Thermodynamics of Molten Pure Rare-Earth Chlorides : LaCl_3 , PrCl_3 , and NdCl_3

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The significant structure theory of liquids has been successfully applied to molten LaCl_3 , PrCl_3 , and NdCl_3 by using the revised partition function which is improved by introducing a correction coefficient. The calculated thermodynamic properties such as the vapor pressure, expansivity, and entropy agree well with the observed values. Finally, the correction coefficient is discussed in details and it is found that the concept of correction function seems to be appropriate.

1 Introduction

A theory of the liquid state is one of the most important problems in statistical mechanics and is essential for further development of many branches of physics and physical chemistry. However, because of the strong interaction between particles and high degree of disorder in the liquid state, the theoretical analysis has remained far behind the theories of the gaseous and crystalline states.

In this decade, the theory has been developed in two ways. The first method, pioneered by Mayer and Kirkwood among others and pursued widely at present, provides the aesthetic pleasure of initial rigor. But approximations always have to be made in this method to make the mathematics tractable. When such difficulties are overcome, a noteworthy advance will be achieved. The second is the approach by use of models, with which one visualizes a physical model of the liquid, translates the picture into a partition function, and then calculates the thermodynamic properties of the liquid. If the model is reasonable and the calculated results agree sufficiently with experimentally determined values, one can assume that the model is an adequate description of the liquid. The model approach to the liquid state has been discussed by many workers¹⁻³⁾. Eyring⁴⁾ proposed his

significant structure theory of liquids, by which calculated values for liquids such as simple argon⁵⁾, organic and inorganic compounds⁶⁻¹⁰⁾ have been obtained in good agreement with the observed ones.

In this paper the authors aim to apply the modified significant structure theory to the molten pure rare-earth chlorides LaCl_3 , PrCl_3 , and NdCl_3 . The calculated thermodynamic properties such as the vapor pressure, expansivity, and entropy will be compared with the literature values.

2 Partition Function

According to the theory of significant structure, a liquid is approximated to have both solid-like and gas-like degrees of freedom. The mole fractions of both degrees of freedom are V_s/V and $(V-V_s)/V$, respectively, where V_s is the molar volume of solid-like molecules in the liquid and V is the molar volume of the liquids itself. Thus, the molar partition function of the liquid is given by

$$f_l = f_s^{N(V_s/V)} \cdot f_g^{N(V-V_s)/V} \quad (1)$$

where N is Avogadro's number, and f_s and f_g are the partition functions for the solid-like and gas-like degrees of freedom, respectively.

If the lattice vibration in the solid-like molecules can be approximated by an Einstein oscillator for a monatomic liquid such as argon, f_s can be written as

$$f_s = \frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \cdot (1 + n_h e^{-\epsilon_h/RT}) \quad (2)$$

where θ is Einstein's characteristic temperature, E_s is the molar sublimation energy, n_h is the

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number of available vacancies per one of the solid-like molecules, and ϵ_h is the energy required for a hole-molecule pair formation through which the exchanging position can be achieved. The n_h and ϵ_h can be written as $n_h = n(V - V_s)/V_s$ and $\epsilon_h = aE_s V_s / n(V - V_s)RT$, n and a being constants. The partition function of the gas-like degree of freedom, f_g , is approximated by the ideal gas partition function for the $(N(V - V_s)/V)$ gas-like molecules moving in the excess volume $(V - V_s)$.

This gives us

$$f_g^{N(V-V_s)/V} = \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \cdot (V - V_s) \right\}^{N(V-V_s)/V} \left\{ \left(\frac{N(V - V_s)}{V} \right)! \right\}^{-1} \quad (3)$$

Substituting equations 2 and 3 into 1, we obtain

$$f_1 = \left\{ \frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \left(1 + n \frac{V - V_s}{V_s} \exp\left(-\frac{aE_s V_s}{(V - V_s)RT} \right) \right) \right\}^{N(V_s/V)} \times \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \right\}^{N(V-V_s)/V} \quad (4)$$

Here, the last term is obtained by using Stirling's approximation $X! = (X/e)^X$ for $(N(V - V_s)/V)!$ in equation 3.

Suppose the structure of rare-earth chlorides LaCl_3 , PrCl_3 , and NdCl_3 may be assumed to have ionic crystals as for the solid-like portion and tetra-atomic molecules as for gas-like portion. The power of solid-like portion of the partition, $N(V_s/V)$, has to be replaced by the power $4N(V_s/V)$ because a mole of rare-earth chloride crystal contains $4N$ particles, provided that all the ions are assumed to be equivalent. The term, E_s/N , is the sublimation energy for a rare-earth chloride molecule. Expressing the sublimation energy per ion, we divide E_s by 4. The partition function of the solid-like degree of freedom, f_s , can be written as follows:

$$f_s = \frac{e^{E_s/4RT}}{(1 - e^{-\theta/T})^3} \left\{ 1 + n \left(\frac{V - V_s}{V_s} \right) \exp\left(-\frac{aE_s V_s}{4(V - V_s)RT} \right) \right\} \quad (5)$$

