

PREDICTIVE THERMODYNAMIC MODELS FOR
MINERAL SYSTEMS. I. QUASI-CHEMICAL ANALYSIS
OF THE HALITE-SYLVITE SUBSOLIDUS

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ABSTRACT

Considerable geochemical application may be made of a model or theory which allows the excess Gibbs energy of mixing to be obtained from the properties of the pure components in a system. Such a model predicts phase relations; chemical partitioning between coexisting mineral pairs is completely specified by such a model, provided that the species of interest is one of the components; geothermometric and geobarometric specifications are given, as well as mixing volume, if the model is pressure dependent. The quasi-chemical model of Guggenheim is shown to be appropriate for subsolidus immiscibility in the system NaCl-KCl. This system is analyzed by means of the solvus curve; and the resulting parameters correctly predict the calorimetrically observed mixing enthalpy, entropy, and heat capacity. The predicted partial molar mixing heats agree to within 12 percent with the results of elaborate lattice energy calculations based on a detailed Born-Mayer model with lattice relaxation. The quasi-chemical model may have broad application to other systems of geochemical importance.

INTRODUCTION

An understanding of the thermodynamics of interphase equilibria is fundamental to the explanation of observed petrological phase relations. Moreover, if petrologists are ever to be able to predict phase relations for unstudied combinations of components, our knowledge of the thermodynamics of mixtures, of both solid and liquid solutions, must be brought to a quantitative level. No matter how accurate or complete the thermodynamic data for pure phases becomes, geochemical calculations will still be crucially limited by a lack of knowledge about knowledge about mixtures, for most mineral systems are crystalline solutions, and few of them are ideal.

If we divide the molar Gibbs energy of an n -component mineral system into its ideal and excess parts,

$$G^{\text{system}} = G^{\text{xs}} + \sum_{i=1}^n x_i [\mu_i^0 + RT \ln(x_i)], \quad (1)$$

(where x_i is the mole fraction of the i^{th} component in the mixture and μ_i^0 is the chemical potential of the pure component) the problem may be formulated as a lack of quantitative or predictive knowledge of the excess Gibbs energy of mixing as a function of temperature, pressure, and composition, $G^{\text{xs}}(T, P, x_i, x_j, \dots, x_{n-1})$.

If the excess free energy of mixing can be calculated from the proper-

ties of the pure components then virtually every physicochemical property of the equilibrium system is immediately obtainable. First, the phase diagram is directly obtainable by the familiar Gibbs (1873) principle of projection of the tangent plane contacts on the free energy surface into P - T -composition space. It should be noted, moreover, that if an analytical expression is known for G^{xs} , it is no more difficult to deal with a large number of components than it is with a binary system. Secondly, the excess chemical potential of each component can be obtained from the excess Gibbs energy and hence the rational activity coefficient of each component in a particular mineral of composition A is known:

$$f_i(x_{iA}) = \exp[\mu_i^{xs}(x_{iA})/RT]. \quad (2)$$

Thirdly, the equilibrium distribution coefficient, which predicts chemical partitioning between coexisting mineral pairs, A and B , is obtainable:

$$D \equiv \frac{(x_i/x_j)_A}{(x_i/x_j)_B} = \exp\left[\frac{(\mu_i^{xs} - \mu_j^{xs})_B - (\mu_i^{xs} - \mu_j^{xs})_A}{RT}\right]. \quad (3)$$

In addition, geothermometry and geobarometry would be specified by the composition of the minerals present and a theoretical basis would be provided for an understanding of non-equilibrium assemblages.

The presentation hereinafter will consist of the development of a theoretical model appropriate to the system under consideration containing certain parameters numerically unspecified by the theory; the determination of the values of these parameters by examination of the phase relations and distribution coefficients in well-studied cases; the correlation of the fitted values of the parameters with the physicochemical properties of the pure components, and the prediction of parameters for unstudied systems; and finally the prediction, by insertion of these assumed values into the theoretical model, of phase relations and thermodynamic properties of unstudied systems of geological interest. This paper will be concerned with the first two of these aspects.

THE QUASI-CHEMICAL MODEL

Scope of the Model. The general problem of the calculation of the free energy of mixtures is a formidable one, involving a detailed knowledge of the energetics and statistics of all the mixture's constituent atoms. However, useful simplifications may be made in statistics, on the one hand, if we restrict our attention to isomorphous solids, and in energetics, on the other hand, if we can restrict ourselves to central force field interactions between the constituent particles. Consequently, the model de-

veloped in this effort will be restricted to subsolidus relations in simple heteropolar solids and, in this paper in particular, to the system halite-sylvite.

Application to Heteropolar Solids. In 1935 Bethe devised a method for deriving the equilibrium properties of a superlattice. Shortly thereafter Rushbrooke (1938) applied the method to the study of mixtures of molecules sufficiently alike in size and shape to be interchangeable on a crystal lattice, but in which the configurational energy depends upon the disposition of the molecules on the lattice. Subsequently Fowler and Guggenheim (1939) showed that the method was equivalent to a much more elegant and direct method which has become known as the quasi-chemical (QC) treatment. The basic assumptions underlying this treatment will be subsequently outlined but detailed derivations must be sought elsewhere.¹ In the QC treatment it is assumed that intermolecular forces are central, short-ranged, and two-body additive, and that consequently the internal energy of the system at the absolute zero of temperature may be evaluated by summing the pair-potentials over all nearest neighbor pairs. It is further assumed that the configurational and vibrational contributions to the partition function (or to the free energy of the mixture) are separable, or equivalently, that the vibrational part of the heat capacity is a linear function of the composition, as suggested by Joule's (1844) rule.² Of these assumptions perhaps the most difficult to justify is the neglect of long range coulombic interactions when dealing with essentially ionic solids.

We believe, however, that although the Madelung term constitutes about 90 percent of the lattice energy of a simple ionic crystal, the coulombic contribution to the *mixing* energy may be neglected in the first approximation for isomorphous solid solutions. The reasons for this are twofold. First, because the formal valence charges on substituting isomorphous species are identical, the crystal structures and the Madelung constants are identical (or, in the case of nonisometric crystal systems, nearly linearly related). Thus the only difference in Madelung energy is due to lattice parameter variations with composition. These differences tend to be minimized due to lattice relaxation around substituting ions.

¹ In particular see Guggenheim (1952) in which the essential features are developed in Chapter 4 and the asymmetrical model, subsequently used here, in Chapter 11. Throughout this paper where equations are equivalent to those of Guggenheim, his equation numbers are shown in square brackets.

² Which rule is sometimes invoked in the names of Neumann (1831), Woestyn (1848), or Kopp (1865).

That is, the anions around a given substituting foreign cation tend to be located at distances from it determined by the pair potential minimum for that given ion pair.

