte is shown in Fig. 2 for NaCl. In this case there is an extensive array of thermodynamic data for NaCl(aq) as reported by Pitzer et al.⁸. Their evaluation of these data yielded a complete set of parameters valid in the region 0-300°C and saturation pressure to 1 kb. As shown in Fig. 2, there is excellent agreement between calculated and experimental solubilities, with a maximum deviation of 1.5% at 275°C.

An example of solubility calculations for a 2:2 electrolyte is shown in Fig. 3 for MgSO₄, using the ion-interaction parameters evaluated by Phutela and Pitzer¹³ from heat capacity, enthalpy, and osmotic coefficient data. Figure 3 shows that the calculated solubilities are in very good agreement with experimental data to 200°C.

Figure 4, for the system NaCl-MgCl₂-H₂O, is an example of calculated solubilities in ternary mixtures. As shown there is good agreement between calculated and experimental values to 200°C.

The mixing terms ϕ_{ij} and ψ_{ijk} complete the parameters necessary to calculate activity or osmotic coefficients in ternary and more complex mixtures. Using the parameters evaluated previously from binary and ternary systems, solubility equilibria in more complex systems can be calculated. An example is shown in Fig. 5 for the quaternary system NaCl-KCl-MgCl₂-H₂O at several isotherms. In this figure, the symbols are experimental data from Boecke²⁵ and the curves represent predicted values.

Vapor Pressure Depression

Vapor pressures of electrolyte mixtures are of interest in industrial technology. Vapor pressures can be calculated from osmotic coefficients and an equation of state for steam. The equation relating vapor pressure and osmotic coefficient is given by Liu and Lindsay²⁶:

$$\phi = \frac{1000}{M_w RT \sum_i m_i} \left[RT \ln \frac{P}{P_0} - \int_{P_0}^P \left(\frac{RT}{P} - V_g^0 \right) dP - \bar{V}_1 (P_0 - P) \right] \quad (8)$$

where V_g^0 is the molar volume of water vapor and \bar{V}_1 is the partial molar volume of water in the electrolyte solution, which can be approximated by the molar volume of pure liquid water. P and P_0 represent the vapor pressure of the solution and of pure water, respectively. The integral term can be evaluated using the equations of Haar et al.²⁰, and Eqn. 8 can be solved iteratively for P knowing the temperature,

solution composition, and the osmotic coefficient calculated from the ion-interaction model.

Predicted vapor pressure lowering values for simulated seawater ($\text{Na}_2\text{SO}_4\text{-NaCl-MgCl}_2\text{-H}_2\text{O}$) to 300°C are compared with experimental data from Liu and Lindsay²⁷ in Columns 3 and 4 of Table 2. The predicted values show excellent agreement with experimental data to 200°C . Calculations above this temperature make use of extrapolations of the temperature functions of the binary ion-interactions parameters for $\text{MgCl}_2(\text{aq})$ and $\text{MgSO}_4(\text{aq})$, but agreement is still relatively good to 300°C .

Boiling point elevation

Boiling point elevations of electrolyte mixtures are also of interest in industry, such as in the design and control of industrial evaporators (Nisenfeld²⁸). Since evaporation processes deal with mixtures that change in composition as evaporation progresses, boiling point elevations become more difficult to calculate accurately using other methods as the solution becomes more concentrated. However, the boiling point rise of the solutions can be obtained from the osmotic coefficient calculated from the ion-interaction model by solving Eqn. 8 for T, with the vapor pressure of pure water, P_0 , set equal to the vapor pressure of the solution, P. A comparison of calculated and experimental boiling point elevation for simulated seawater are shown in Columns 5 and 6 of Table 2. Again, there is good agreement between calculated and experimental values to 300°C .

ACKNOWLEDGEMENT

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Table 1. Binary electrolyte solutions with available high-temperature data.

