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Mass-spectrometric Measurement of Activities in Both Solid and Liquid Solutions of the KCl–NaCl System

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The activities of the KCl–NaCl system were mass-spectrometrically determined by the ion-current-ratio method in the temperature range from 793 to 1083 K. As a result, the activities of KCl or NaCl in the solid solution showed greatly positive deviations from Raoult's law while the liquid solution at 1083 K gave slightly negative values. The heats of mixing in the solid solution were calculated from the temperature dependence of the modified ion-current ratios, $[(I_{\mathrm{Na_2Cl^+}}/X^2_{\mathrm{NaCl}})/(I_{\mathrm{K_2Cl^+}}/X^2_{\mathrm{KCl}})]$. The excess entropy of mixing in the solid solution was attributed to the change in the vibrational spectrum, and the vibrational contribution to the heat of mixing was evaluated.

The Knudsen-cell mass-spectrometric method developed by Belton and Fruehan[1] has been applied to the determination of the thermodynamic properties of metallic solutions at elevated temperatures and has proved to be very useful. However, there have been few reports concerning the application of this method in activity measurements in inorganic-solid-solution systems between compounds. In the case of the activity measurement of a solid-solution system, a difficult problem is a surface depletion caused by the preferential vaporization of certain components.

In this study, the applicability of the mass-spectrometric method has been checked for the measurement of activities in the KCl–NaCl system. This system is proper for a discussion of the adaptability of the mass spectrometry to the activity measurements in an inorganic-solid-solution system because of the relatively small difference in the vapor pressures of the components (the ratio of the vapor pressure of KCl to that of NaCl is about two) and the ease of thermodynamical analysis from the observed data.

Experimental

The instrument used was a doubly focused mass spectrometer (JEOL JMS-01/BK) with a Knudsen-cell source (*cf.* Fig. 1). The Knudsen cell(G), made of alumina, had dimensions of 8 mm I.D. by 8 mm in height and had a cylindrical orifice 0.2—0.7 mm in diameter bored in the center of a lid about 1 mm thick. The cell was heated by radiation from tungsten ribbon heaters(H). The temperature of the cell was measured with a W5%Re–W26%Re thermocouple attached at the inner bottom of the outer cell(F), which had been calibrated in advance from the difference in the temperatures between the inside and outside of the cell (containing a sample), the difference having been determined using a PR13 thermocouple (0.2 mm in diameter) inserted through the orifice. Samples in the KCl–NaCl solid solutions were prepared by the melting a mixture of exactly weighted KCl and NaCl powders dried in a vacuum for a day and by then quenching them to room temperature in a quartz tube. They were crushed to powder just before the measurement, and about 300 mg was used in the Knudsen cell for each run of an experiment.

The ion intensity for the derived species was measured by the usual mass-spectrometrical technique in the temperature range from 793 to 1083 K, changing the temperature in steps of 40 K intervals. The temperature was held for about 15 min at each temperature level in order to obtain the constant ion intensity indicating the chemical equilibrium. The total weight loss of the sample after each run was about 0.1 mg in the solid state and about 3 mg in the liquid state. If a perfect shutter effect could not be obtained because of the contamination by alkali halide vapors, the ion source was completely cleaned. The ionization potential of 25 eV was used.

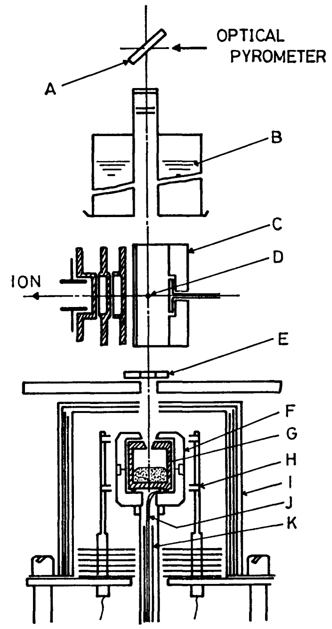

Fig. 1. Scheme of the mass spectrometer with Knudsen cell ion source.
A: Mirror, B: liquid N_2 trap, C: ion source chamber, D: electron beam, E: shutter slit, F: outer cell, G: Knudsen cell, H: filament, I: radiation shield, J: W5%Re–W26%Re thermocouple, K: ThO_2-tube.