Detailed direct calculations by Douglas (1966) for very dilute crystalline alkali halide solutions, based on the Born-Mayer (1932, 1933) potential function, show that in these face-centered cubic systems interchange of Na^+ and K^+ is accompanied by an increased energy of about 5 kcal per mole of replacing ion (although the lattice energies of the pure salts are of the order of -170 kcal mole $^{-1}$).¹ Of that 5 kcal mixing energy, by far the most important contribution is from short range overlap repulsion. On the basis of less elaborate calculations Durham and Hawkins (1951) had earlier concluded that the treatment of the specific repulsion constant was the factor having the greatest effect on the heat of mixing in alkali halide solid solutions. They attributed the success of their model to allowances made for fluctuations in interionic distance. Still earlier Wallace (1949) attributed the failure of his attempt to calculate heats of mixing from the Born-Mayer model without lattice relaxation to inadequate representation of the repulsive potential. Wasastjerna (1944, 1949) has produced experimental evidence suggesting the existence of some local order in alkali halide solid solutions. He has developed a model which allows the ions to be displaced from average lattice positions in the mixed crystal depending upon their size and upon the degree of short range order. With later modifications suggested by Hovi (1950) the model has been used to calculate excess enthalpy in alkali halide systems with some degree of success. (*cf.* Lister and Myers, 1958, for a comparison with experiment.) The principal point of failure of this model is the overestimation of local order near the composition of order ($x_2=0.5$), and the invariable prediction of negative excess mixing entropy.

In view of the relative importance of lattice configuration, relaxation, and short range repulsion, as well as the relative unimportance of coulombic interaction in determining the mixing energy, the nearest neighbor interaction model may not be as outrageous as it first appears.

Properties of the Quasi-chemical Model. If we restrict our attention to condensed phases at moderate pressures, the distinction between the Gibbs and Helmholtz energy of mixing becomes negligible, especially for isomorphous solids, which have small mixing volumes. Then the QC expression for the molar excess Gibbs (or Helmholtz) energy of mixing in a binary model with ideal athermal terms (*i.e.*, we assume that the solution becomes ideal as the interchange energy vanishes) is given by

¹ Throughout this paper cal = 4.184 J, gibbs = 4.184 J °K $^{-1}$.

$$\frac{G^{xs}}{RT} = \frac{Z}{2} \left\{ x_1 q_1 \ln \left[1 + \frac{\phi_2(\beta - 1)}{\phi_1(\beta + 1)} \right] + x_2 q_2 \ln \left[1 + \frac{\phi_1(\beta - 1)}{\phi_2(\beta + 1)} \right] \right\}, \quad (4), [11.08.4]$$

where Z is the number of nearest neighbors of each component, the subscripts [1] and [2] refer to the components, q_1 and q_2 are constants which we shall refer to as contact factors¹, the contact fractions ϕ_1 and ϕ_2 are defined by

$$\phi_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}, \quad (5a), [11.03.13]$$

$$\phi_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}, \quad (5b)$$

and β is a measure of the tendency toward non-randomness in the mixture ($\beta = 1$ for a perfectly random mixture, $\beta > 1$ indicates a tendency for clustering, and $\beta < 1$ indicates a trend toward compound formation):

$$\beta = \{1 - 4\phi_1\phi_2[1 - \exp(2W_G/ZRT)]\}^{\frac{1}{2}}, \quad (6), [11.07.12]$$

where $2W_G$, the molar interchange energy, is a parameter of the theory which measures the energy requirement to effect the interchange of a [1] and a [2] atom between two pure crystals.

An approximate form of the QC mixing expression may be derived for the limiting case of small interchange energy, W_G , or high temperature. In this case we note that the expression in square brackets in (6) is small. Expanding β in binomial series yields

$$\begin{aligned} \frac{\beta - 1}{\beta + 1} &= \phi_1\phi_2 \left[\frac{2W_G}{ZRT} + \frac{1}{2} \left(\frac{2W_G}{ZRT} \right)^2 + \dots \right] \\ &\quad - 2\phi_1^2\phi_2^2 \left[\left(\frac{2W_G}{ZRT} \right)^2 + \dots \right] + \dots \end{aligned} \quad (7)$$

Finally, expanding the logarithmic terms about unity one obtains correct to second powers of W_G/T :

$$\frac{G^{xs}}{RT} \simeq \frac{x_1 x_2 q_1 q_2}{x_1 q_1 + x_2 q_2} \left(\frac{W_G}{RT} \right) - \frac{x_1^2 x_2^2 q_1^2 q_2^2}{Z(x_1 q_1 + x_2 q_2)^2} \left(\frac{W_G}{RT} \right)^2 + \dots \quad (8)$$

¹ For a discussion of the significance of the contact factors as molecular configurational partition functions, the reader is referred to Rushbrooke (1938) and to Guggenheim (1952, p. 186).

The first term on the right will be recognized as a form of the van Laar (1906, 1910)-Hildebrand (1929) expression for the enthalpy of mixing if we take the contact factors, $q_1/q_2 = V_1/V_2$, to be proportional to the molar volumes of the components. The second term on the right can be identified with Lumsden's (1952, p. 318) correction term for nonrandomness if we take the contact factors to be proportional to the $\frac{4}{3}$ power of Lumsden's atomic radii: $q_1/q_2 = (r_1/r_2)^{\frac{4}{3}}$. Thus it is seen that the van Laar-Hildebrand and Lumsden treatments may be considered to be limiting forms of the QC model.

For our purposes, however, it is no more difficult to work with the full QC expression (4), and the approximate relations (8) will not be treated further. The enthalpy of mixing may be obtained from (4) using a version of the Gibbs-Helmholtz relation,

$$\frac{d(G^{xs}/RT)}{d(1/RT)} = H^{xs}. \quad (9)$$

However, before doing so it is useful to define two new quantities:

$$W_H = W_G - T \frac{dW_G}{dT}, \quad (10a), [4.27.1]$$

$$W_S = - \frac{dW_G}{dT}, \quad (10b)$$

related to the interchange energy W_G as enthalpy and entropy are related to the Gibbs energy. Then we obtain

$$H^{xs} = \frac{2x_1x_2q_1q_2W_H}{(x_1q_1 + x_2q_2)(\beta + 1)}, \quad (11)$$

and the excess entropy may be evaluated from

$$S^{xs} = \frac{H^{xs} - G^{xs}}{T}. \quad (12)$$

The excess chemical potentials may be obtained from the Gibbs energy surface by differentiation of (4) with respect to composition. Considering that ϕ_1 , ϕ_2 , and β are all functions of composition, it is a pleasure to note the surprisingly simple form of the chemical potential expressions,

$$\frac{\mu_1^{xs}}{RT} = \frac{Zq_1}{2} \ln \left[1 + \frac{\phi_2(\beta - 1)}{\phi_1(\beta + 1)} \right], \quad (13a), [11.08.2]$$

$$\frac{\mu_2^{xs}}{RT} = \frac{Zq_2}{2} \ln \left[1 + \frac{\phi_1(\beta - 1)}{\phi_2(\beta + 1)} \right]. \quad (13b)$$