Temperature range (°C)		Ref.	Temperature range (°C)		Ref.
1:1 Electrolytes			1:2 or 2:1 Electrolytes		
HCl	0 - 375	6, 7	Li ₂ SO ₄	0 - 225	10
LiCl	0 - 250	3	Na ₂ SO ₄	0 - 225	10
NaCl	0 - 300	8	K ₂ SO ₄	0 - 225	10
NaI	25 - 100	6	Cs ₂ SO ₄	0 - 225	10
NaOH	0 - 350	9	MgCl ₂	25 - 200	11, 12
KCl	0 - 325	3, 4	CaCl ₂	25 - 200	11, 12
CsF	25 - 100	6	SrCl ₂	25 - 200	11
CsCl	0 - 250	3			
CsI	25 - 100	6	2:2 Electrolytes		
			MgSO ₄	25 - 200	13

Table 2. Experimental and Calculated Vapor Pressure Depression and Boiling Point Elevation for Simulated Seawater (NaCl-Na₂SO₄-MgCl₂-H₂O).

Temp (°C)	Concentrate Multiple of Simulated Seawater	V. Press. Lowering $\Delta p = p^{\circ} - p$ (mm. Hg)		Boiling Pt. Elev. $\Delta t = t - t^{\circ}$ (°C)	
		Expt.	Calc.	Expt.	Calc.
75	2.8476	15	16	1.29	1.36
75	5.8158	35	36	3.05	3.14
100	1.4884	19	21	0.72	0.79
100	2.8528	41	42	1.54	1.50
100	5.8377	92	94	3.58	3.64
106	1.4888	24	26	0.76	0.82
125	1.4907	46	48	0.86	0.90
125	2.8630	94	96	1.80	1.82
125	5.8811	212	212	4.18	4.18
150	1.4949	95	99	1.01	1.04
150	2.8813	194	195	2.07	2.09
150	5.9597	436	434	4.79	4.78
175	1.5018	181	186	1.16	1.19
175	2.9128	367	368	2.38	2.38
175	6.1004	824	820	5.50	5.47
200	1.5126	323	328	1.34	1.36
200	2.9630	650	649	2.73	2.72
200	6.3279	1467	1460	6.33	6.31
225	1.5291	541	548	1.53	1.55
225	3.0415	1098	1089	3.15	3.12
225	6.6980	2517	2499	7.43	7.37
250	3.1648	1782	1768	3.62	3.60
250	7.3078	4224	4183	8.89	8.80
275	3.3622	2844	2810	4.26	4.21
275	8.3482	7083	6953	11.04	10.82
300	3.6957	4570	4436	5.19	5.03
300	10.2027	12244	11391	14.61	13.51

Actual composition of experimental solutions are given by the concentrations listed below multiplied by the concentrate multiple of simulated seawater given in the second column of the table (data from Liu and Lindsay²⁷).

NaCl = 0.42663 m
Na₂SO₄ = 0.02976 m
MgCl₂ = 0.06726 m

Figure Captions

- Fig. 1 Calculated vapor pressure depressions, ΔP (vapor pressure of pure water - vapor pressure of solution) for aqueous KCl solutions compared with experimental data from Wood et al.²⁹ and Zarembo et al.³⁰. The vapor pressures were calculated using the equations of Pabalan and Pitzer⁴.
- Fig. 2. Calculated halite (NaCl) solubilities in the binary NaCl-H₂O system compared to experiment. The solubility data from 75-300°C are from Liu and Lindsay²⁶, and those below 75°C are from Linke and Seidell³¹.
- Fig. 3 Calculated solubilities in the system MgSO₄-H₂O compared to experimental data from Linke and Seidell³¹.
- Fig. 4. Calculated and experimental solubilities in the NaCl-MgCl₂-H₂O system. Experimental data below 100°C are from Linke and Seidell³¹, while those above 100°C are from Akhumov and Vasil'ev³².
- Fig. 5. Predicted solubilities in the quaternary system NaCl-KCl-MgCl₂-H₂O at 15, 40, 65, and 90°C. The solid symbols are experimental data from Boecke²⁵.

