

Transient State Theory of Significant Liquid Structure Applied to Alkali Earth Chlorides

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용융 알칼리토금속 염화물에 대한 천이상태 이론의 적용

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초 록

액체구조의 천이상태 이론을 알칼리토금속 염화물에 적용시켜서 상태함울 유도하였다. 이 상태함으로부터 SrCl₂ 와 BaCl₂ 의 증기압, 몰부피, 엔트로피등의 열역학적 성질을 계산하여 실험치와 비교하였으며, 천이상태 이론이 용융염에도 잘 적용된다는 결론을 얻었다.

INTRODUCTION

As it is revealed in the x-ray analysis, when ionic liquids melt the internuclear distance and the coordination number are decreased; and they show a local order.¹⁾ On the other hand, the density is decreased largely upon melting.²⁾ The transient state theory of significant liquid structure, proposed by S. Chang *et al.*, which assumes the introduction of Frenkel and Schottky type holes in ionic liquids, explains the above experimental facts very well.³⁾

Authors in cooperation with a few other scientists applied the theory to fused alkali halides.⁴⁾ This work is the further application of the theory to alkali

earth halides, as liquids of alkali earth halides have much more complicated structures.

THEORY

According to the transient state theory of significant liquid structure, as in the case of significant liquid structure theory,⁵⁾ molecular-size holes are introduced upon fusion and the number of the holes increase with the elevation of temperature. In ionic liquids, it is assumed that the holes are Frenkel and Schottky types as in the case of lattice defects in solids. However, since the number of the holes, or vacancies, are much larger in liquids than in solids, the formation of vacancies which are sufficiently large to accommodate a triple ions (MX₂) can be expected. Accordingly, although the ionic liquids are composed

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of ions and neutral triple ions (MX_2), the diffusive movement is supposed to involve a simultaneous movement of neutral triple ions. In this movement, it can be assumed that a fraction of such a MX_2 type cation hole is exclusively available to cations only in order to retain local order. This fraction results from a cation hole. Considering geometrical hindrance and strong interactions among the neighboring ions, an anion cannot enter and occupy any $\frac{1}{2}$ portion of the remaining fraction, but can enter into a particular $\frac{1}{2}$ portion which only is geometrically allowable.

Chlorides of barium and strontium have fluorite type structures; in other words, a face-centered cubic lattice of cations are interpenetrated by a simple cubic lattice of chloride ions.⁶⁾ Accordingly, a cation has 12 nearest neighbors, while an anion has 6 first nearest neighbors which are most closely located, 12 second nearest neighbors which are less closely located, and 8 third nearest neighbors which are still less closely located in a perfect lattice. Owing to the strong ionic interactions, it is probable that the holes in the first nearest neighbors are only available to an anion. Therefore, the coordination numbers of cation and anion can be given by $12V_s/V_{t+}$ ($=n_+$) and $6V_s/V_{t-}$ ($=n_-$), respectively. Here, V_s and $V_{t\pm}$ are molar volumes of solid and that of liquid at the melting point, respectively. Since $N(V-V_s)/V_s$ holes are introduced in a mole of liquid, the number of available holes to a cation is $n_+(V-V_s)/V_s$, and that of an anion is $n_-(V-V_s)/V_s$.

Considering the above facts, the partition function according to the transient state theory can be written as

$$F = \frac{(N_{s+} + N_{t+})!}{N_{s+}! N_{t+}!} \left[\left(\frac{T}{\theta_{s+}} \right)^3 e^{E_{s+}/RT} \right]^{N_{s+}} \left[n_+ \frac{V-V_s}{V_s} \left(\frac{T}{\theta_{t+}} \right)^3 e^{E_{t+}/RT} \right]^{N_{t+}} \left[\frac{T}{\theta_{s-}} \right]^3 e^{E_{s-}/RT} \left[\frac{(N_{s-} + N_{t-})!}{N_{s-}! N_{t-}!} \left[\left(\frac{T}{\theta_{t-}} \right)^3 e^{E_{t-}/RT} \right]^{N_{t-}} \left[n_- \frac{V-V_s}{V_s} \left(\frac{T}{\theta_{s-}} \right)^3 e^{E_{s-}/RT} \right]^{N_{s-}} \right]^{N_{s-}} \left[\frac{(2\pi mkT)^{3/2} (V-V_s)}{h^3} \frac{8\pi^2 IkT}{2h^2} \prod_{i=1}^3 \frac{1}{1 - e^{-h\nu_i/kT}} \right]^{N_s} \frac{1}{N_s!} \quad (1)$$

where,

$$N_{s+} = \frac{1}{2} N_{s-} = N \frac{V_s}{V}$$

$$N_{t+} = \frac{1}{2} N_{t-} = N \frac{V_s}{V} (1 - \alpha)$$

$$N_s = N \frac{V - V_s}{V}$$

Here, E_{s+} and E_{s-} are the ground state energies of the solid-like cations and anions, respectively. θ_{s+} and θ_{s-} are the Einstein characteristic temperatures of the solid-like cations and the transient state cations, respectively. θ_{t+} and θ_{t-} represent same properties for anions. Since the liquids are in the high temperature range, the solid-like and the transient state ions are represented as classical oscillators. D is the dissociation energy of the neutral triple ions. And the remaining notations have usual physical meanings. Throughout the notation, the subscripts + and - stand for cations and anion, respectively.

Although ions move predominantly as neutral triple ions into the MX_2 type holes, it is still possible for an ion to move into a single hole by gaining enough energy to overcome the electrostatic atmosphere. These ionic species may be MX^+ and X^- in large, and a few other types.⁷⁾ The contribution of these species to the partition function is neglected, because the fraction of these species can be negligible due to the extremely high energy of dissociation of the triple ions.