It is well known that the van Laar and Lumsden binary models predict a miscibility gap for positive W_G , so it is not surprising that the QC model does also. The consolute conditions of temperature and composition, T_c , x_{1c} , x_{2c} , could, in principle, be evaluated from the conditions,

$$\left(\frac{\partial^2 G^{\text{system}}}{\partial x_i^2}\right)_{T_c} = \left(\frac{\partial^3 G^{\text{system}}}{\partial x_i^3}\right)_{T_c} = 0, \quad (14)$$

where the derivatives are the total compositional derivatives ($dx_1 = -dx_2$) at constant temperature, evaluated at composition x_{1c} , x_{2c} . In practice, however, the derivatives become progressively less attractive beyond the first. It is easier to employ another mathematically equivalent device. We shall find the spinodal curve, defined as that temperature determined by

$$\left(\frac{\partial \mu_i}{\partial x_i}\right)_{T_s} = 0, \quad (15)$$

and then find the maximum in the spinodal where

$$\frac{dT_s}{dx_i} = 0. \quad (16)$$

Differentiating (13a) with respect to x_2 and noting that $x_1 = 1 - x_2$ in the binary system, we obtain

$$\frac{1}{RT} \left(\frac{\partial \mu_1}{\partial x_2}\right)_{T_s} = 0 = \frac{1}{x_1} \left[-1 + \frac{Zq_1q_2(\beta - 1)}{2(x_1q_1 + x_2q_2)\beta} \right], \quad (17)$$

where the first term in the square brackets arises from the ideal contribution and the second from the excess potential of (13a). The spinodal curve is thus defined by

$$\beta(T_s) = \frac{q_1q_2Z}{q_1q_2Z - 2(x_1q_1 + x_2q_2)}, \quad (18)$$

Differentiating again with respect to x_2 and setting $dT_s/dx_2 = 0$ we obtain by combination of (6) and (18)

$$\left(\frac{\partial \beta}{\partial x_2}\right)_{T_s} = \frac{(\beta^2 - 1)(\phi_1 - \phi_2)}{2\beta x_1 x_2} = \frac{2q_1q_2Z(q_2 - q_1)}{[q_1q_2Z - 2(x_1q_1 + x_2q_2)]^2}, \quad (19)$$

which may be rearranged in combination with (6) to give

$$[x_2q_2 - x_1q_1][q_1q_2Z - (x_1q_1 + x_2q_2)][q_1q_2Z - 2(x_1q_1 + x_2q_2)] + [(q_2 - q_1)q_1^2q_2^2Z^2x_1x_2] = 0. \quad (20)$$

This relation involves only q_1 , q_2 , and Z ; and thus the critical consolute composition is defined in terms of these parameters. The relation is, however, cubic in x_1 ; and as a consequence the simplest methods of solution will be numerical rather than analytical. Having found the consolute composition it is a straightforward procedure to substitute this value in (18) to obtain the consolute temperature.

ANALYSIS OF THE HALITE-SYLIVITE SYSTEM

Previous Work and Sources of Data. One of the principal reasons for choosing the NaCl-KCl system as an initial effort in applying the QC model was the recent appearance of an interesting analysis of this same system by Thompson and Waldbaum (1969) who used Hardy's (1953) essentially empirical subregular (SR) model. Although they find that the halite-sylvite phase relations may be fitted to the SR model parameters in a simple smooth fashion, the resulting thermodynamic consequences bear a rather disappointing correspondence with the available calorimetric data. We had hoped that the QC model might prove more fruitful in this regard, and will show subsequently that this hope was not without foundation.

For other reasons as well, the halite-sylvite system is ideal as an initial choice for demonstration of the method. The bonding and structure in these solids, being octahedrally coordinated atoms with almost purely ionic interactions, are among the simplest kinds known to chemistry. The system is isomorphous and among the best studied of all solid solutions. Although of limited geological application it is of some interest as a comparison with other mineral pairs in which Na-K substitution occurs.

In order to facilitate direct comparison of results the choice of solvus data will be the same as that of Thompson and Waldbaum (1969). As they have discussed the available measurements at some length the data will not be reviewed again here. The 15 critically chosen data points are listed in Table I.

Evaluation of the Quasi-chemical Parameters. In correspondence with Thompson and Waldbaum we take component [1] to be NaCl and [2] to be KCl and identify the Na-rich phase and K-rich phase as *A* and *B*, respectively. If we take the standard state of each component, regardless of its concentration, to be the respective pure phase¹, and if the system is adequately described by the QC model, we may write for interphase equilibria at any appropriate constant temperature

¹ In which case the activity coefficient of a component at infinite dilution will not in general be unity.

$$\frac{\mu_{1A}}{RT} = \frac{\mu_{1B}}{RT}, \quad (21a)$$

$$\begin{aligned} & \ln(x_{1A}) + \frac{Zq_1}{1} \ln \left[1 + \frac{\phi_{2A}(\beta(x_A) - 1)}{\phi_{1A}(\beta(x_A) + 1)} \right] \\ = & \ln(x_{1B}) + \frac{Zq_1}{2} \ln \left[1 + \frac{\phi_{2B}(\beta(x_B) - 1)}{\phi_{1B}(\beta(x_B) + 1)} \right], \end{aligned} \quad (21b)$$

$$\frac{\mu_{2A}}{RT} = \frac{\mu_{2B}}{RT}, \quad (21c)$$

$$\begin{aligned} & \ln(x_{2A}) + \frac{Zq_2}{2} \ln \left[1 + \frac{\phi_{1A}(\beta(x_A) - 1)}{\phi_{2A}(\beta(x_A) + 1)} \right] \\ = & \ln(x_{2B}) + \frac{Zq_2}{2} \ln \left[1 + \frac{\phi_{1B}(\beta(x_B) - 1)}{\phi_{2B}(\beta(x_B) + 1)} \right]. \end{aligned} \quad (21d)$$

These two independent relations involve 3 unknown parameters: q_1 , q_2 , and W_G . However, the contact factors, q_1 and q_2 , are not independent. It is required that $q_1/q_2 \rightarrow 1$ as either become unity. Any number of functional relations might satisfy this simple requirement. We shall make the *ad hoc* assumption that the geometric mean of the contact factors is unity,

$$\sqrt{q_1 q_2} = 1, \quad (22)$$

as this choice allows considerable algebraic simplification. In view of the fact that the ratio q_1/q_2 does not deviate widely from unity, it appears that this assumption is not critical. Moreover parallel analyses which we have performed under the assumption that the arithmetic mean of the contact factors is unity,

$$q_1 + q_2 = 2, \quad (23)$$

produce essentially identical results. For this octahedrally coordinated *fcc* system we take $Z = 6$. With the aid of (22), the two chemical equilibrium equations (21) are reduced to the two unknowns (q_1/q_2) and W_G . Although transcendental in these parameters the unknowns may be obtained by standard Newton-Raphson methods. The results are shown in Table I, columns 6 and 7. It is expected from QC theory that the ratio q_1/q_2 depends only upon the geometry of the substituting chemical species and is essentially independent of temperature. We find that this is the case; the contact ratio displays no obvious trend with increasing temperature and there is no reason to fit to the data a functional form other

than a constant. The mean value for this constant and its root-mean-square (standard) deviation are,

$$q_1/q_2 = 0.692 \pm 0.023. \quad (24)$$

Guggenheim (1944) takes the contact factors to be proportional to the surface area of a molecule involved in contacts with dissimilar molecules. Thus he shows for simply branched polymer chains of length r_i ,

$$q_i = \frac{2 + r_i(Z - 2)}{Z}. \quad (25), [11.01.1]$$

For compact molecules of molar volume V_i , however, probably a better surface area representation would be

$$q_i = KV_i^{2/3}, \quad (26)$$

where K is some geometrical constant. This would be in correspondence with Langmuir (1925) who found for mixtures of rather large organic molecules the ratio $H^{xs}(x_1 \rightarrow 0)/H^{xs}(x_2 \rightarrow 0)$ to be equal to the ratio $(V_1/V_2)^{2/3}$, provided that the molecules of the two species have approximately the same shape. The representations of van Laar (1910), Hildebrand (1929), and Lumsden (1952) have been discussed in a previous section. For the NaCl-KCl system we find, from the tabulations of Robie, *et al.* (1967),

$$V_1/V_2 = 0.7199, \quad (27a)$$

$$V_1^{2/3}/V_2^{2/3} = 0.8033. \quad (27b)$$

If we consider atomic sizes rather than molar volumes we find, using octahedral ionic radii of Pauling (1948, p. 246),

$$r_{\text{Na}^+}/r_{\text{K}^+} = 0.714, \quad (28a)$$

$$r_{\text{Na}^+}^2/r_{\text{K}^+}^2 = 0.510. \quad (28b)$$

The observed contact ratio is very close to either the molar volume or cation radius ratios. We shall defer, however, any attempt to correlate the q -factors with physical properties of the components until a later paper in this series. We prefer at this time to consider q_1/q_2 simply a parameter which may be evaluated from the QC model and the solvus data. For the system under discussion we shall take its value to be the mean of the estimates (24).

