

Transient State Theory of Significant Liquid Structure Applied to Fused Salts

by

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액체 구조의 천이상태이론의 용융에 대한 적용

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요 약

액체 구조의 천이상태 이론을 용융염에 확장시켜서 액체염의 상태함수를 유도하였다. 이 상태함수를 액체할로젠화알칼리들에 적용시켜 증기압, 몰부피, 엔트로피 등의 열역학적 성질을 계산한 결과 측정치와의 좋은 일치를 보여주었다.

Introduction

The ionic liquids are composed of ions and ion pairs. The main difference between the structure of ionic liquids and molecular liquids is that the ions are surrounded by oppositely charged particles in the nearest neighbor. The attractive force between particles of the opposite sign and the repulsive force between particles of the same sign are very strong. Therefore, a cation will predominantly have anions in the closest neighbor, and vice versa. However, the main diffusive movements in ionic liquids are supposed to involve the simultaneous movement of cation and anion in the same direction, as was suggested by G. J. Dienes for solids.⁽¹⁾

In 1957 J. O'M. Bockris and N. E. Richards

reported their theoretical works on ionic liquids.⁽²⁾ Since then, many others tried to improve the partition function for ionic liquids;⁽³⁾ among them, noted is the C. M. Carlson's proposal for the partition function of ionic liquids according to the "Significant Liquid Structure Theory".⁽⁴⁾ Although C. M. Carlson's work results in good agreement with experimental data, it fails to predict the equilibrium vapor pressures. Besides, the original assumption in formulating partition function to treat the ionic liquids same as molecular liquid raises many debatable questions in a sense of physical picture, because the attractive force which forms the ion pairs is electrostatic in nature. Moreover, they did not consider the dissolving process of ionic compound in a polar solvent in formulating the partition function.

Authors treated the fused alkali halides according to the transient state theory of significant liquid structure.

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re, as the first trial, because their physical properties are considerably well known. ^(5,6,7)

Partition Function

In formulating the partition function for the fused alkali halides, it is assumed that the holes are Schottky and Frenkel type, and cation holes, for example, are exclusively available for cations only. Considering a salt of NaCl, for example, the occupation of an anion hole by a cation requires an energy of approximately 200 k cal/mole, as may be estimated from the electrostatic theory, which is very much higher than either heat of fusion, 6.8 k cal/mole, or heat of vaporization, 40.5 k cal/mole. ⁽⁸⁾

Although ions move predominantly as ion pairs into the paired holes, it is still possible for an ion to move into a single hole by gaining enough energy to overcome the electrostatic atmosphere.

Since the alkali halide liquids are in the high temperature range, the solid-like and the transient molecules can be considered as the classical oscillators.

Considering the above facts, in formulating the partition function for this work, alkali halides are treated similar to the equimolar binary mixtures of respective cations and anions. ^(5,6,7)

$$\begin{aligned}
 F = & \frac{(N_{s+} + N_{t+})!}{N_{s+}! N_{t+}!} \left[\left(\frac{T}{\theta_{s+}} \right)^3 e^{E_{s+}/RT} \right]^{N_{s+}} \\
 & \cdot \left[n \frac{V - V_s}{V_s} \left(\frac{T}{\theta_{t+}} \right)^3 e^{E_{t+}/RT} \right]^{N_{t+}} \\
 & \cdot \frac{(N_{s-} + N_{t-})!}{N_{s-}! N_{t-}!} \left[\left(\frac{T}{\theta_{s-}} \right)^3 e^{E_{s-}/RT} \right]^{N_{s-}} \\
 & \cdot \left[n \frac{V - V_s}{V_s} \left(\frac{T}{\theta_{t-}} \right)^3 e^{E_{t-}/RT} \right]^{N_{t-}} \\
 & \cdot \left[\frac{(2\pi m k T)^{3/2} (V - V_s)}{h^3} \right]^{N_{g+}} \\
 & \cdot \frac{1}{N_{g+}!} \left[\frac{(2\pi m k T)^{3/2} (V - V_s)}{h^3} \right]^{N_{g+}} \\
 & \cdot \frac{1}{N_{g-}!} \left[e^{-D/RT} \right]^{N_{g+}} \\
 & \cdot \left[\frac{(2\pi m k T)^{3/2} (V - V_s)}{h^3} \frac{8\pi^2 I k T}{h^2} \frac{1}{1 - e^{-h\nu/kT}} \right]^{N_{g-}} \\
 & \cdot \frac{1}{N_{g-}!} \dots \dots \dots (1)
 \end{aligned}$$

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

$$N_{g+} = N_{g-} = N \frac{V - V_s}{V} \tau, \quad N_{g-} = N \frac{V - V_s}{V} (1 - \tau)$$

The numbers of cations and anions in each state, i. e. solid-like, transient, and gas-like, are considered

to be equal, since cations and anions are supposed to move simultaneously. Of the gas-like portion, $N(V - V_s)/V$, τ is the fraction of free ions and the remaining $(1 - \tau)$ is the fraction of ion pairs. E_i is the ground state energies of the solid-like ions. θ_s and θ_t are the Einstein characteristic temperatures of the solid-like ions and the transient state ions, respectively. n is the number of the nearest neighboring sites around a given ion. D is the dissociation energy of the gas-like molecule, i. e. ion pair. And the other notations have usual physical meanings. Throughout the notation, the subscripts + and - stand for cation and anion, respectively.