Results and Discussion

The detected ion species were Na^+, K^+, $NaCl^+$, KCl^+, Na_2Cl^+, K_2Cl^+, $NaKCl^+$, and Cl^+. Their apperance potentials, referred to H_2O^+, were 10.3, 11.0, 10.0, 10.5, 10.0, 10.8, 10.5, and 15.5 eV respectively. The ion intensities of the $Na_3Cl_2^+$ and $K_3Cl_2^+$ trimers were under 1/100 for those of the Na_2Cl^+ and K_2Cl^+.

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Both by considering the temperature dependences of the ion currents and by using an analogy with other chlorides,[2,3] the formation processes of ions from the alkali-halide vapors were estimated to be as follows:

$$MCl + e^- = M^+ + Cl + 2e^-, \quad (1)$$

$$MCl + e^- = MCl^+ + 2e^-, \quad (2)$$

$$M_2Cl_2 + e^- = M_2Cl^+ + Cl + 2e^-, \quad (3)$$

$$MM'Cl + e^- = MM'Cl^+ + Cl + 2e^-, \quad (4)$$

$$Cl + e^- = Cl^+ + 2e^-, \quad (5)$$

where M and M′ stand for Na or K. That is to say, MCl^+, M_2Cl^+, and $MM'Cl^+$ were the molecular(or parent) ions formed by the simple ionization, while M^+ and Cl^+ were the fragment ions. Therefore, we considered that the sum of the ion currents of M^+ and MCl^+ was proportional to the vapor pressure of MCl(g).

In order to confirm the equilibrium in the cell, the dimer ion-current ratio, $I_{Na_2Cl^+}/I_{K_2Cl^+}$ was measured at 913 K as a function of the orifice diameter, as shown in Fig. 2. From the results, the equilibrium in the cell was confirmed.

Belton and Fruehan[1] have derived expressions relating to the activity of a solution which is favorable to mass spectrometry. The activity in the system was determined using the expression for the ion-current ratios of any two peaks for Na_2Cl^+, K_2Cl^+, or $NaKCl^+$. For example, the activity coefficient for the KCl component, γ_{KCl}, is given by:

$$\ln\gamma_{KCl} = -\int_{X_{KCl}=1}^{X_{KCl}} \frac{X_{NaCl}}{2} \times d\{\ln(I_{Na_2Cl^+}/I_{K_2Cl^+}) - \ln(X_{NaCl}/X_{KCl})^2\}, \quad (6)$$

where X_i is the mole fraction. This equation means that the activity can be determined from the ion-current ratio, $I_{Na_2Cl^+}/I_{K_2Cl^+}$, as a function of the composition. The experimental results are shown in Fig. 3 as plots of $\ln(I_{Na_2Cl^+}/I_{K_2Cl^+})$ *vs.* $1/T$. These plots for each composition fall on straight lines, the slopes of which are given in Table 1. The broken lines in Fig. 3, located on the gaps between the two straight lines in the lower and higher temperature sides, correspond to the regions where the solid and liquid coexist. The solidus and liquidus temperatures obtained from this figure agreed approximately with those in the phase diagram.[4] In order to graphically integrate Eq. 6, the term of $\{\ln(I_{Na_2Cl^+}/I_{K_2Cl^+}) - \ln(X_{NaCl}/X_{KCl})^2\}$ was plotted against the composition, X, as is illustrated in Fig. 4. Using this figure, the

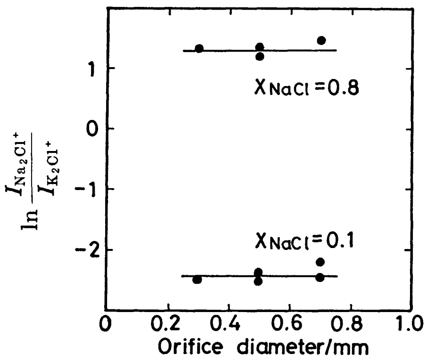

Fig. 2. Orifice diameter dependence of $\ln(I_{K_2Cl^+}/I_{Na_2Cl^+})$.