Having taken this value we can use the two equations (21) to obtain two independent estimates of W_G . These are also shown in Table I, columns 8 and 9. The variance between these two independent estimates allows an objective evaluation of the conformance of the solvus data

TABLE I. OBSERVED AND CALCULATED TWO-PHASE COMPOSITIONS AND CALCULATED QUASI-CHEMICAL PARAMETERS

Temp. °C	Compositions: mole fraction				QC Parameters			References	
	x_{2A}		x_{2A}		q_1/q_2	W_G/RT			
	Ob- served	Calcu- lated	Ob- served	Calcu- lated		Calculated with q_1/q_2 at left	Assuming $q_1/q_2=0.692$		
250		0.010		0.944					
275		0.014		0.927					
309	0.021	0.022	0.889	0.897	0.670	3.460	3.425	3.509	Bunk and Tichelaar (1953)
335	0.020	0.031	0.880	0.867	0.648	3.433	3.365	3.535	Nacken (1918)
367	0.044	0.045	0.830	0.822	0.698	3.074	3.080	3.065	Barrett and Wallace (1954a)
367	0.044	0.045	0.830	0.822	0.698	3.074	3.080	3.065	Barrett and Wallace (1954a)
391	0.061	0.061	0.771	0.779	0.684	2.870	2.866	2.882	Bunk and Tichelaar (1953)
400	0.060	0.068	0.740	0.760	0.649	2.810	2.791	2.878	Nacken (1918)
422	0.096	0.089	0.709	0.708	0.710	2.698	2.703	2.677	Barrett and Wallace (1954a)
422	0.096	0.089	0.712	0.708	0.707	2.693	2.697	2.676	Barrett and Wallace (1954a)
447	0.137	0.125	0.634	0.633	0.712	2.556	2.556	2.537	Bunk and Tichelaar (1953)
462	0.139	0.157	0.612	0.574	0.695	2.530	2.529	2.527	Barrett and Wallace (1954a)
462	0.138	0.157	0.612	0.574	0.696	2.529	2.529	2.525	Barrett and Wallace (1954a)
465	0.150	0.165	0.560	0.560	0.670	2.467	2.474	2.489	Nacken (1918)
466	0.195	0.168	0.542	0.556	0.716	2.447	2.439	2.429	Bunk and Tichelaar (1953)
472	0.191	0.187	0.521	0.525	0.693	2.427	2.426	2.426	Bunk and Tichelaar (1953)
496	0.292		0.436		0.734	2.382	2.363	2.360	Barrett and Wallace (1954a)

with the QC model. The model is relatively insensitive to small changes in the contact ratio. We have obtained essentially the same estimates of W_G by setting the contact ratio equal to the molar volume ratio (27a). This insensitivity is seen by comparison of the data of Table I, column 7, with the mean from columns 8 and 9 (*cf.* Figure 1). In contrast, examination of the data shows that the parameter W_G/RT is clearly dependent upon temperature. The values are plotted against reciprocal absolute temperature in Figure 1, where the straight line represents the linear least-squares fit to the data of Table I, columns 8 and 9, weighed according to the reciprocal variance between the two observations at each temperature. The resulting best linear equation is

$$W_G = W_H - TW_s, \quad (29)$$

$$W_H = 5559. \pm 565 \text{ cal mole}^{-1}, \quad (30a)$$

$$W_s = 2.630 \pm 0.759 \text{ gibbs mole}^{-1}. \quad (30b)$$

COMPARISON OF THE MODEL PROPERTIES WITH EXPERIMENT

The Phase Diagram. The determined values of q_1/q_2 (24) and W_G (30) may now be entered into (4) and the excess Gibbs energy of mixing calculated at any temperature or composition. The binodal curve or solvus bounding the two-phase region may be determined by the graphical

double tangent method or by equivalent iterative numerical methods. The calculated two-phase compositions are shown in Table I, columns 3 and 5; and the calculated binodal is shown by the solid line in Figure 2, where are also plotted the original data and the boundary calculated by Thompson and Waldbaum (1969) with the SR model. As was discussed above, the critical conditions may be obtained by substitution of (24) into (20). The functional relation of (20) is shown in Figure 3 for several

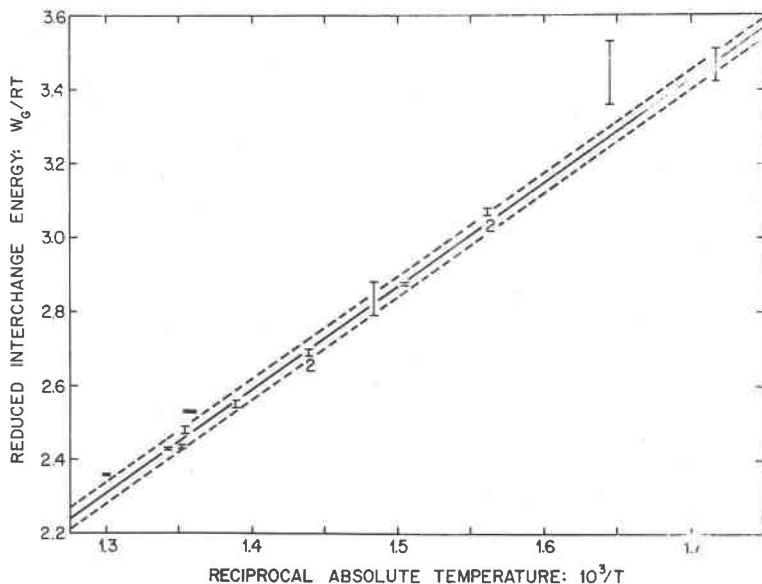


FIG. 1. Reduced interchange energy for NaCl-KCl crystalline solutions. Vertical bars connect the two independent calculations. The solid line is the best linear weighted-least-squares fit. The dashed lines bound the 95% confidence limits (two standard deviations).

different coordination numbers. For $Z=6$ and q_1/q_2 as determined (24), we find

$$x_{2c} = 0.338. \quad (31)$$

The critical consolute temperature depends upon both the parameters q_1/q_2 and $W_G(T)$. However, the reduced consolute temperature, as defined by $2RT_c/W_G$ and of the order of unity, may be represented in terms of q_1/q_2 . This function is shown in Figure 4 for several different coordination numbers. It will be noted that greater asymmetry in the system tends to raise the reduced consolute temperature slightly. For perfectly symmetrical systems ($q_1/q_2 = 1$) Guggenheim (1952, p. 41) has shown