Using the thermodynamic equilibrium condition, $\frac{\partial \ln F}{\partial \alpha} = 0$, equation (1) can be simplified as follows;

$$\begin{aligned}
 F = & \left[\left(\frac{T}{\theta_{s+}} \right)^3 \left(\frac{T}{\theta_{s-}} \right)^3 e^{E_s/RT} (1 + \lambda(x-1)e^{-\omega/RT})^2 \right]^{N/2} \\
 & \cdot \left\{ \frac{(2\pi \sqrt{m_+ m_-} k T)^{3/2}}{h^3} e^{-D/2RT} \frac{eV}{N\tau} \right\}^{2N(1-\frac{1}{2})\tau} \\
 & \cdot \left\{ \frac{(2\pi m k T)^{3/2}}{h^3} \frac{eV}{N(1-\tau)} \frac{8\pi^2 I k T}{h^2} \right. \\
 & \cdot \left. \frac{1}{1 - e^{-h\nu/kT}} \right\}^{N(1-\frac{1}{2})(1-\tau)} \dots \dots \dots (2)
 \end{aligned}$$

where $\lambda = n \left(\frac{\theta_{s+}}{\theta_{t+}} \right)^3 = n \left(\frac{\theta_{s-}}{\theta_{t-}} \right)^3$

$$x = \frac{V}{V_s}$$

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

$$\omega = \frac{\epsilon}{n(x-1)} = E_{s-} - E_{t+} = E_{t-} - E_{s+}$$

It is assumed, also, that the energy differences between the solid-like and the transient state are the same in both of cation and anion, and are inversely proportional to the neighboring vacancies $n(x-1)$, ϵ being the proportionality constant.

Calculation and Result

Helmholtz free energy is related to the partition function as follows;

$$A = -kT \ln F \dots \dots \dots (3)$$

Differentiating equation (3) with respect to τ and putting the results equal to zero, the following equation is obtained;

$$\frac{\tau^2}{1-\tau} = \frac{\left\{ \frac{(2\pi \sqrt{m_+ m_-} k T)^{3/2}}{h^3} \frac{eV}{N} \right\}^2 e^{-D/RT}}{\frac{(2\pi m k T)^{3/2}}{h^3} \frac{8\pi^2 I k T}{h^2} \frac{1}{1 - e^{-h\nu/kT}} \frac{eV}{N}} \dots \dots \dots (4)$$

The parameters included in the partition function are determined at the triple point according to the way proposed by S. Chang et al. (6) Here, an additional consideration special to the salt is counted in this work. In ionic liquids, a given solid-like ion oscillate harmonially at the equilibrium position. Accordingly, the Einstein characteristic temperature of the ion is inversely proportional to the square root of the mass, and proportional to the square root of the ground state energy. (9)

$$\frac{\theta_{s+}}{\theta_{s-}} = \sqrt{\frac{m_-}{m_+}} = \frac{\theta_{t+}}{\theta_{t-}}$$

$$\sqrt{\frac{E_{s-}}{E_{t-}}} = \frac{\theta_{s-}}{\theta_{t-}} = \frac{\theta_{s+}}{\theta_{t+}} = \sqrt{\frac{E_{s+}}{E_{t+}}} = \sqrt{\frac{E_s}{E_t}} = \sqrt{\frac{E_s}{E_t - \omega}}$$

Therefore

$$\lambda = n \left(1 - \frac{\omega}{E_s} \right)^{-3/2}$$

The values of parametrs determined and some other properties which appear in the partition functions are listed in Table 1.

From equations (3) and (4), various thermodynamic properties are calculated by the use of thermodynamic relations. The calculated values are listed in Tables 2, 3, 4, and 5 with the experimentally observed values for the comparison.

Table 1. Parameters and some physical properties

	NaCl	KCl	NaBr	KBr
θ_{s+} , °K	194.35	136.79	166.57	97.60
θ_{s-} , °K	156.50	143.65	89.34	68.27
θ_{t+} , °K	192.72	135.53	165.02	96.60
θ_{t-} , °K	155.19	142.32	88.51	67.57
E_s , k cal/mole	56.07	54.15	51.91	48.08
ϵ , k cal/mole	0.628	0.743	0.704	0.770
V_s^{\ddagger} , c. c./mole	35.46	45.97	41.45	52.48
n	11.62	11.57	11.59	11.57

Table 2. Thermodynamic properties of NaCl

T/T_f^*	P ^{oim} calc.	P ^{oim 8} obs.	V ^{cc} calc.	V ^{cc 8} obs.	S ^{e. u.} calc.	S ^{e. u.} obs.
1.0	0.00026	...	37.55	37.55	36.39	40.8
1.1	0.00235	0.00295	38.54	39.01	38.56	42.4
1.2	0.0125	0.0137	39.36	40.58	40.08	43.8
1.3	0.0496	0.0499	40.21	42.30	41.86	45.3
1.4	0.1603	0.1611	41.48	44.16	43.33	...
1.5	0.4147	0.4343	42.12	46.19	44.69	...
1.607**	1.000	...	43.26	...	46.06	...