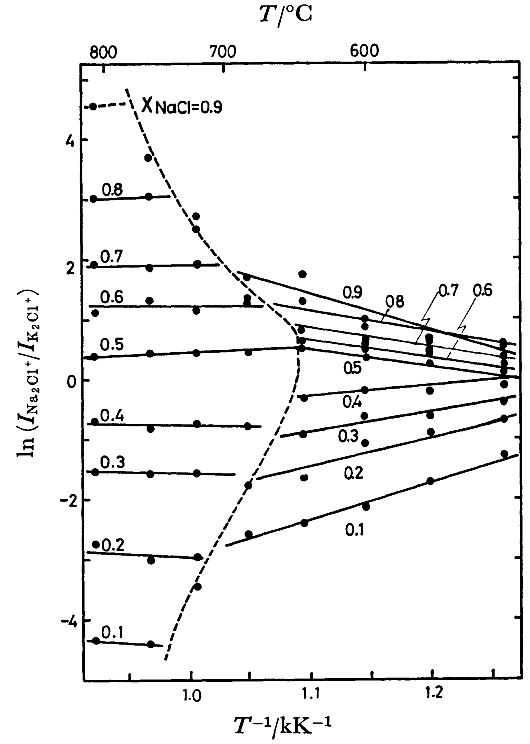

Fig. 3. The observed ion current ratio of dimer ions in the KCl–NaCl system.

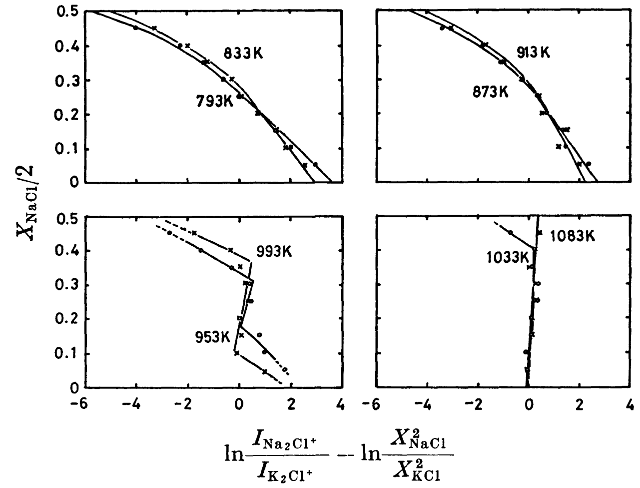

Fig. 4. Preliminary curves for the graphical integration in Eq. 6.

TABLE 1. VALUES OF SLOPES FOR THE LINES DRAWN IN FIG. 3

X_{NaCl}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$d\ln\left(\frac{I_{Na_2Cl^+}}{I_{K_2Cl^+}}\right)/d(1/T)$	6250	5030	3050	1240	−470	−990	−2970	−4310	−6830

activity coefficients for NaCl and KCl are calculated by the graphical integration on the basis of Eq. 6. The results are shown in Fig. 5.