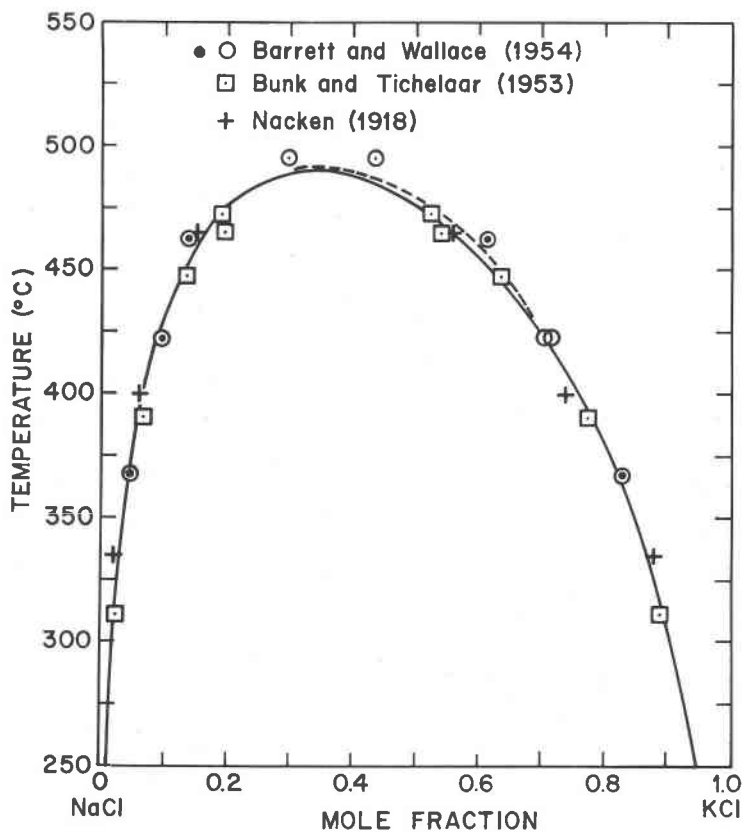


FIG. 2. Observed two-phase data and binodal curves calculated from QC model (solid line) and SR model (dashed line) where the latter diverges from the former.

$$\frac{2RT_c}{W_G} = \frac{2}{Z \ln \left[\frac{Z}{Z-2} \right]}, \quad \text{when } q_1/q_2 = 1, \quad (32), \quad [4.12.13]$$

which tends to unity as Z becomes large. For Z and q_1/q_2 of the halite-sylvite system we determine from Figure 4:

$$\frac{2RT_c}{W_G} = 0.8538. \quad (33)$$

Substitution of (30) into (33) yields

$$T_c = 763.0^\circ \text{K}. \quad (34)$$

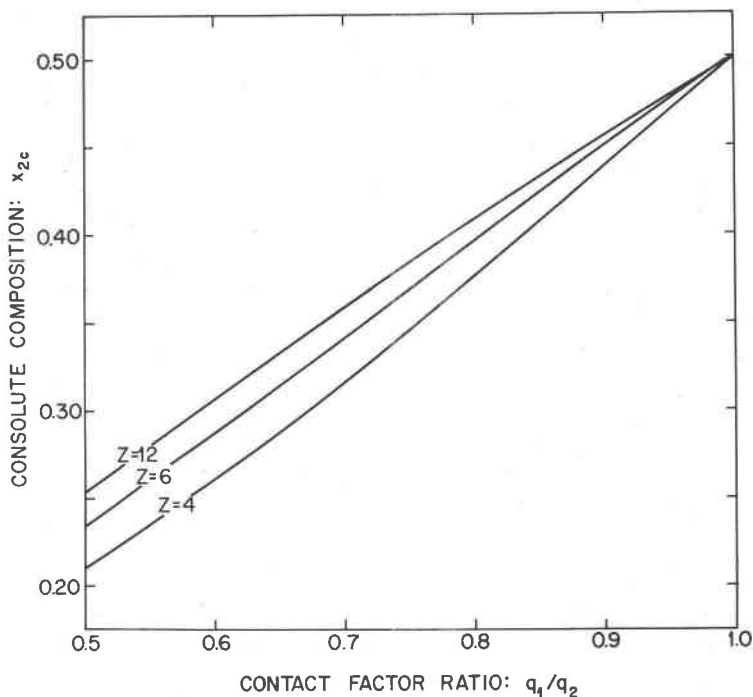


FIG. 3. Consolute composition (mole fraction of component two in the binary system at the maximum temperature at which two separate phases co-exist) as calculated from the QC model for various coordination numbers.

The critical conditions determined, (31) and (34), are very close to those yielded by the SR model of Thompson and Waldbaum (1969), $x_{2c} = 0.448$, $T_c = 765.2^\circ\text{K}$.

It is seen that both the QC and SR models represent the data well (although the QC model does so with one less parameter) and that on this basis alone there is little to recommend one model over the other. Such is not the case, however, when the thermodynamic predictions of the models are compared with the experimental calorimetric data.

Calorimetric Measurements. Barrett and Wallace (1954a) have measured the enthalpy of mixing in the system NaCl-KCl using a differential calorimeter and obtaining heat of solution differences between solid solutions and mechanical mixtures of the same composition. Their measurements were made at 25°C but some discussion of the measurement temperature is in order to allow a correct interpretation of the observed enthalpy. NaCl-KCl crystalline solutions are thermodynamically un-

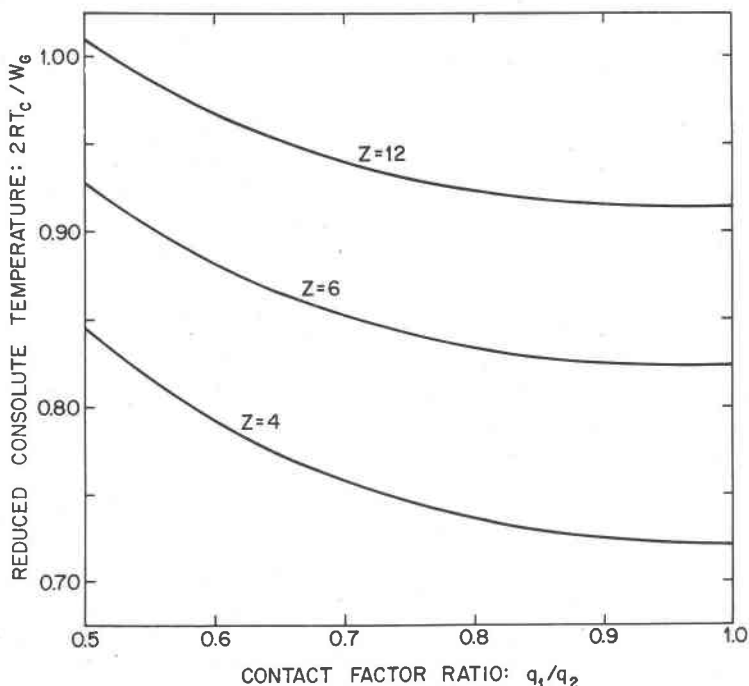


FIG. 4. Reduced consolute temperature as calculated from the QC model for various coordination numbers.

stable at room temperature. The measurements were made on the metastable phase which had been homogenized and annealed at 630°C, then rapidly quenched to room temperature. Consequently while the vibrational contribution to the measured enthalpy was that characteristic of 25°C, the configurational contribution was that which was frozen-in at 630°C or slightly below. Barrett and Wallace (1954b) assumed that C_p for the solid solution *at constant configuration* is given by the Joule rule so that the purely vibrational contribution to the excess enthalpy is near zero. This is not to imply that C_p^{ss} is zero, since negative excess heat capacity may arise from configurational changes such as order-disorder transitions or declustering. Positive excess heat capacity may result from other configurational changes, *e.g.*, the appearance in the solid of equilibrium defects. What it does imply is that the excess enthalpy measured is the 630°C enthalpy and any comparison with theory should be made at that temperature.