* T_f : 1073.0 °K, ** T_b , calc.; 1724.3 °K (T_b obs. †; 1712.2 °K)

ΔS_f calc.; 5.06 e. u., ΔS_b calc.; 24.16 e. u.

ΔS_f obs. †; 6.3 e. u., ΔS_b obs. †; 23.5 e. u.

Table 3. Thermodynamic properties of KCl

T/T_f^*	P ^{oim} calc.	P ^{oim 8} obs.	V ^{cc} calc.	V ^{cc 8} obs.	S ^{e. u.} calc.	S ^{e. u.} obs.
1.0	0.00035	0.00061	49.02	49.02	39.02	42.2
1.1	0.00264	0.00376	50.24	51.06	40.77	43.8
1.2	0.0135	0.0172	51.37	53.28	42.85	45.2
1.3	0.0522	0.0615	52.58	55.70	44.47	46.6
1.4	0.1608	0.1637	53.83	58.36	45.93	...
1.5	0.4166	0.4133	55.16	61.27	47.30	...
1.639**	1.000	...	56.68	...	48.67	...

* T_f : 1049.0 °K, ** T_b , calc.; 1687.7 °K (T_b obs. †; 1689.2 °K)

ΔS_f calc.; 5.57 e. u., ΔS_b calc.; 23.58 e. u.

ΔS_f obs. †; 5.8 e. u., ΔS_b obs. †; 23.1 e. u.

Table 4. Thermodynamic properties of NaBr

T/T_f^*	$P_{calc.}^{atm}$	$P_{obs.}^{atm}$	$V_{calc.}^{cc}$	$V_{obs.}^{cc}$	$S_{calc.}^{e.u.}$	$S_{obs.}^{e.u. 10}$
1.0	0.00034	...	44.15	44.15	40.27	42.4
1.1	0.00248	0.00369	45.22	45.75	42.31	44.0
1.2	0.0123	0.0156	46.42	47.46	44.18	45.4
1.3	0.0468	0.0526	47.25	49.31	45.60	46.7
1.4	0.1421	0.1492	48.25	51.31	46.98	...
1.5	0.3629	0.3687	49.41	53.48	48.32	...
1.639**	1.000	...	50.90	...	49.88	...

* T_f : 1023.0 °K, ** T_f calc.; 1667.1 °K (T_b obs.; 1666.0 °K)

ΔS_f calc.; 19.18 e. u., ΔS_b calc.; 22.91 e. u.

ΔS_f obs.; 6.0 e. u., ΔS_b obs.; 23.2 e. u.

Table 5. Thermodynamic Properties of KBr

T/T_f^*	$P_{calc.}^{atm}$	$P_{obs.}^{atm}$	$V_{calc.}^{cc}$	$V_{obs.}^{cc}$	$S_{calc.}^{e.u.}$	$S_{obs.}^{e.u. 10}$
1.0	0.00037	0.00045	56.14	56.14	44.90	45.6
1.1	0.00268	0.00281	57.61	58.36	46.93	47.2
1.2	0.0120	0.0128	58.81	60.76	48.57	48.6
1.3	0.0413	0.0464	60.04	63.37	50.04	50.0
1.4	0.1192	0.0948	61.49	66.21	51.46	...
1.5	0.5883	0.5630	62.61	69.32	52.62	...
1.677**	1.000	...	65.06	...	54.66	...

* T_f : 1008.0 °K, ** T_f calc.; 1690.0 °K (T_b obs.; 1653.0 °K)

ΔS_f calc.; 8.81 e. u., ΔS_b calc.; 29.58 e. u.

ΔS_f obs.; 6.94 e. u., ΔS_b obs.; 22.4 e. u.

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Discussion

Owing to the strong interactions between the neighboring ions, the short range order is still maintained in the ionic liquids. This fact is confirmed by the X-ray analysis.⁽¹¹⁾ It is conceivable, therefore, that the number of the nearest neighboring sites are close to 12, which is exhibited in the crystal lattice of alkali halides.

In the ordinary liquid ranges of the ionic liquids, τ being order of 10^{-10} , is negligibly small, which means that the most of the moving units are ion pairs. This fact is due to the extremely high heat of dissociation of the ion pairs, which is about 100 kcal/mole.

The calculated thermodynamic properties are in good agreement with experiments. This means that the proposed model for the fused alkali halides is very well applicable.

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