

《Original》 **Fusion Mechanism of Liquid according
to the Significant Liquid Structure Theory**

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(Received December 26, 1970)

Abstract

With the use of the significant structure theory of liquid, the fusion criteria has been successfully explained. To test the theory of fusion, the excess volume upon melting has been calculated for some liquids such as simple liquids and fused salts.

The results obtained show good agreements between theory and experiment. The theoretical study on the fused salt may be useful to understand the properties and structure of high temperature liquids in the atomic reactor.

요 약

액체에 대한 Significant Structure 이론을 토대로 하여 용해의 기본적 원리를 성공적으로 논의 하였다.

용해의 이론을 실증하는 보기로서 용접에서의 부피의 팽창을 용융열등 몇가지 액체에 대해 계산하였다.

계산결과와 실험치와 이론치 사이에 좋은 일치율을 보여주고 있다.

용융열의 연구는 원 자료에 쓰는 고온도 액체의 성질과 구조를 이해 하는데 도움을 줄 것이다.

I. Introduction

Any acceptable liquid theory should predict the experimental observations as well as lead to the quantitative calculations of thermodynamic and transport properties. Significant structure theory¹⁾ is such a model and has been most widely applied to the various liquids among other theories.²⁻⁵⁾

In this paper, we discuss the mechanism of fusion according to the significant liquid structure theory. The most striking characteristics upon melting are a marked volume change and a marked increase in fluidity. The fact that X-ray diffraction⁶⁾ indicate little change in the nearest neighbor distance with melting suggests a retention of small regions of solid-like structure interspersed with loose, gas-like regions where molecules unsupported by nearest

neighbors fall freely for short distances.

In alternative languages, this can be understood if some of the molecules are replaced by "fluidized vacancies" which are quite different from the essentially static locked in vacancies of the solid state and is moved by cooperative action of all neighbors.

The detailed discussion of so called "fluidized vacancies" is omitted here and reviewed elsewhere¹⁾ This fine grained heterogeneity is attested to by the fact that liquids contain no solid-like or gas-like nuclei large enough to form foci for either supercooling or bumping of liquids.

In order that loose gas-like regions can exist in a liquid state without collapse must be a local balance between the kinetic energy density tending to make a region expand and the potential energy density tending to make these regions collapse.

This balance is necessary for a phase to be dynamically stable and accounts for the existence of melting. In the solid range, the fluidized vacancies is not stable since this balance is not established. This criteria accounts for the melting phenomena. According to the significant liquid structure theory, the fusion criteria is due to the stability of this excess loose region (i.e., fluidized vacancies) upon melting.

It is not because the molecules start colliding with their neighbors⁷⁾, nor because the lattice allows a minimum of the pressure for the change in the volume⁸⁾, nor because the lattice is unstable under a shearing stress⁹⁾, nor because the solid is at a critical temperature in which the structure goes from an ordered state to disorder structure goes from an ordered state to disorder¹⁰⁾, nor because the particle becomes unstable under the action of its neighbors.¹¹⁾

To test the fusion criteria from the significant liquid structure model, the deduced partition function is used to evaluate the excess volume

upon melting

II. The partition function deduced from the model

Straight forward considerations from the model lead to the values of $\frac{V-V_s}{V}$ for the mole fraction of degrees of gas-like molecules and the remainder $\frac{V_s}{V}$ are solid like¹⁾. Here, V and V_s are the molar liquid volume and the molar solid like volume.

Vacancies confer positional degeneracy on the solid like molecules. The number of additional sites will be the number of vacancies around solid like molecules $n_h = n(V - V_s)/V_s$ multiplied by the probability that the molecules has the required energy E to preempt the site from competing neighbors. E is inversely proportional to n_h and directly proportional to the energy of sublimation, E_s .