Lister and Meyers (1958) have made a comparable set of measurements in a very similar manner. Their annealing temperature was 600°C.

TABLE 2. CALORIMETRIC DATA FOR NaCl-KCl CRYSTALLINE SOLUTIONS

Mole Fraction of KCl x_2	Reduced Excess Enthalpy, kcal mole ⁻¹ H^{xs}/x_1x_2	Reduced Excess Entropy, gibbs mole ⁻¹ S^{xs}/x_2x_2	Reduced Heat Capacity between 500° and 630°C, gibbs mole ⁻¹ C_p^{xs}/x_1x_2
BARRETT AND WALLACE (1954), 630°C			
0.10	5.16	0.56	
0.30	4.18	1.24	
0.50	4.18	1.12	0.40
0.70	4.09	1.14	
0.90	4.47	-0.22	
LISTER AND MEYERS (1958), 600°C			
0.04	4.58		
0.11	4.16		
0.15	4.35		
0.26	3.92		
0.34	4.39		
0.42	4.21		
0.55	4.08		
0.68	4.27		
0.90	3.71		
0.95	4.91		
0.98	4.57		

The excess heat capacity estimate of Barrett and Wallace (1954b) suggests that the correction of the 600° data to 630°C would amount to an addition of only 0.01 kcal. As this is no doubt smaller than the uncertainty in the data, we will compare them without making this adjustment. The two sets of measurements are in good agreement with the early work of Zhemchuzhnuii and Rambach (1910) and the more recent work of Popov *et al.* (1940a, b), who found the equimolar reduced excess enthalpy to be 4.20 and 4.23 kcal, respectively.

In Table II are listed the Barrett-Wallace (1954a) and the Lister-Meyers (1958) data recalculated on a reduced basis, H^{xs}/x_1x_2 . Figure 5 shows, in addition to this, the mixing enthalpy obtained from the QC model (11), (24), and (30), as well as the value predicted by the SR model as analyzed by Thompson and Waldbaum (1969). It is seen that the calorimetric data is remarkably well represented by the QC model, especially considering that the representation is obtained by an extrapolation over 130° from the nearest data point. The QC model may be

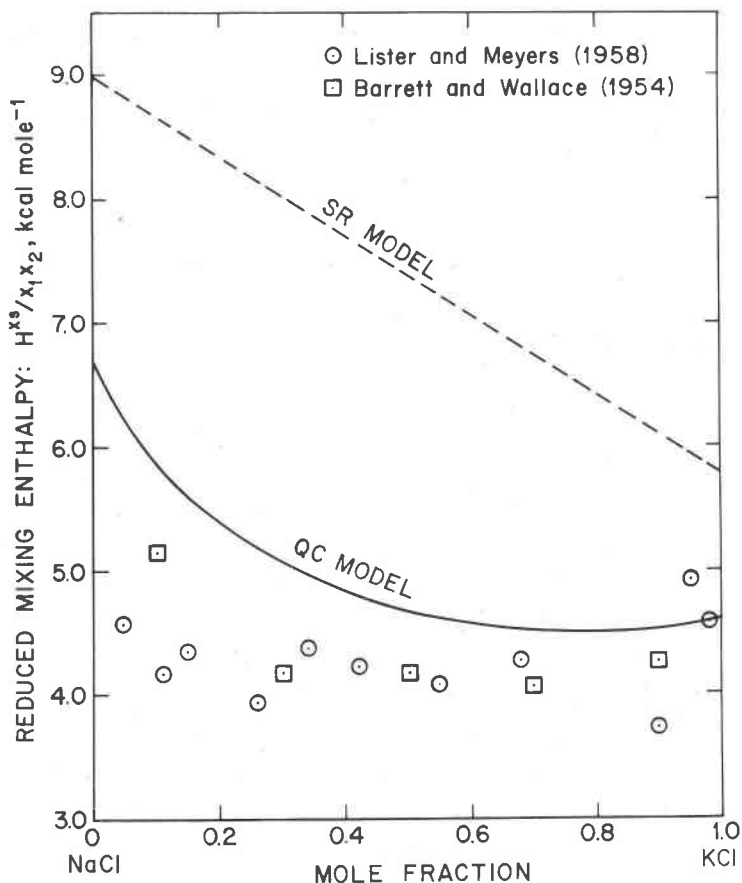


FIG. 5. Reduced enthalpy of mixing for NaCl-KCl crystalline solutions at 630°C. The solid line represents the QC model (this work), the dashed line is the SR model (Thompson and Waldbaum, 1969), and the points are the calorimetric observations.

systematically slightly high. The SR model is considerably less satisfactory. Not only is the predicted excess enthalpy almost twice too large, but the SR model totally fails to provide a reasonable representation of the enthalpic compositional dependence.

Barrett and Wallace (1954b) have also calculated excess entropies of mixing in this system by combining their enthalpy data and the solvus curve, using a reversal of the method of double tangents. Their entropy data recalculated to an excess, reduced basis, S^{xs}/x_1x_2 , is shown in Table II and in Figure 6 together with the QC and SR predictions. Because of the awkward way these data were obtained, it is difficult to assess their

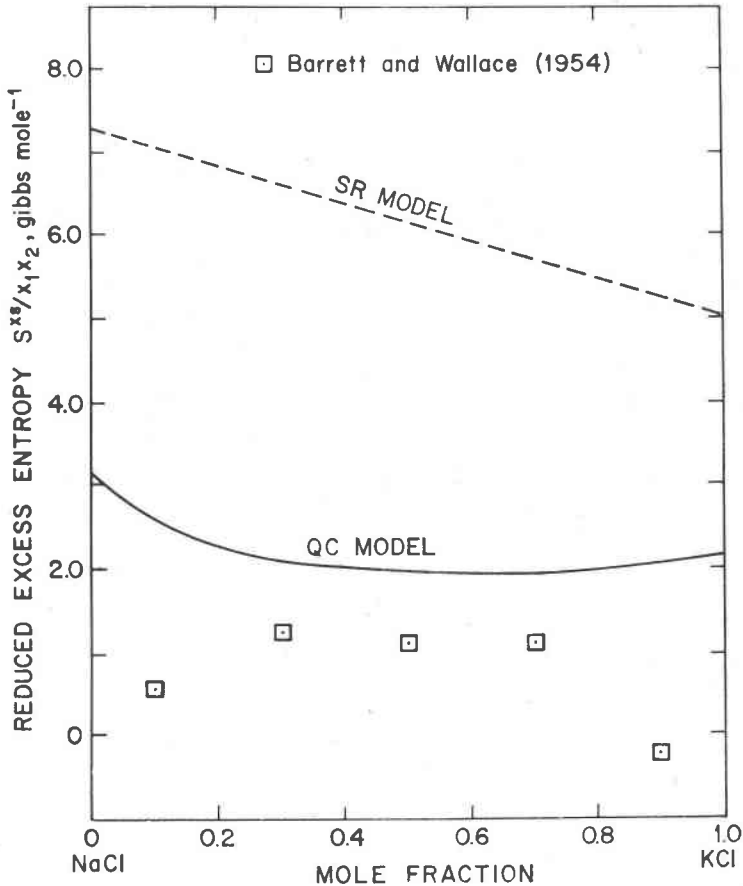


FIG. 6. Reduced excess entropy of mixing of NaCl-KCl crystalline solutions at 630°C. The solid line represents the QC model (this work), the dashed line is the SR model (Thompson and Waldbaum, 1969), and the points are the available measurements.

reliability. The probability of systematic error in these values, moreover, does not allow us to make meaningful detailed comparisons. Even so, the QC model is again clearly superior with respect to the magnitude of the entropy, and the agreement with the experiment is not too bad considering the method in which the comparison data were obtained.