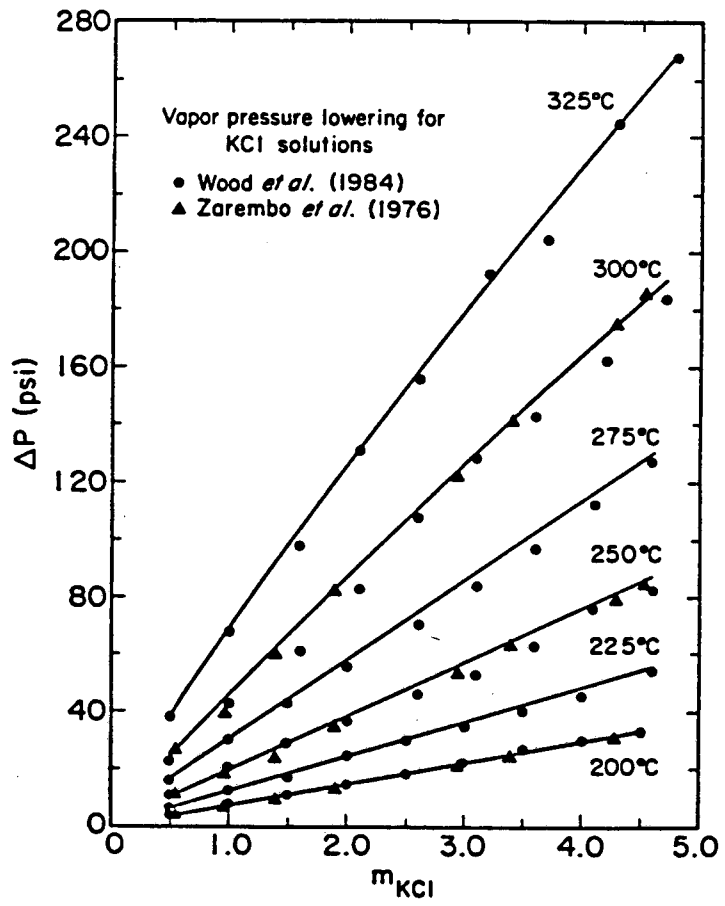


Fig. 1

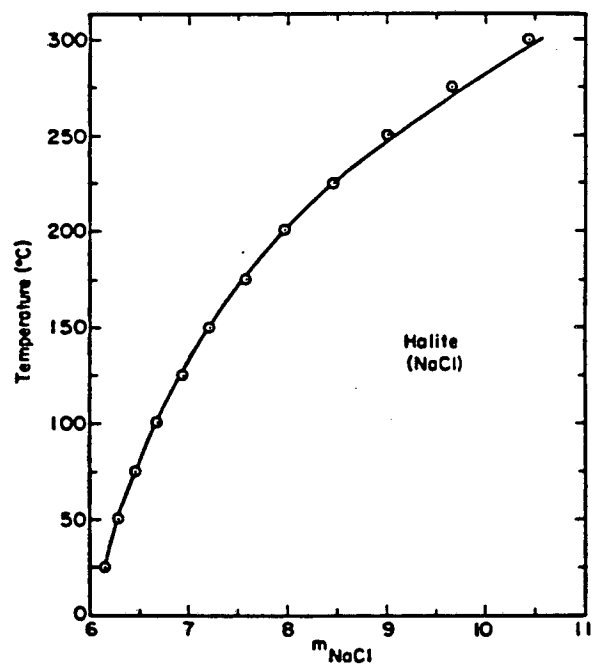


Fig. 2

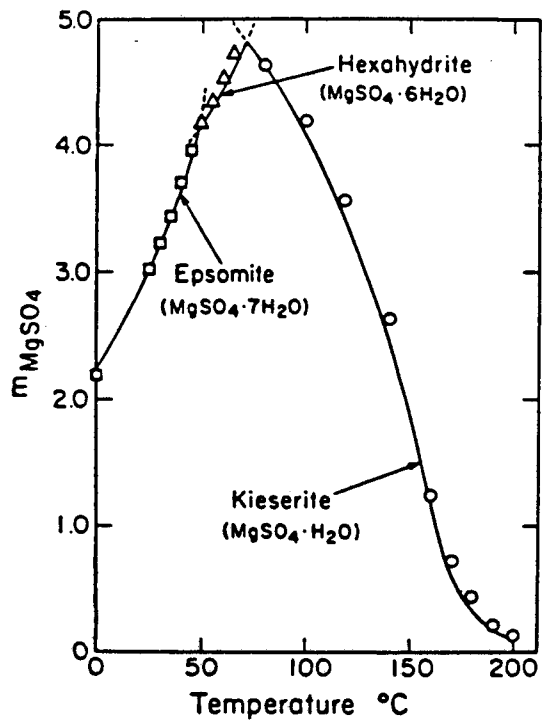


Fig. 3