The activity can be obtained also using a complex dimer, $NaKCl_2(g)$, in the following manner. The equilibrium reaction between the gas and the condenced phases containing the complex vapor:

$$Na_2Cl_2(g) + KCl(c) = NaKCl_2(g) + NaCl(c) \tag{7}$$

gives another expression for the activity coefficient corresponding to Eq. 6:

$$\ln\gamma_{KCl} = -\int_{X_{KCl}=1}^{X_{KCl}} X_{NaCl} \times d\{\ln(I_{NaKCl^+}/I_{K_2Cl^+}) - \ln(X_{NaCl}/X_{KCl})\}. \tag{8}$$

The obtained ion-current ratios *vs.* $1/T$ and the $\{\ln(I_{NaKCl^+}/I_{K_2Cl^+}) - \ln(X_{NaCl}/X_{KCl})\}$ *vs.* composition are shown in Figs. 6 and 7. The activities derived from Fig. 7 are shown in Fig. 8; they are in close agreement with those shown previously in Fig. 5. The closed circles in Fig. 8 indicate that the activities of NaCl at 1083 K were determined by the monomer-dimer method,[5] in which the following equation was used:

$$a_{NaCl} = (I_{Na_2Cl^+}/I_{NaCl^+})_{solution}/(I_{Na_2Cl^+}/I_{NaCl^+})_{pure}. \tag{9}$$

The plots were in good agreement with the values determined by the ion-current-ratio method. This fact supports the idea that the following fragmentation can be neglected:

$$Na_2Cl_2 + e^- \rightarrow Na^+ + NaCl + Cl + 2e^-, \tag{10}$$

$$Na_2Cl_2 + e^- \rightarrow NaCl^+ + NaCl + 2e^-. \tag{11}$$

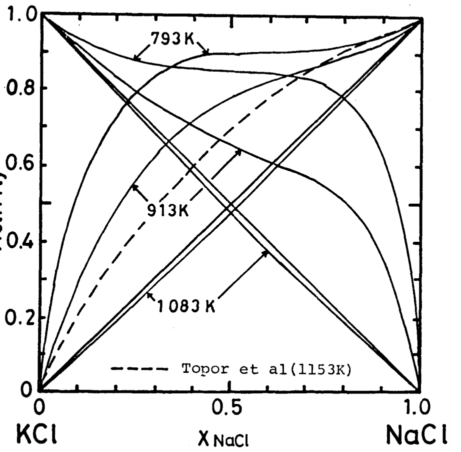

Fig. 5. Activities in the KCl–NaCl system.

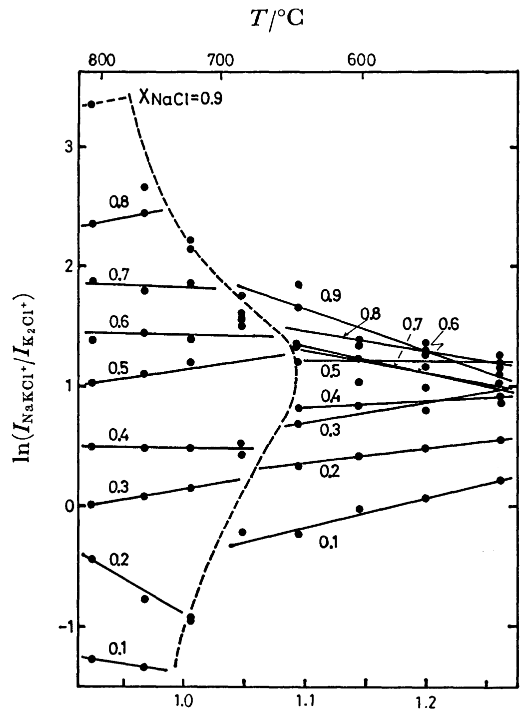

Fig. 6. The observed ion current ratio of dimer ions in the KCl–NaCl system.

Topor and Topor[6] have determined the activity of the KCl–NaCl system at 1153 K by means of the galvanic-cell method. The activity reported by them (Fig. 5) shows a great positive deviation from that for the ideal solution, while their values disagree with those extrapolated from our data up to 1153 K. When the excess partial entropy of mixing was evaluated using Topor and Topor's activity data and Hersh and Kleppa's calorimetric data,[7] the value of −0.72

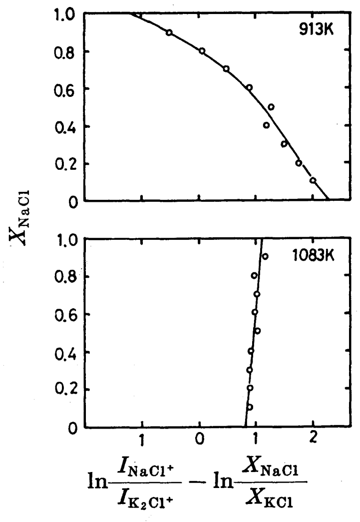

Fig. 7. Preliminary curves for the graphical integration in Eq. 8.