For the description of the partition of the gas-like significant structure of the tetra-atomic rare-earth chloride molecules it is assumed that the moments of inertia and ground state vibrational frequencies are the same as in the vapor

phase:

$$f_g = \frac{(2\pi mkT)^{3/2} eV}{h^3 N} \cdot \frac{8\pi^2 (8\pi^3 I_{xyz})^{1/2} (kT)^{3/2}}{\sigma h^3} \prod_i \left\{ 1 - \exp\left(-\frac{h\nu_i}{kT} \right) \right\}^{-1} \quad (6)$$

Here, σ and I_{xyz} are the symmetry number and moment of inertia of the gas-like molecules, respectively, and ν_i is a ground state vibrational frequency. The first term is due to the translational, the second to the rotational, and the third to the vibrational motion. In combining equations 5 and 6, we write equation 7 in the form of

$$f_1 = \left\{ \frac{e^{E_s/4RT}}{(1 - e^{-\theta/T})^3} \left(1 + n \left(\frac{V - V_s}{V_s} \right) \exp\left(-\frac{aE_s V_s}{4(V - V_s)RT} \right) \right) \right\}^{4N(V_s/V)} \times \Omega \left\{ \frac{(2\pi mkT)^{3/2} eV}{h^3 N} \cdot \frac{8\pi^2 (8\pi^3 I_{xyz})^{1/2} (kT)^{3/2}}{h^3} \cdot \prod_i \left(1 - \exp\left(-\frac{h\nu_i}{kT} \right) \right)^{-1} \right\}^{N(V-V_s)/V} \quad (7)$$

In this equation, a correction coefficient, Ω , attributed to the restrictions of the motions of the gas-like molecules and the formation of dimer, trimer, and so on appears.

3 Calculations

The Helmholtz energy, A , written in terms of the partition function is

$$A = -kT \ln f_1 \quad (8)$$

Fig. 1 Isotherm for the Helmholtz energy vs. molar volume

Table 1 Constants and parameters for LaCl_3 , PrCl_3 , and NdCl_3

	LaCl_3	PrCl_3	NdCl_3
Molecular weight, M	245.27	247.27	250.60
Symmetry number*, σ	3	3	3
Principal moment**, $I_{xyz} = I_x \cdot I_y \cdot I_z / 10^{-111} \text{g} \cdot \text{cm}^2$	0.97623	0.90458	0.89072
Sublimation energy***, $E_s / \text{erg} \cdot \text{mol}^{-1}$	3.8450×10^{12}	2.3806×10^{12}	2.3597×10^{12}
Molar volume of solid ⁺ , $V_s / \text{cm}^3 \cdot \text{mol}^{-1}$	63.7	61.51	60.62
Molar volume of liquid ⁺ , $V_m / \text{cm}^3 \cdot \text{mol}^{-1}$	77.3	76.6	75.9
Averaged coordination number ⁺⁺ , Z	10.5	10.5	10.5
Parameter, n	8.652651	8.431521	8.386161
Parameter, a	0.013688	0.017102	0.017848
Parameter of Einstein temperature ⁺⁺⁺ , θ_0 / K	188.463	211.864	204.091
θ_1 / K	-0.025002	-0.023939	-0.0227605

* It was assumed that the gas molecule has the pyramidal tetra-atomic molecule.

** As the origin the center of gravity of molecule is taken.

*** Ref. 21)

+ Ref. 23)

++ The values calculated from the ionic radius of solid atom.

+++ Ref. 20)

Since the Hemholtz energy is calculated by using equations 7 and 8, they are plotted as a function of volume at a constant temperature, as shown in Fig. 1. If a common tangent to the points corresponding to the liquid and vapor phases can be drawn Fig. 1, the vapor pressure is given by the slope of the common tangent and the volume of the liquid and vapor, V_l and V_g , are obtained from the abscissas of the two points of contact. The vapor pressure, P , expansivity, α , and entropy, S , of liquids are given by the following equations, which are evaluated by using equations 7 and 8:

$$\begin{aligned}
 P &= -\left(\frac{\partial A}{\partial V}\right)_T \\
 \alpha &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = -\frac{(\partial P / \partial T)_V}{V(\partial P / \partial V)_T} \\
 &= -\frac{1}{V} \frac{(\partial / \partial T)(kT)(\partial \ln f_i / \partial V)_T}{kT(\partial^2 \ln f_i / \partial V^2)_T} \\
 S &= -\left(\frac{\partial A}{\partial T}\right)_V = k \left\{ \frac{\partial (T \ln f_i)}{\partial T} \right\}_V \quad (9)
 \end{aligned}$$

The parameters used for the calculations are listed in Table 1. The calculations were carried out by using HITAC 8700 of Tokyo Institute of Technology. The parameters n and a , shown in Table 1, can be determined easily by using the coordination number Z , the molar volumes of solid and liquid at melting point, V_s and V_m

(see Appendix). Since the gas molecules included no light atoms such as hydrogen, carbon, and oxygen display the vibrational spectra in the far infrared region, the six values of ground state vibrational frequencies of 350, 250, 150, 150, 100 cm^{-1} were used for the calculation of f_g (Since such six ground state vibrational frequencies are not changed markedly with rare-earth chlorides, it may be reasonable to choose above frequencies for the calculation of f_g).

