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Quasilattice Interpretation of the Thermodynamic Properties of Mixing of Binary Alkali-Metal Systems

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Quasilattice theory was applied to heats of mixing in the six systems formed from the binary combinations of Na, K, Rb, and Cs. The alkali-metal systems are particularly well suited for a critical test of the quasicrystalline assumption since the theoretical model for these systems is relatively simple and the thermodynamic data are fairly complex. Very good fits of the heat-of-mixing data were achieved by assuming that the larger atom in the binary system covered multiple sites on the quasilattice. The values of the empirically determined constants appear to fit the physical significance accorded to them by the quasilattice model. Values for the excess free energies of the Na–K system, calculated from the parameters of heat of mixing data, were in semiquantitative agreement with experimental data.

The generalized quasilattice model described by Barker[1,2] has been used with some success in our laboratory[3–5] to correlate and semiquantitatively predict values for the thermodynamic properties of mixing of simple organic molecules. The use of molecular species, especially those with more than one type of interaction site, generates so many arbitrarily adjustable parameters that the extent to which the quasilattice assumption may be valid is obscured. Binary solutions of alkali metals, on the other hand, because of the simplicity of the model and the difference in size of the atoms are particularly well suited for a test of the theory.

Adding to the interest of these systems is the variation found in the symmetry of their heat-of-mixing vs-mole-fraction curves, which vary from the almost perfectly symmetrical K–Rb system to the badly skewed curve of the Na–Cs system. We have with the alkali-metal systems, therefore, a case where a relatively simple model must account for fairly complex thermodynamic information.

QUASILATTICE MODEL

In general, application of quasilattice theory requires a knowledge of the number and types of contact sites on each molecule and the energies for all possible interactions of these sites. Three lattice parameters and one energy of interaction need to be specified to provide this information for the systems under discussion. The lattice parameters are z, the coordination number of the quasilattice; r_s, the number of lattice sites occupied by the smaller atoms in the binary system; and r_L, the number of sites occupied by the larger atom. The number of interaction sites Q of the atom can then be calculated from the relation

$$Q=rz-2r+2. \tag{1}$$

The lattice model that we have used assigns one site on a fourfold coordinated lattice to the smaller atom in each system, i.e., $z=4$, $r_s=1$. The value of r_L, as will be explained more fully later, was determined from experimental heat-of-mixing data.

The energy of interaction required in the theory is the energy of the quasichemical process

$$\tfrac{1}{2}(i-i)+\tfrac{1}{2}(j-j)\rightarrow i-j,$$

in which i and j represent contact sites on unlike atoms. Hence, for binary mixtures of the alkali metals, a single interaction energy U is all that needs to be considered. Its value, as with r_L, was obtained empirically from experimental heat-of-mixing data.

COMPUTATIONS

The quasilattice equations that apply to the alkali-metal systems are given below:

$$\Delta H_x^m \cong \Delta E_x^m = -2RT(\mathrm{x}_{\mathrm{Na}}\mathrm{x}_{\mathrm{K}}\eta_{\mathrm{Na-K}}\ln\eta_{\mathrm{Na-K}}), \tag{2}$$

$$\Delta G_x^E \cong \Delta A_x^E = x_s\mu_s^E + x_L\mu_L^E, \tag{3}$$

$$\mu_s^E = RT[4\ln(\mathrm{x}_s/x_s\mathrm{x}_s') + \ln(r_L x_L + x_s)], \tag{4}$$

$$\mu_L^E = RT\{Q_L\ln(\mathrm{x}_L/x_L\mathrm{x}_L') + r_L\ln[(x_s+r_Lx_L)/r_L]\}. \tag{5}$$

The heat of mixing per mole of solution, ΔH_x^m, is so nearly equal to the energy of mixing (which is actually calculated from the theory) that the two can be used interchangeably in these systems. The same applies for the excess Gibbs free energy ΔG_x^E, and the excess Helmholtz free energy ΔA_m^E. L and s signify the larger and smaller atom, respectively, in the mixture. The quantities μ_L^E and μ_s^E then are the excess partial molal Helmholtz free energies or approximately excess chemical potentials of the large and small atoms; η is $\exp(-U/RT)$; x_L and x_s are mole fractions; and Q

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[2] J. A. Barker, J. Chem. Phys. **21**, 1391 (1953).
[3] J. R. Goates, R. L. Snow, and M. R. James, J. Phys. Chem. **65**, 335 (1961).
[4] J. R. Goates, R. L. Snow, and J. B. Ott, J. Phys. Chem. **66**, 1301 (1962).
[5] J. B. Ott, J. R. Goates, and R. L. Snow, J. Phys. Chem. **67**, 515 (1963).

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TABLE I. Parameters for the quasilattice model.