Finally, it is of interest to compare estimates of excess heat capacity, obtained by differential calorimetry on equimolar NaCl-KCl solutions annealed at 500°C, with the predictions of the models. The SR model does not predict an excess heat capacity. The QC model excess heat capacity may be obtained by temperature differentiation of (11) to yield

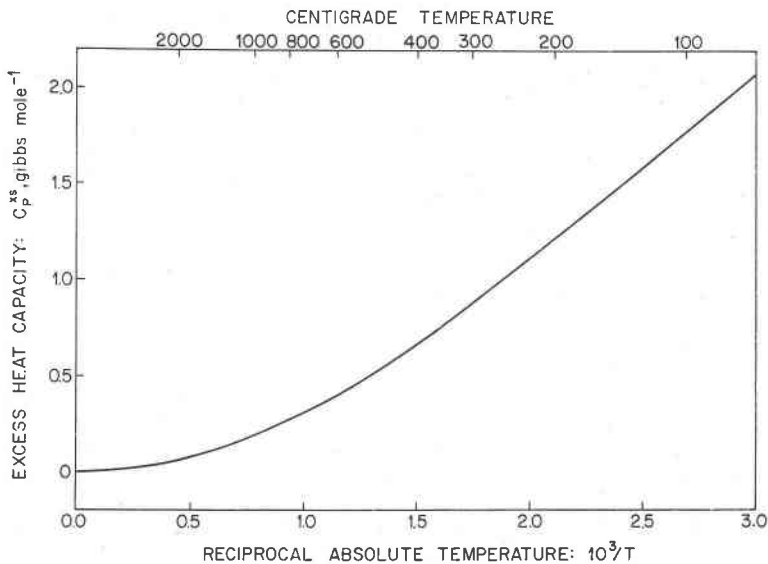


Fig. 7. Excess heat capacity of mixing for equimolar NaCl-KCl crystalline solutions as calculated from the QC model.

$$\frac{C_p^{xs}}{R} = \frac{2q_1q_2x_1x_2[\beta^2 - (\phi_1 - \phi_2)^2]}{Z(x_1q_1 + x_2q_2)(\beta + 1)^2\beta} \left(\frac{W_H}{RT}\right)^2 \quad (35)$$

for the case where $dW_H/dT=0$. This function is shown in Figure 7 for the equimolar solid as calculated from (35) using (24) and (30). Between 500° and 600°C the model predicts the equimolar excess heat capacity to be about 0.44 gibbs mole $^{-1}$. This is a substantially larger value than the experimental 0.10 gibbs mole $^{-1}$, but it should be noted that the heat capacity is related to the second temperature derivative or curvature of the Gibbs energy surface and somewhat larger errors in this function are to be expected.

Other Theoretical Calculations. Although derived from a statistical mechanical framework, the QC model, as applied here, is essentially a macroscopic model; that is, the parameters which enter into it are obtained from classical macroscopic properties of the components. It is of interest, therefore, to compare its predictions with those of an atomic model. The high temperature, infinite dilution, partial molar heats of mixing in this system have been calculated by Douglas (1966) as discussed earlier. The same quantities may be obtained from (11) by differentiation:

$$\bar{h}_2^{xs}(x_2 \rightarrow 0, T \rightarrow \infty) = q_2 W_H = \frac{W_H}{\sqrt{q_1/q_2}} = 6.68 \text{ kcal mole}^{-1} \quad (36a)$$

$$\bar{h}_1^{xs}(x_1 \rightarrow 0, T \rightarrow \infty) = q_1 W_H = \sqrt{q_1/q_2} W_H = 4.63 \text{ kcal mole}^{-1}. \quad (36b)$$

The values Douglas obtains are 6.04 and 4.09 kcal mole⁻¹, respectively, for \bar{h}_2^{xs} and \bar{h}_1^{xs} . Again the agreement is quite remarkable.

SUMMARY AND CONCLUSIONS

In the foregoing, some of the model properties of the quasi-chemical theory of mixtures have been developed and applied to an analysis of the subsolidus miscibility gap in the system NaCl-KCl. It has been noted that high temperature values of the excess thermodynamic parameters, G^{xs} , H^{xs} , S^{xs} , C_p^{xs} , are surprisingly well-predicted by the model and model parameters. These parameters are derived from phase diagram data at temperatures 130° to 320° lower than the calorimetric data. From examination of this single system it is difficult to say to what extent the agreement is fortuitous and to how wide an extent the model may be applied. These questions will be examined in a succeeding paper. It may be noted here, however, that allowing temperature dependence of the interchange

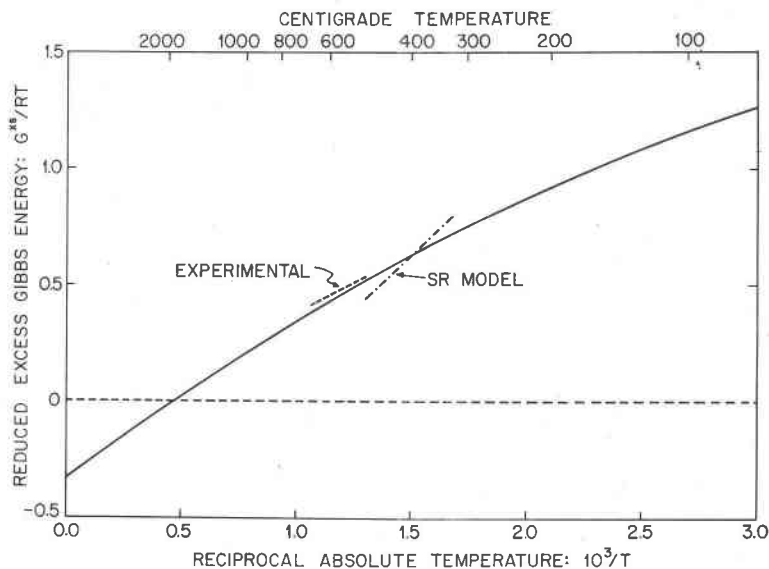


FIG. 8. Reduced excess Gibbs energy of mixing for equimolar NaCl-KCl crystalline solutions. The solid line represents the QC model (this work), the dot-dashed line is the prediction of the SR model (Thompson and Waldbaum, 1969), and the dashed line represents the experimental observations (Barrett and Wallace; 1954a, b).

energy term allows a great deal of flexibility in the theory; and it is probably this feature as well as the model's general appropriquity for cooperative phenomena that is responsible for its success here.

