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Mass-spectrometric Measurements of Enthalpy and Entropy Changes for the Mixed Dimer Reaction: $Na_2Cl_2(g)+K_2Cl_2(g)=2NaKCl_2(g)$

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Synopsis. The enthalpy(ΔH°_r) and entropy(ΔS°_r) changes for the mixed dimer formation reaction, $Na_2Cl_2+K_2Cl_2=2NaKCl_2$, have been measured by mass-spectrometry in the temperature range of 793 to 1083 K. $\Delta H^\circ_r=-1.67$ kJ mol^{-1} and $\Delta S^\circ_r=5.69$ J K^{-1} mol^{-1} were obtained. These very small values were referred both to the mainly ionic-bonding structure in the related dimers and to preserving the isobonding through the reaction.

Hastie[1] has recently summarized the empirically based rules for complex halide formation. From these it is derived that isobonding mixed-dimer reactions such as $(AX)_2+(BX)_2=2ABX_2$, where A and B are different alkali metals and X is a halogen, should occur with very little enthalpy and entropy changes. However, in practice, the enthalpy changes have ranged from about 0 to approximately -340 kJ/2 mol-complex due to the excess stability associated with the mixed dimer formation.[1]

The following reaction:

$$Na_2Cl_2(g)+K_2Cl_2(g)=2NaKCl_2(g)\,, \tag{1}$$

was chosen in this study to examine the energetic situation in the mixed dimer formation reaction because of its simplicity in chemical bondings.

Experimental

A series of mass-spectrometric experiments was carried out on the solid solutions of NaCl and KCl with different compositions ranging from 10 to 90 mol% NaCl. A method of detection and identification of species was described in detail elsewhere.[2,3] Approximately 50 mg of the mixed salt was placed in a Knudsen-cell made of pure alumina.

The ions of Na_2Cl^+, K_2Cl^+, and $NaKCl^+$ were determined as the parent ions produced from Na_2Cl_2, K_2Cl_2, and $NaKCl_2$ molecular vapors, respectively.[2] The equilibrium partial pressure of i-th vapor, p_i, is given by $p_i=C_iTI(i^+)$ where $I(i^+)$ is the parent ion intensity, T is the absolute temperature and C_i is a constant involving the ionization cross section(σ_i), the isotopic ratio(γ_i), the collection efficiency (S_i) in the first step of an electron multiplier, and the potential difference (ΔE_i) between an ionizing- and appearance-potentials of i-th ion, and an apparatus constant(k):$C_i=k(\sigma_i\gamma_iS_i\Delta E_i)^{-1}$ for the i-th ion.

The equilibrium constant, K_p, for Eq. 1 can be written as:

$$K_p=\frac{[p(NaKCl_2)]^2}{p(Na_2Cl_2)p(K_2Cl_2)}=\frac{C[I(NaKCl^+)]^2}{I(Na_2Cl^+)I(K_2Cl^+)}\,, \tag{2}$$

where,

$$C=\frac{[C(NaKCl_2)]^2}{C(Na_2Cl_2)C(K_2Cl_2)}=\frac{\sigma(Na_2Cl_2)\sigma(K_2Cl_2)}{[\sigma(NaKCl_2)]^2}\times\frac{\gamma(^{23}Na_2{}^{35}Cl_2)\gamma(^{39}K_2{}^{35}Cl_2)}{[\gamma(^{23}Na^{39}K^{35}Cl_2)]^2}\times\frac{S(Na_2Cl^+)S(K_2Cl^+)}{[S(NaKCl^+)]^2}\times\frac{\Delta E(Na_2Cl^+)\Delta E(K_2Cl^+)}{[\Delta E(NaKCl^+)]^2}\,. \tag{3}$$

Assuming that S-values are almost identical for Na_2Cl^+, K_2Cl^+, and $NaKCl^+$ ions and using our previous data[2] for σ and ΔE, $C=1.06$ was obtained.

Vapor equilibrium in the Knudsen cell was ensured by our previous mass-spectrometric measurements of activities of the NaCl–KCl system[2,4] carried out by taking advantage of the ion intensity of Na_2Cl^+, K_2Cl^+, and $NaKCl^+$ which came from Na_2Cl_2, K_2Cl_2, and $NaKCl_2$ molecules: the activity coefficient determined from the ion current ratios of $I(Na_2Cl^+)/I(K_2Cl^+)$ was in close agreement with that obtained from the ratios of $I(NaKCl^+)/I(K_2Cl^+)$. This shows attainment of equilibria between gas phases in Eq. 1.