In view of the above, the partition function f_N for a mole of liquid at the melting temperature can be expressed as

$$f_N = (f_s)^{NV_s/V_m} (f_g)^{N(V-V_s)/V_m} \dots \dots \dots (1)$$

Here N is Avogadro's number, V_m is the molar liquid volume at melting temperature, f_s and f_g are the partition function of solid-like molecules with the degeneracy factor and that of gas-like molecules.

Usually, the Einstein oscillator is represented for the solid like molecules, while the non-localized independent ideal gas partition function is used for the gas-like molecules.

For a simple liquid such as argon, we can write the partition function at melting temperature f_l as follows.¹²⁾

$$f_l = \left\{ \frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \left(1 + n \frac{\Delta V}{V_s} e^{-\frac{e E_s V_s}{\Delta V RT}} \right) \right\}^{-\frac{V_s}{V_s + \Delta V} N} \left\{ \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} \frac{e^{(V_s + \Delta V)}}{N} \right\}^{-\frac{\Delta V}{V_s + \Delta V} N} \dots (2)$$

Here $\Delta V = V_m - V_s$

The values of sublimation energy E_s , Einstein characteristic temperature θ , and the molar

solid like volume V_s are obtained from the solid state and the values of a and n are evaluated theoretically.

The other symbols has their usual significance. Near the melting point, the fraction of the neighboring positions, Z , which are empty and therefore available for occupancy is

$$Z \left(\frac{V_m - V_s}{V_m} \right) = Z \left(\frac{V_s}{V_m} \right) \frac{V_m - V_s}{V_s} \\ = n \frac{V_m - V_s}{V_s}, \text{ hence } n = Z \frac{V_s}{V_m} \dots\dots (3)$$

We next calculate a . The average solid like molecule has kinetic energy equal to $\frac{3}{2}RT$

If a molecule is to preempt a neighboring position in addition to its original position, it must have additional position, it must have additional kinetic energy $\frac{1}{2} \left(\frac{3}{2}RT \right) \frac{n-1}{Z}$. This value is equivalent to

$$\epsilon = \frac{aE_s V_s}{V_m - V_s} = \frac{1}{2} \left(\frac{3}{2}RT \right) \frac{n-1}{Z} \dots\dots (4)$$

here

$$E_m = \frac{3}{2}RT = \frac{(V_m - V_s)}{V_m} E_s$$

Then, we obtain

$$a = \frac{n-1}{Z} \cdot \frac{1}{2} \cdot \frac{(V_m - V_s)^2}{V_m V_s} \dots\dots\dots (5)$$

For fused salt¹³⁾, the following partition function at melting temperature is used;

$$f_l(\text{salt}) = \left\{ \frac{e^{(E_s/RT) \left(\frac{V_s + \Delta V}{V_s} \right)^{\frac{1}{3}}}}{(1 - e^{-\theta/T})^3} \right. \\ \left. \left[1 + n \frac{\Delta V}{V_s} \exp \frac{aE_s \left(\frac{V_s + \Delta V}{V_s} \right)^{\frac{1}{3}}}{2RT \Delta V} V_s \right] \right\}^{2NV_s/V_s + \Delta V} \\ \times \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \cdot \frac{8\pi^2 IkT}{h^2} \frac{1}{1 - e^{-h\nu/kT}} \right\}^N \frac{V}{V_s + \Delta V} \dots\dots\dots (6)$$

Here, I and ν are the moment of inertia, and the ground state vibrational frequency respectively. The other notations have been defined previously.

III. Evaluation of excess volume upon melting

From thermodynamics, we could calculate the excess volume upon melting ΔV considering the condition that the chemical potential at the

solid (μ_s) is equal to that of the liquid (μ_l).