The model always predicts a positive excess heat capacity (35) if W_H is not strongly temperature dependent. This does not imply, however, that S^{xs} is always positive; in the high temperature limit S^{xs} will have the same sign as W_s . This is because $S^{xs}(T \rightarrow 0)$ does not vanish for constant composition but remains finite due to the "frozen-in" disequilibrium composition. Figure 8 displays the function G^{xs}/RT versus reciprocal temperature for the equimolar model system halite-sylvite, $x_2=0.5$. It should be noted that the slope of this curve at any temperature is equal to H^{xs}/R and that the extrapolated intercept of the slope tangent is equal to $-S^{xs}/R$. The curve is concave downwards for positive C_p^{xs} . Above $1/T = 1.33 \times 10^{-3} \text{K}^{-1}$ (below 477°C) the system is metastable, as determined by the phase diagram. Above $1/T = 2.15 \times 10^{-3} \text{K}^{-1}$ (below 193°C) the excess entropy becomes negative due to configurational effects, although it will be observed that the excess heat capacity is everywhere positive.

The extent of the model's low temperature agreement with thermodynamic parameters derived from aqueous-solid distribution coefficients will be reviewed in a subsequent paper. The high temperature correspondence between model and experiment leads us to suggest that progress may be made toward theoretical prediction of phase diagrams by consideration of appropriate thermodynamic models.

REFERENCES

- BARRETT, W. T., AND W. E. WALLACE (1954a) Studies of NaCl-KCl solid solutions. I. Heats of formation, lattice spacings, densities, Schottky defects and mutual solubilities. *J. Amer. Chem. Soc.* **76**, 366-369.
- , AND ——— (1954b) Studies of NaCl-KCl solid solutions. II. Experimental entropies of formation and a comparison of certain thermodynamic properties with values calculated from Wasastjerna's theory. *J. Amer. Chem. Soc.* **76**, 379-373.
- BETHE, H. A. (1935) Statistical theory of superlattices. *Proc. Roy. Soc. London A*, **150**, 552-575.
- BORN, M., AND J. E. MAYER (1932) Zur Gittertheorie der Ionenkristalle. *Z. Physik*, **75**, 1-18.
- BUNK, A. J. H., AND G. W. TICHELAAK (1953) Investigations in the systems NaCl-KCl. *Kon. Ned. Akad. Wetensch. Proc. B.*, **56**, 375-384.
- DOUGLAS, T. B. (1966) Calculated heats of dilute solid solution among the alkali halides other than cesium salts. *J. Chem. Phys.* **45**, 4571-4585.
- DURHAM, G. S., AND J. A. HAWKINS (1951) Solid solutions of the alkali halides II. The theoretical calculation of lattice constants, heats of mixing, and distributions between solid and aqueous phases. *J. Chem. Phys.* **19**, 149-156.
- FOWLER, R. H., AND E. A. GUGGENHEIM (1939) Statistical thermodynamics of superlattices. *Proc. Roy. Soc. London A*, **174**, 189-206.
- GIBBS, J. W. (1873) A method of geometrical representation of the thermodynamic properties of substances by means of surfaces. *Trans. Conn. Acad. Arts Sci.* **2**, 382-404.

- GUGGENHEIM, E. A. (1944) Statistical thermodynamics of mixtures with zero energies of mixing. *Proc. Roy. Soc. London A*, **183**, 203–227.
- (1952) *Mixtures*. Clarendon Press, Oxford.
- HARDY, H. K. (1953) A “sub-regular” solution model and its application to some binary alloy systems. *Acta Met.* **1**, 202–209.
- HILDEBRAND, J. H. (1929) Solubility XII. Regular Solutions. *J. Amer. Chem. Soc.* **51**, 69–80.
- HÖVI, V. (1950) Wasastjerna's theory of the heat of formation of solid solutions. *Soc. Sci. Fenn. Commentat. Phys. Math.* **15** (12), 1–14.
- JOULE, J. P. (1844) On specific heat. *Phil. Mag.* **25**, 334–337.
- KOPP, H. (1865) Investigations of the specific heat of solid bodies. *Phil. Trans.* **155**, 71–202.
- LANGMUIR, I. (1925) The distribution and orientation of molecules. *Colloid Symposium Monograph*, **3**, 48–75.
- LISTER, M. W., AND N. F. MEYERS (1958) Heats of formation of some solid solutions of alkali halides. *J. Phys. Chem.* **62**, 145–150.
- LUMSDEN, J. (1952) *Thermodynamics of Alloys*. Institute of Metals, London.
- MAYER, J. E. (1933) Dispersion and polarizability and the van der Waals' potential in the alkali halides. *J. Chem. Phys.* **1**, 270–279.
- NACKEN, R. (1918) Über die Grenzen der Mischkristallbildung zwischen Kaliumchlorid und Natriumchlorid. *Sitzungsber. Preuss. Akad. Wiss., Phys. Math. Kl.* 192–200.
- NEUMANN, F. E. (1831) Untersuchung über die spezifische Wärme der Mineralien. *Ann. Phys. Chem.*, **23**, 1–39.
- PAULING, L. (1948) *The Nature of the Chemical Bond*, 2nd ed., Cornell University Press, Ithaca.
- POPOV, M. M., S. M. SKURATOV, AND I. N. NIKANOWA (1940a) Investigations of mixed crystals III. *Zh. Obshch. Khim.* **10**, 2017–2022.
- , ———, AND M. M. STREL'TSOVA (1940b) Investigations of mixed-crystals IV. *Zh. Obshch. Khim.* **10**, 2023–2027.
- ROBIE, R. A., P. M. BETHKE AND K. M. BEARDSLEY (1967) Selected x-ray crystallographic data, molar volumes, and densities of minerals and related substances. *Bull. U.S. Geol. Surv.* **1248**, 87 pp.
- RUSHBROOKE, G. S. (1938) A note on Guggenheim's theory of strictly regular binary liquid mixtures. *Proc. Roy. Soc. London, A*, **166**, 296–315.
- THOMPSON, J. B., JR., AND D. R. WALDBAUM (1969) Analysis of the two-phase region halite-sylvite in the system NaCl-KCl. *Geochim. Cosmochim. Acta*, **33**, 671–690.
- VAN LAAR, J. J. (1910) Über Dampfspannung von binären Gemischen. *Z. Phys. Chem.* **72**, 732–751.
- (1906) *Sechs Vorträge über das thermodynamische Potential*. Vieweg und Sohn, Braunschweig.
- WALLACE, W. E. (1949) The Born-Mayer model for ionic solids and the heats of formation and lattice spacings of alkali halide solid solutions. *J. Chem. Phys.* **11**, 1095–1099.
- WASASTJERNA, J. A. (1949) The theory of the heat of formation of solid solutions. *Sci. Fenn., Commentat. Phys. Math.* **15** (3), 1–13.
- (1944) An X-ray investigation of the solid solutions KCl-KBr and KCl-RbCl. *Acta Soc. Sci. Fenn.* **3A** (8), 1–17.
- WOESTYN, A. C. (1848) Note sur les chaleurs spécifiques. *Ann. Chem. Phys.* **23**, 295–302.
- ZHEMCHUZHNUH, S., AND J. RAMBACH (1910) Schmelzen der Alkalichloride. *Z. Anorg. Chem.* **65**, 403–428.