Results and Discussion

Figure 1 shows the temperature dependence of K_p calculated from Eq. 2 using the mass-spectrometrically observed data. Some K_p data reported by Milne and Klein[5] are also presented in the figure. The least squares treatment gave:

$$\log K_p=0.5945(\pm0.936)+\frac{175.1(\pm101.7)}{T}\,. \tag{4}$$

Therefore, the Gibbs energy for the mixed dimer reaction (Eq. 1) is calculated as follows:

$$\Delta G^\circ_r=-RT\ln K_p=-3352(\pm1947)-11.38(\pm1.79)T \quad [\text{J/2 mol-complex}]\,. \tag{5}$$

Thus, from the relation of $\Delta G^\circ_r=\Delta H^\circ_r-T\Delta S^\circ_r$, the

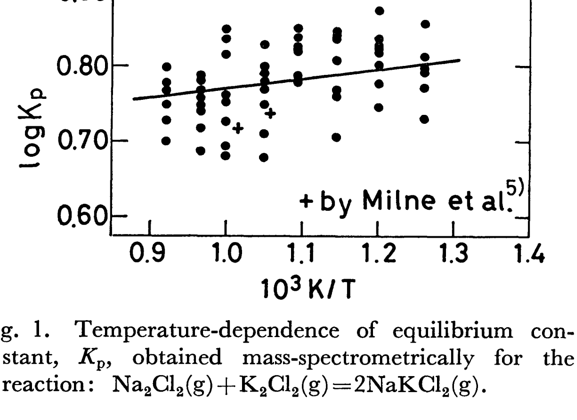

Fig. 1. Temperature-dependence of equilibrium constant, K_p, obtained mass-spectrometrically for the reaction: $Na_2Cl_2(g)+K_2Cl_2(g)=2NaKCl_2(g)$.

enthalpy and entropy changes at the central temperature in the experimental temperature range were:

$$\Delta H^\circ_{\mathrm{r},940\,\mathrm{K}} = -1.67\pm0.97\ [\mathrm{kJ\,mol^{-1}}], \tag{6}$$

$$\Delta S^\circ_{\mathrm{r},940\,\mathrm{K}} = 5.69\pm0.90\ [\mathrm{J\,K^{-1}\,mol^{-1}}]. \tag{7}$$

The formation energy of $\mathrm{NaKCl_2(g)}$, ΔU, in the following gaseous reaction:

$$\frac{1}{2}\begin{bmatrix}\mathrm{Na^+\text{-}Cl^-} \\ | \qquad | \\ \mathrm{Cl^-\text{-}Na^+}\end{bmatrix} + \frac{1}{2}\begin{bmatrix}\mathrm{K^+\text{-}Cl^-} \\ | \qquad | \\ \mathrm{Cl^-\text{-}K^+}\end{bmatrix} = \begin{bmatrix}\mathrm{Na^+\text{-}Cl^-} \\ | \qquad | \\ \mathrm{Cl^-\text{-}K^+}\end{bmatrix} + \Delta U, \tag{8}$$

was calculated from the equation:

$$\Delta U = U_{\mathrm{NaKCl_2}} - \frac{1}{2}(U_{\mathrm{Na_2Cl_2}} + U_{\mathrm{K_2Cl_2}}), \tag{9}$$

where U denotes the potential energy of each ionic dimer compared to the completely separated ions. The values of $U_{\mathrm{Na_2Cl_2}}$ and $U_{\mathrm{K_2Cl_2}}$ were given to be -1266 and $-1119\ \mathrm{kJ\,mol^{-1}}$ respectively by Milne and Cubicciotti.⁶⁾ They also provided the following equation for $U_{\mathrm{NaKCl_2}}$:

$$U_{\mathrm{NaKCl_2}} = \left(-\frac{2}{a} - \frac{2}{b} + \frac{1}{c} + \frac{1}{d} + \frac{153.3}{a^{8.6}} + \frac{401.3}{b^{8.6}} + \frac{22.86}{c^{8.6}} + \frac{439.4}{d^{8.6}}\right) \times 1389\ [\mathrm{kJ\,mol^{-1}}], \tag{10}$$