Then, we have

$$\mu_s = \left(\frac{\partial G_s}{\partial N} \right)_{T, P} = \mu_l = \left(\frac{\partial G_l}{\partial N} \right)_{T, P} \dots\dots\dots (7) \\ -kT \ln f_{solid} + \frac{PV_s}{N} = -kT \ln f_l + \frac{P(V_s + \Delta V)}{N}$$

Here f_{solid} is given as f_l at $\Delta V=0$

For simple liquid like Argon, Equation (7) can be rewritten as

$$\ln \frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \\ = \ln \left[\frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \left(1 + n \frac{\Delta V}{V_s} e^{-\frac{aE_s V_s}{\Delta V RT}} \right) \right]^{\frac{V_s}{V_s + \Delta V}} \\ + \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{e(V_s + \Delta V)}{N} \right] \frac{\Delta V}{V_s + \Delta V} - \frac{P \Delta V}{RT} \dots\dots\dots (8)$$

Equation (8) may be expressed in the following simplified notations.

$$\ln f_{solid} = \frac{V_s}{V_s + \Delta V} \ln f_s + \frac{\Delta V}{V_s + \Delta V} \ln f_g - \frac{P \Delta V}{RT} \dots\dots\dots (9)$$

$$\text{where } f_{solid} = \frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3}$$

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

and

$$f_g = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{e(V_s + \Delta V)}{N}$$

Solving for $\Delta V/V_s$, then, we obtain

$$\frac{\Delta V}{V_s} = \frac{\ln f_s - \ln f_{solid} - P \Delta V / RT}{\ln f_{solid} - \ln f_g + P \Delta V / RT} \dots\dots\dots (10)$$

Eq. (10) is the condition for the excess volume upon melting. This transcendental equation can not be solved directly. The values of f_s and f_g are to be evaluated in terms of ΔV and V_s for a given temperature.

In alternative manner, the excess volume upon melting ΔV may be easily evaluated by plotting the Helmholtz free energy, A against volume V at melting temperature, and finding out the condition that $\left(\frac{\partial A}{\partial V} \right)_T = 0$.

Here, Helmholtz free energy, A is given by $A = kT \ln f_l$.

IV. Results and Discussion

With the use of Eq. (2), the excess volume upon melting is calculated for simple liquids

such as Argon, Krypton and Xenon to justify our explanation of the fusion of liquid.

In this calculations, the values of E_s , V_s and θ are obtained from solid state¹²⁾ and Eqs. (3) and (5) were used to calculate n and α in Eq. (2). Thus, the introduction of adjustable parameters is avoided. In Table 1, the Helmholtz free energy of liquid Argon versus ΔV at $T=T_m$ is shown. The calculated results obtained are shown in Table 2. Good agreement was obtained between experiment and theory.

As a further check of the applicability of the theory, the excess volume upon melting for fused salts have been evaluated. In Eq. (6), the values of E_s , θ , V_s , and n are obtained from solid data¹³⁾ and the Eq. (2). The theoretical value of Argon for α is used.

The other notations has their usual statistical mechanical significance and can be easily obtained.

The calculated results are summarized in Table 3 and one sees good agreement between theory and experiment.

Acknowledgement

The authors express their appreciation to the donors of the Petroleum Research Funds administered by the American Chemical Society for support of this research.

Table 1. The values of Helmholtz free energy of liquid Argon with increasing ΔV at $T=T_m$

$\Delta V(\text{cc})$	$A_1(\text{cal/mole})$
2.50	-2218
3.00	-2219
3.50	-2220
4.00	-2219
4.50	-2218

Table 2. Excess volume upon melting of liquid A, Kr and Xe

	$\Delta V/V_m(\text{Calc.})$ (%)	$\Delta V/V_m(\text{Obs.})$ (%)
A	12.49	10.88

Kr	11.28	13.27
Xe	9.42	14.47

*Taken from reference 12.

Table 3. Excess Volume upon melting of fused salts KCl, KBr and NaBr.

	$\Delta V(\text{Calc.})$ (cc)	$\Delta V(\text{Obs.})$ (cc)
KCl	7.00	7.23
KBr	7.00	7.89
NaBr	5.00	7.93

*Taken from reference 14.

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