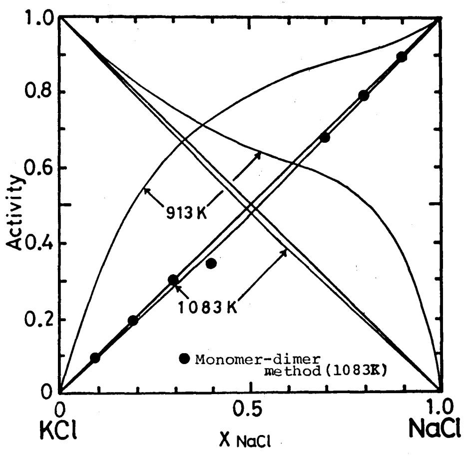

Fig. 8. Activities in the KCl–NaCl system.

e.u. was obtained for the composition of $X_{\mathrm{NaCl}}=0.5$. This value, however, is considered to be too large for this simple system.

The heats of mixing, ΔH^{M}, for the solid solution were determined by a graphical integration of Eq. 12:[1]

$$\Delta\bar{H}_{\mathrm{KCl}} = -R\int_{X_{\mathrm{KCl}}=1}^{X_{\mathrm{KCl}}} \frac{X_{\mathrm{NaCl}}}{2} \times \mathrm{d}\left[\frac{\mathrm{d}\ln\{I_{\mathrm{Na_2Cl^+}}\cdot X_{\mathrm{KCl}}^2/I_{\mathrm{K_2Cl^+}}\cdot X_{\mathrm{NaCl}}^2\}}{\mathrm{d}(1/T)}\right], \tag{12}$$

using the values of the slope given in Table 1. The integration along the curve in Fig. 9 yields Fig. 10. The large positive heat of mixing in the solid solution system probably arises from the difference in radius between the radii of $\mathrm{Na^+}$ (0.96 Å) and $\mathrm{K^+}$ (1.33 Å). As is shown in Fig. 10, $\Delta\bar{H}_{\mathrm{KCl}}$ is larger than $\Delta\bar{H}_{\mathrm{NaCl}}$. This is due to a requirement of a larger energy than that for the case of a small ion for the introduction of a large ion into a lattice. If the ionic radii in the state of solid solution and bulk moduli of the ions are known, the contribution of the strain energy to the heat of mixing can be estimated. In the KCl–NaCl system, the cations may take an arrangement with a short-range order in order to reduce the strain energy.

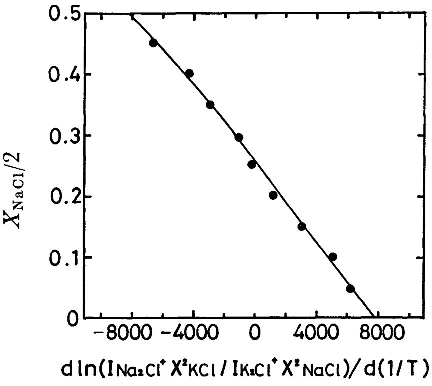

Fig. 9. Integration plot for the KCl–NaCl system.