System[a]	r_L	Q_L	U
Na–K	2.0	6	164
Na–Rb	3.5	9	244
Na–Cs	5.0	12	161
K–Rb	1.0	4	31.4
K–Cs	2.0	6	22.0
Rb–Cs	1.0	4	−29.0

[a] $z=4$, $r_s=1$, and $Q_s=4$ apply to all six systems.

and r are as described earlier. The $\mathbf{x}$ functions are obtained from the simultaneous solution of the following equations:

$$\mathbf{x}_s(\mathbf{x}_s+\mathbf{x}_L\eta)=\tfrac{1}{2}(Q_s x_s), \tag{6}$$

$$\mathbf{x}_L(\mathbf{x}_L+\mathbf{x}_s\eta)=\tfrac{1}{2}(Q_L x_L). \tag{7}$$

The values for U and r_L were determined by curve fitting, using the experimental heat-of-mixing data of Yokokawa and Kleppa.[6] Since the value of r_L affects only the height of the heat-of-mixing–composition curve, it was possible to obtain a unique "best fit" for any specified set of lattice parameters. The computations were made with an IBM 360 computer, which was programmed to include in its output a plot of the heat-of-mixing curve showing both experimental and calculated data points. This made a quick visual analysis all that was necessary to bracket a narrow range of possible best values for U and r_L. Final selection of "best fit" was made on the basis of the root-mean-square deviation from the experimental curve at nine points spaced at 0.1-mole-fraction intervals. To make this comparison the experimental points of Ref. 6 were smoothed with a least-squares plot of $\Delta H_x^M/x_1x_2$ vs x_1. The values of ΔH at the 0.1-mole-fraction intervals were then calculated from the least-squares equation.

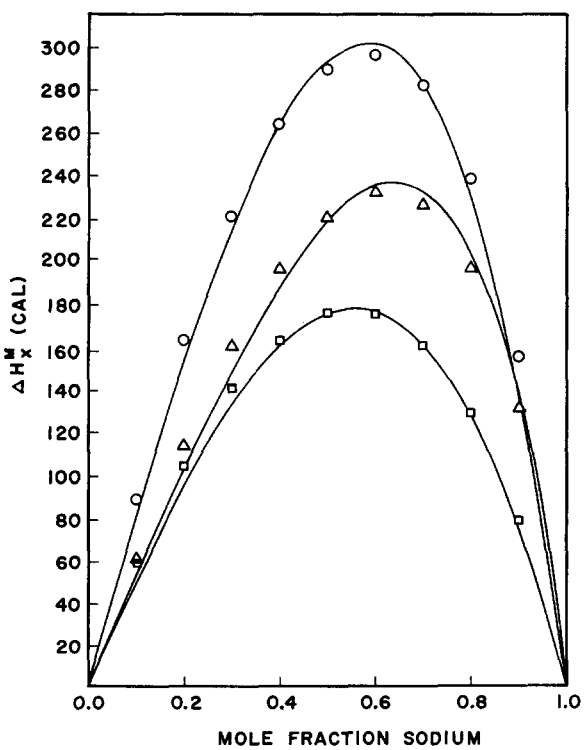

FIG. 1. Comparison of quasilattice theory (solid lines) and smoothed experimental heats of mixing (data points). ○, Sodium–rubidium system; △, sodium–cesium system; □, sodium–potassium system.

[6] T. Yokokawa and O. J. Kleppa, J. Chem. Phys. **40**, 46 (1964).

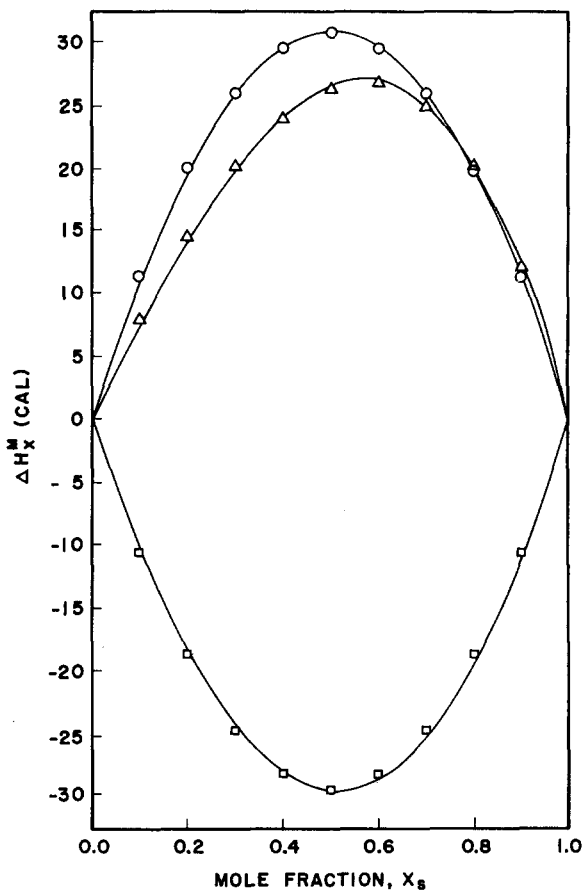

FIG. 2. Comparison of quasilattice theory (solid line) and smoothed experimental heats of mixing (data points). ○, Potassium–rubidium system; △, potassium–cesium system; □, rubidium–cesium system.