Using the thermodynamic equilibrium condition, $\frac{\partial \ln F}{\partial \alpha} = 0$, and Stirling's approximation for factorial terms, equation 1 can be simplified as

$$F = \left(\frac{T}{\theta_{s+}} \right)^3 \left(\frac{T}{\theta_{s-}} \right)^3 e^{E_s/RT} [1 + \lambda_+(x-1)e^{-\omega_+}]^3 \left[\frac{(2\pi mkT)^{3/2} eV}{h^3} \frac{8\pi^2 IkT}{N} \frac{1}{2h^2} \prod_{i=1}^3 \frac{1}{1 - e^{-h\nu_i/kT}} \right]^{N_s} \quad (2)$$

where,

$$x = V/V_s$$

$$E_s = E_{s+} + 2E_{s-} - D$$

$$\lambda_+ (= \lambda_-) = \frac{1}{4^{1/2}} \frac{\theta_{s+} \theta_{s-}^2}{\theta_{t+} \theta_{t-}^2} e^{D/kT}$$

$$\omega_+ = \frac{a_+}{n_+} \frac{E_s}{(x-1)RT}, \quad \omega_- = \frac{a_-}{n_-} \frac{E_s}{(x-1)RT}$$

Here, n_+ stands for $n_+(V-V_s)/V_s$. It is assumed that the energy differences between the solid-like and the transient state are the same in both of cation and anion, and are proportional to E_s , heat of MX_2 type vacancy formation, and inversely proportional to the neighboring vacancies, $n_+(x-1)$, a_+ and a_- being the proportionality constants.

CALCULATIONS AND RESULTS

The parameters in the partition function are determined by the similar way used for alkali halides.⁽⁴⁾ The obtained values are listed in Table 1.

TABLE 1. Parameters and some Physical Properties.

	BaCl ₂	SrCl ₂
θ_{r+} (°K)	127.31	186.07
θ_{r-} (°K)	250.58	292.51
θ_{v+} (°K)	126.44	177.77
θ_{v-} (°K)	248.87	279.47
E_s (Kcal/mole)	79.78	78.75
n_+	10.886	10.661
$(a/n_+) \times 10^3$	0.68814	1.49390
V_s (c. c./mole)	59.55	51.65

Since the partition function is related to Helmholtz free energy as

$$A = -kT \ln F, \quad (3)$$

various thermodynamic properties can be calculated by the use of thermodynamic relations. Calculations are made at several temperatures. The calculated results are plotted and compared with experimentally observed values in Figure 1, 2, and 3.

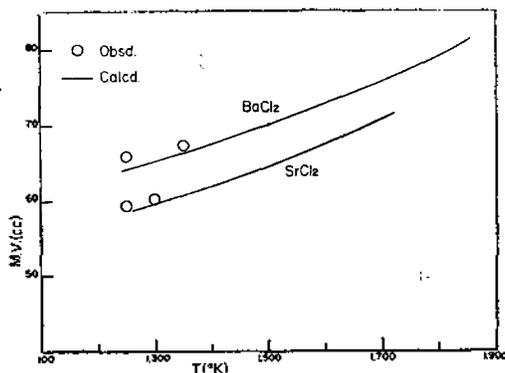


Fig. 1. Molar Volume vs. Temperature Curves

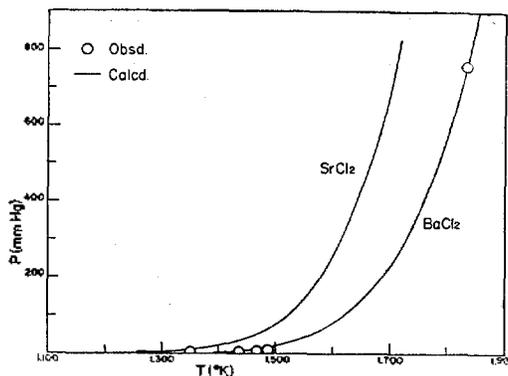


Fig. 2. Vapor Pressure vs. Temperature Curves.

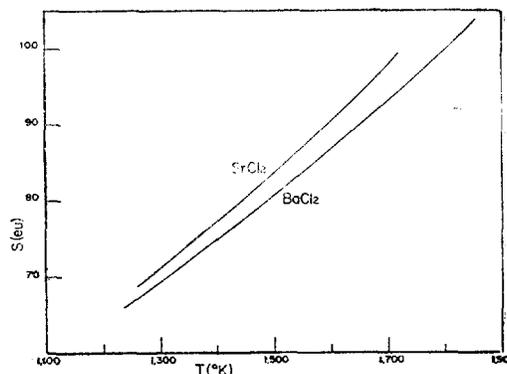


Fig. 3. Entropy vs. Temperature Curves

DISCUSSION

The calculated values agree well with experimentally observed values. However, only the experimental values available are in the vicinity of the melting point;⁽⁵⁾ and could not compare at any other points.

Experimental boiling point data vary widely depending on the experimental method, ranging from 1523 to 2150 °K for SrCl₂ and ranging from 1833 to 2100 °K for BaCl₂.^(6,7) The calculated values are 1710 and 1833 °K for SrCl₂ and BaCl₂, respectively. Accordingly the comparison seems meaningless.

The liquid entropies are calculated. Again the comparison is not possible since no experimental data are available. Considering high temperature, the calculated values are reasonable.

The calculated thermodynamic properties are satisfactory in general. In view of the fact that the pro-

posed model works very well to the chlorides 2A and the halides belonging to 1A group⁹⁾ it can be concluded that the model is appropriate for ionic liquids on the whole.

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