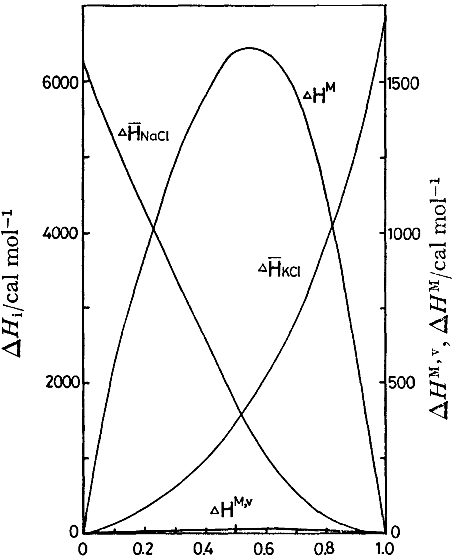

Fig. 10. Heats of mixing in the KCl–NaCl solid solution system.

The entropy of mixing, ΔS^{M}, in the solid solution was calculated from the well-known thermodynamic relation:

$$\Delta S^{\mathrm{M}} = -(\Delta H^{\mathrm{M}}-\Delta G^{\mathrm{M}})/T. \tag{13}$$

It is shown in Fig. 11. If the arrangement of the cations is close to the random state in the solid solution, the entropy is given by only the ideal configurational term, $\Delta S_{\mathrm{ideal}}^{\mathrm{M}}$:

$$\Delta S_{\mathrm{ideal}}^{\mathrm{M}} = -R(X_{\mathrm{KCl}}\ln X_{\mathrm{KCl}}+X_{\mathrm{NaCl}}\ln X_{\mathrm{NaCl}}). \tag{14}$$

$\Delta S_{\mathrm{ideal}}^{\mathrm{M}}$ is also plotted in Fig. 11. Then the excess entropy, $\Delta S_{\mathrm{excess}}^{\mathrm{M}}$, is given by:

$$\Delta S_{\mathrm{excess}}^{\mathrm{M}} = \Delta S^{\mathrm{M}} - \Delta S_{\mathrm{ideal}}^{\mathrm{M}}. \tag{15}$$

The entropy of mixing in the liquid solution shown in Fig. 11 was calculated from the activities from Hersh and Kleppa's calorimetric data. The small excess entropy of mixing and the small heat of mixing suggest that the liquid solution is nearly an ideal solution. The large positive excess entropy of mixing in the solid solution is considered to arise from a change in the vibrational entropy associated with a change in the vibrational spectrum. The vibrational entropies(ΔS^{M}) of KCl and NaCl can be calculated from Debye's theory[8] using the Debye temperatures[9–11] of KCl (235 K) and NaCl (321 K). The vibrational entropy of solid solution(S^{V}) is the mean vibrational entropy, $S_{\mathrm{mean}}^{\mathrm{v}}(=X_{\mathrm{KCl}}S_{\mathrm{KCl}}^{\mathrm{v}}+X_{\mathrm{NaCl}}S_{\mathrm{NaCl}}^{\mathrm{v}})$, plus the excess entropy, $\Delta S_{\mathrm{excess}}^{\mathrm{M}}$. The calculated S^{v}'s are shown in Fig. 12. The Debye temperature of the solid solution was calculated from the S^{v}; it is shown in Fig. 13, along with the Debye temperature, θ_{D}, corresponding to the $S_{\mathrm{mean}}^{\mathrm{v}}$. It is also possible to calculate the heat capacity, C_{v}, for the KCl–NaCl solid solution. The change in the heat capacity to form the solid solution is:

$$\Delta C_{\mathrm{v}} = C_{\mathrm{v,solid\ solution}} - X_{\mathrm{KCl}}C_{\mathrm{v,KCl}} - X_{\mathrm{NaCl}}C_{\mathrm{v,NaCl}}. \tag{16}$$

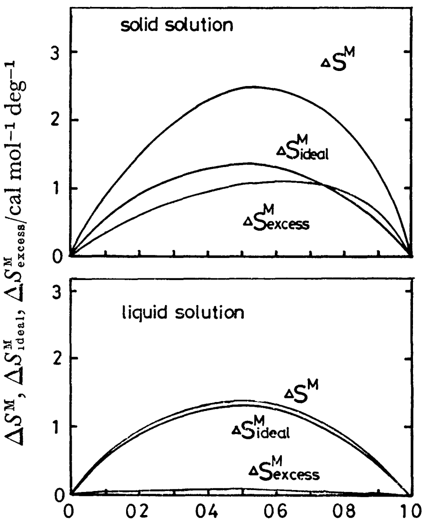

Fig. 11. Entropies of mixing in the KCl–NaCl solid solution and liquid solution systems.