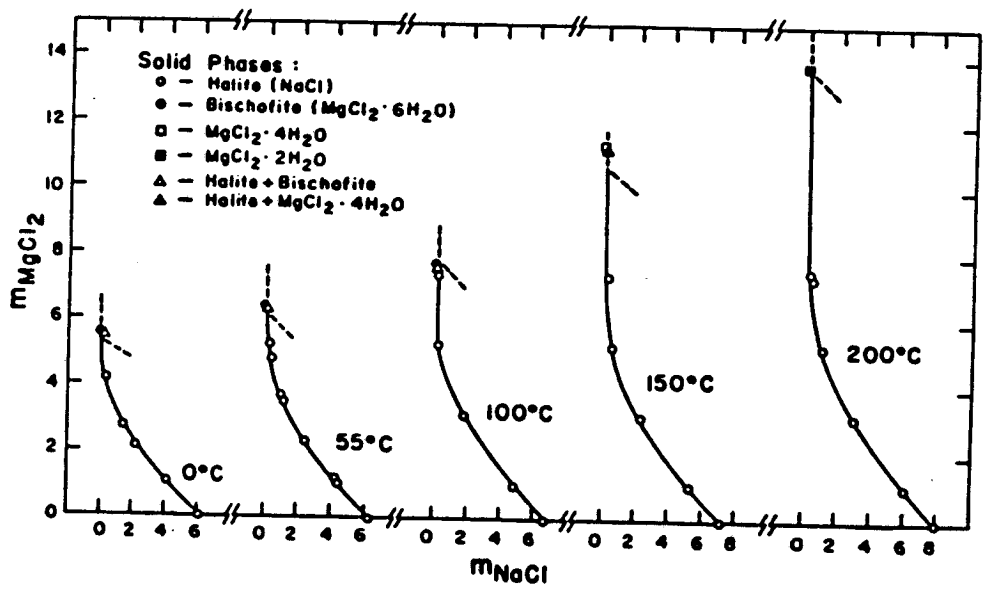


Fig. 4

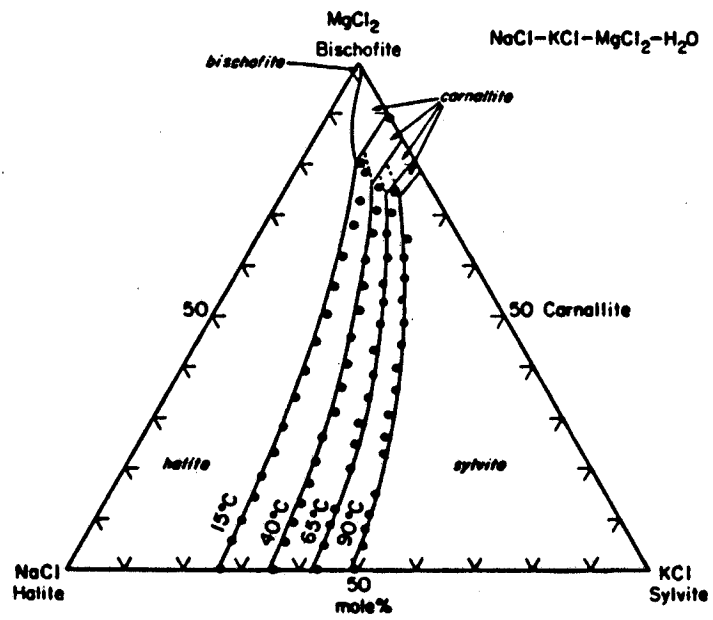


Fig. 5

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