RESULTS AND DISCUSSION

Table I lists the values of the lattice parameters and the energies of interaction obtained for the six binary mixtures of Na, K, Rb, and Cs. Figures 1 and 2 are plots of the heats of mixing calculated from the data of Table I. The theory is represented by the solid line, and the smoothed experimental data are plotted as circles. The agreement between theory and experiment is good, in most cases the fit being well within the limits of the scattering of actual experimental data points.

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We next checked the resonableness of the empirically measured values. The number of lattice sites covered by the larger atom, r_L, should bear some relationship to the size of the atom if the empirically determined constant is to have the physical significance assigned to it by the theory. In Fig. 3 we have plotted the ratio of the number of sites covered by the unlike atoms against the ratios of the volumes of the atoms. The slope of the line is too steep for a 1:1 correspondence; but, qualitatively, the relationship is correct. Since all errors inherent in the theory that affect the symmetry of the heat-of-mixing data are absorbed into the single empirically determined constant r_L, the straight-line relationship is rather satisfying.

The values of the interaction energies in Table I fall roughly into two groups: (a) relatively high endothermic values in the three systems containing sodium, and (b) low values (both exothermic and endothermic) for those systems composed of the elements in the lower part of Group IA of the periodic table.

This grouping is in line with what one might expect from a consideration of the variations in physical properties of the four metals. An abrupt break in the otherwise gradual change in properties as one goes down the IA Group from Na to Cs occurs between Na and K. For example, the bond energies in kilocalories per mole are Na–Na, 17.3; K–K, 11.8; Rb–Rb, 10.8; and Cs–Cs, 10.4. A similar relationship can be seen with the melting points, heats of fusion, boiling points, and heats of vaporization. Since the physical properties that are related to attractive forces are quite similar for K, Rb, and Cs, one might expect their mixtures to have low interaction energies. On the other hand, energies for interactions between less similar atoms, the condition that exists in the Na-containing systems, would be expected to be relatively high. Thus, from at least a qualitative point of view, the values found for U are also reasonable.

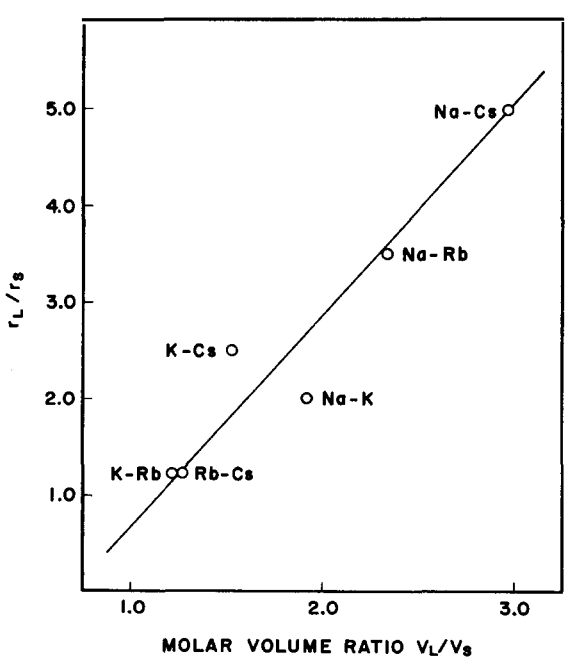

FIG. 3. Comparison of occupied sites vs atomic volumes.

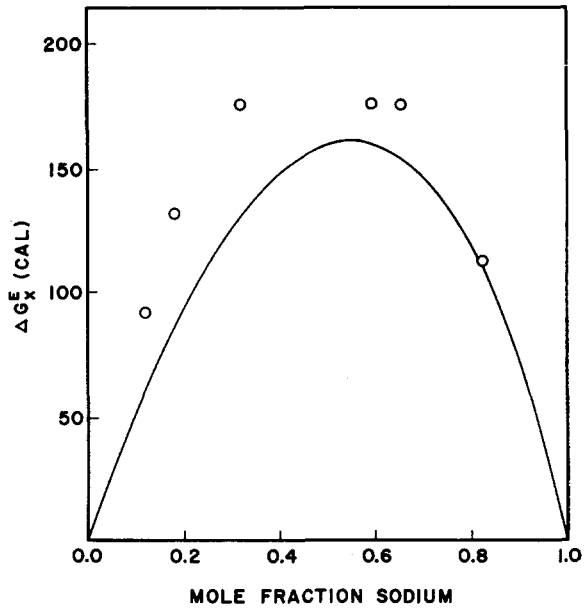

FIG. 4. Comparison of experimental excess free energies of mixing (data points) and quasilattice theory prediction (solid line) for mixtures of sodium and potassium.

After the parameters of Table I had been established from the heat-of-mixing studies, the same data were used to calculate excess chemical potentials and excess free energies of mixing. The results are shown in Fig. 4 for the one system, Na–K, for which we had experimental data.[7] Inasmuch as no consideration was given to the free-energy data in establishing the values of the constants in Table I, the agreement between theory and experiment is considered satisfactory. The calculated curve is low at its peak by 12%–15% and appears to be skewed to the right.

ACKNOWLEDGMENTS

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[7] F. A. Cafasso, V. M. Khanna, and H. M. Feder, Advan. Phys. 16, 535 (1967).

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