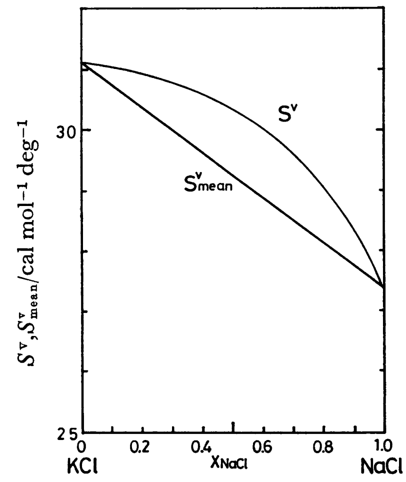

Fig. 12. Vibrational entropy and mean entropy of the KCl–NaCl solid solution system.

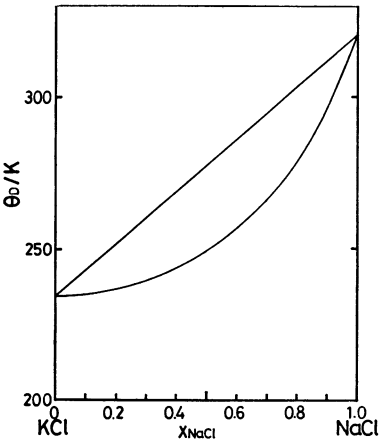

Fig. 13. Debye temperature for the KCl–NaCl solid solution system.

The change in the heat of mixing caused by the change in the vibrational spectrum is calculated using the following equation:

$$\Delta H^{\mathrm{M,v}} = \int_0^T \Delta C_p \mathrm{d}T. \tag{17}$$

The results are shown in Fig. 10. For the purposes of this study, it is possible to estimate that ΔC_p is close to ΔC_v. As is shown in Fig. 10, $\Delta H^{\mathrm{M,v}}$ makes only a small contribution to ΔH^{M}.

Conclusion

(1) The activities of KCl and NaCl in the solid solution showed greatly positive deviations from Raoult's law, while the liquid solution gave slightly negative values.

(2) The large positive heat of mixing in the solid solution was attributed to the strain energy which arises from the difference in radius between the radii of Na^+ and K^+.

(3) The large positive excess entropy of mixing in the solid solution is considered to arise from a change in the vibrational spectrum.

References

1) G. R. Belton and R. J. Fruehan, *Metall. Trans.*, **2**, 291 (1971).

2) J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, **29**, 653 (1958).

3) T. A. Milne and H. M. Klein, *J. Phys. Chem.*, **64**, 1628 (1960).

4) R. G. Wolston and W. Kobes, *Mater. Res. Bull.*, **2**, 263 (1967).

5) J. Berkowitz and W. A. Chupka, *Ann. N. Y. Acad. Sci.*, **79**, 1073 (1960).

6) T. Topor and L. Topor, *J. Chim. Phys.*, **69**, 1465 (1972).

7) S. Hersh and O. J. Kleppa, *J. Chem. Phys.*, **42**, 247 (1965).

8) D. E. Gray, "American Institute of Physics Handbook," 3rd ed, McGraw-Hill (1972).

9) W. T. Bergand and J. A. Morrison, *Proc. R. Soc. London Ser. A*, **242**, 467 (1957).

10) P. H. Keeson and N. Pearman, *Phys. Rev.*, **91**, 1054 (1953).

11) F. J. Werb and J. Wilks, *Proc. R. Soc. London, Ser. A*, **230**, 549 (1955).