The correction coefficient, Ω , was determined from the molar volume of liquids, V_l , which was calculated from the density published in the previous papers^{22, 23}.

Now if the correction coefficient depends only on the temperature, one curve can be drawn, as given by the isotherm in Fig. 1, by substituting the temperature and correction coefficient to equations 7 and 8. In this case, if the value of the correction coefficient is selected accurately, the calculated V_l should agree with the one measured. In this study, the molar volumes of liquids, V_l , could be calculated by using the arbitrarily chosen several correction coefficients, Ω , at constant temperature and then the correction coefficient was determined so that the calculated molar volume coincides with the observed molar volume of liquid at the same tempera-

ture.

4 Results and Discussion

4.1 Correction coefficient

The correction coefficients corresponding to the observed molar volumes of the molten PrCl_3 at various temperatures are shown in Fig. 2. The correction coefficients for the molten LaCl_3 and NdCl_3 are also given in Fig. 2. It is seen from Fig. 2 that obtained correction coefficient for the molten PrCl_3 and NdCl_3 is smaller than 1, and it is larger than 1 for the molten LaCl_3 . It is also seen from Fig. 2 that these correction coefficients tend to approach to 1 when the temperature increases. This suggests that the restrictions of motion of the gas-like particles in the

Fig. 2 Variation of the correction coefficient Ω with the temperature

molten chlorides are relaxed gradually with temperature, and that the gas-like particles in the molten chlorides at very high temperatures may move in the same way as the gas molecules.

4.2 Thermodynamic properties of the molten LaCl_3 , PrCl_3 , and NdCl_3

The vapor pressures, expansivities, and entropies of the molten pure rare-earth chlorides, such as LaCl_3 , PrCl_3 , and NdCl_3 , are evaluated by using equation 9 and the calculated correction coefficients. In Figs. 3, 4, and 5 are shown the evaluated and observed values²⁰⁻²³⁾ of these mol-

Fig. 3 Calculated and observed vapor pressures for PrCl_3 and NdCl_3 melts

Fig. 4 Calculated and observed expansivities for PrCl_3 and NdCl_3 melts

ten chlorides. The calculated values agree well with the observed ones.

5 Appendix

The parameters n and a in equation 7 can be calculated as follows. Near the melting point, the liquid approximates an expanded solid-like lattice with the addition of vacancies. Thus, near the melting point, the fraction of the

Fig. 5 Calculated and observed entropy for LaCl_3 , PrCl_3 , and NdCl_3 melts

neighboring sites, Z , which is empty and therefore available for occupancy is

$$Z\left(\frac{V_m - V_s}{V_m}\right) = \left(Z \frac{V_s}{V_m}\right) \cdot \left(\frac{V_m - V_s}{V_s}\right) \\ = n \frac{V_m - V_s}{V_s}$$

Hence,

$$n = Z \frac{V_s}{V_m}$$

The averaged solid molecule has kinetic energy equal to $(3/2)kT$. Now if a molecule is to occupy a neighboring position, additional kinetic energy should be equal to or in excess of the value of kinetic energy, which is required for the movement of the other $(n-1)$ neighboring molecule into this vacancy. If an average molecule shares its retention time equally between two neighboring positions, its energy density has to be divided by two. Since a molecule will move in the time of $(1/Z)$ th of its retention time in the direction of any neighbor, the average kinetic energy of $(n-1)$ ordinary molecules will provide a vacancy with kinetic energy $(1/2)(3/2)kT(n-1)/Z$. This is the value of $aE_s V_s / (V_m - V_s)N$ which must have at the melting point

$$\epsilon_h = \frac{aE_s V_s}{V_m - V_s} = \frac{1}{2} \left(\frac{3}{2} N k T \right) \frac{n-1}{Z}$$

Since the entropy of melting per molecule is

very close to $(3/2)k = E_m/NT$ and since the energy of melting per mole, E_m , is due to introducing vacancies into the solid with no change in kinetic energy, we have $E_m = (V_m - V_s)E_s/V_m$. Accordingly, we can write

$$\frac{aE_s V_s}{V_m - V_s} = \frac{1}{2} E_m \frac{n-1}{Z} = \frac{1}{2} \frac{V_m - V_s}{V_m} E_s \frac{n-1}{Z}$$

Hence,

$$a = \frac{1}{2} \frac{n-1}{Z} \frac{(V_m - V_s)^2}{V_m V_s}$$

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