by assuming pure ionic-bonding in all dimers and a diamond-shaped structure for $\mathrm{NaKCl_2}$, as shown in Fig. 2, and by employing a model suggested by Pauling.⁷⁾ Numerical analyses for Eq. 10 gave a set of the geometrical parameters: $a=2.49$, $b=2.85$, $c=3.70$, and $d=3.83$ Å which resulted in the minimum energy of the $\mathrm{NaKCl_2}$ mixed dimer; $U^{\mathrm{MIN}}_{\mathrm{NaKCl_2}}=-1195$ kJ mol⁻¹. Consequently, we obtained $\Delta U \simeq -2.5$ kJ mol⁻¹ from Eq. 9.

On the other hand, a combination of Eq. 6 with the heats of formation⁸⁾ for $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Cl^+}$, $\mathrm{Na_2Cl_2}$, and $\mathrm{K_2Cl_2}$, leads to $\Delta H^\circ_{\mathrm{f},940\mathrm{K}}=-1248\ \mathrm{kJ\,mol^{-1}}$ for the heat of formation of the mixed dimer $\mathrm{NaKCl_2}$ from separation $\mathrm{Na^+}$, $\mathrm{K^+}$, and $\mathrm{Cl^-}$ ions. If the heat capacities of the dimer molecules are the same, the values of ΔU and $U^{\mathrm{MIN}}_{\mathrm{NaKCl_2}}$ may be compared directly with those of the $\Delta H^\circ_{\mathrm{r},940\mathrm{K}}$ and $\Delta H^\circ_{\mathrm{f},940\mathrm{K}}$ mentioned above. The direct comparison gave good agreement which strongly suggests that each bond in the dimer molecules of $\mathrm{Na_2Cl_2}$, $\mathrm{K_2Cl_2}$, and $\mathrm{NaKCl_2}$ is almost ionic and that the mixing of $\mathrm{Na^+}$, and $\mathrm{K^+}$ ions in the mixed dimer $\mathrm{NaKCl_2}$ contributes to a lesser extent to the enhancement of bond strength.

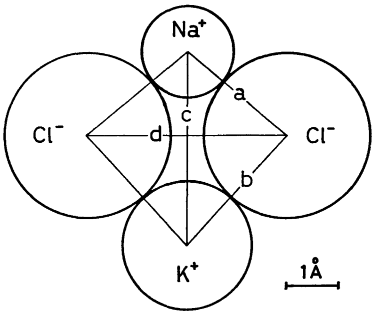

Fig. 2. Schematic representation for a structure of $\mathrm{NaKCl_2}$ molecule.

Table 1. Calculated entropy values for gaseous dimers, $\mathrm{Na_2Cl_2}$, $\mathrm{K_2Cl_2}$, and $\mathrm{NaKCl_2}$, at 940 K

Dimers	S_{trans} / kJ K mol⁻¹	S_{rot} / kJ K mol⁻¹	S_{vib} / kJ K mol⁻¹
$\mathrm{Na_2Cl_2}$	191.989	119.997	102.462
$\mathrm{K_2Cl_2}$	195.025	128.440	126.194
$\mathrm{NaKCl_2}$	193	128	116.7[a]

[a] Estimated from the equation: $S_{\mathrm{vib,NaKCl_2}}=\Delta S^\circ_{\mathrm{r},940\,\mathrm{K}}+(S_{\mathrm{total,Na_2Cl_2}}+S_{\mathrm{total,K_2Cl_2}})/(S_{\mathrm{trans,NaKCl_2}}+S_{\mathrm{rot,NaKCl_2}})$.

Table 1 shows the translational, ratational, and vibrational entropies for the $\mathrm{NaKCl_2}$ molecule at 940 K calculated on the basis of the statistical thermodynamics⁹⁾ using the molecular weight, the vapor pressure, the product of the moment of inertia ($I_AI_BI_C=1.224\times10^{-38}\ \mathrm{kg^3\,m^6}$) and the $\Delta S^\circ_{\mathrm{r},940\mathrm{K}}$, along with those for $\mathrm{Na_2Cl_2}$ and $\mathrm{K_2Cl_2}$ dimers calculated using the required data from the JANAF Tables.⁸⁾ It can be seen from the table that the entropy change in the isobonding mixed-dimer reaction, Eq. 1, is very small and that this small entropy change is brought about mainly by the change in the rotational entropy.

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