

The Significant Structures of Liquid Fluorine

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액체 플루오르의 구조에 관하여

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요 약

H. Eyring 등에 의하여 제안된 액체구조에 관한 이론에 따라서 액체의 partition function을 정하였다. parameter E_s , V_s , θ , a 는 앞서 저자들에 의해 제안된 방법에 의하여 정하였고, 이렇게 정해진 partition function을 써서 액체의 몰부피, 증기압, 한계점, 증발엔트로피 및 표면장력등을 계산한 결과 실험치와 잘 맞는 값을 얻었다.

Abstract

The partition function of liquid fluorine were developed by applying the theory of significant structures in liquids. The molar volume, vapor pressure, entropy of vaporization and surface tension of the liquid were calculated over a wide temperature range. The critical properties for the liquid were also calculated. The results show good agreement with experimental observations.

Partition Function

With the use of the significant structure theory of liquids proposed by H. Eyring and coworkers^{2) 3) 4)}, T. R. Thomson and coworkers⁵⁾ developed the partition function of liquid fluorine. They calculated thermodynamic properties and surface tension which have given good agreement with experimental values. But they employ, in their calculation, for parameter n the value of 14.3 which is contrary to the common understandings.

Applying the modified theory of significant liquid structure proposed by Chang *et al*¹⁾, the authors cal-

culated the following properties with reasonably good agreements with observed values: vapor pressure, molar volume, entropy of vaporization, critical constants, surface tension.

This report is one of a series of studies applying the modified theory of significant liquid structures to various liquids, and is the last of the sequence on the halogens.

Fluorine has a normal entropy of fusion (2.278 e. u.) and has a solid state transition at about 8° below its melting point. This indicates that fluorine molecules probably rotate in the solid state at the melting point.

This has led the authors to assume that both the solid-like molecules as well as the gaslike molecules rotate freely, and for simplicity, the solid is treated as a

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three-degree Einstein oscillator. Accordingly, the following form of partition function is assumed for the liquid fluorine.

$$f = \left[\frac{\exp(E_s/RT)}{[1 - \exp(-\theta/T)]^3} \left\{ 1 + n \left(\frac{V - V_s}{V_s} \right) \exp \left(- \frac{aE_s V_s}{n(V - V_s)RT} \right) \right\} \right]^{N \frac{V_s}{V}} \left[\frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \right]^{N \frac{V - V_s}{V}} \left[\frac{1}{1 - e^{-h\nu/kT}} \cdot \frac{8\pi^2 IkT}{2h^2} \right]^N$$

where E_s , θ , V_s are parameters corresponding respectively to the heat of sublimation, Einstein characteristic temperature and molar volume of the solid-like molecules in the liquid. And a is a parameter involved in the strain energy term $\frac{aE_s V_s}{n(V - V_s)}$ for a shifting molecule to one of the available neighboring sites. The moment of inertia, I ,⁶⁾ is 25.3×10^{-40} gr. cm² and the molecular vibration frequency, $\omega = \frac{\nu}{c}$,⁷⁾ is 892.1 cm⁻¹.

Results

Assuming the relation $n = 12 \times \frac{V_s}{V_m}$, the parameters for liquid fluorine are determined in a similar manner developed by Chang *et al.*¹⁾ where V_s is the molar volume of solid like molecule in the liquid and V_m is the molar volume of liquid under the equilibrium between the liquid and vapor at the melting point. The results are given in Table 1.

Table 1. Melting point and parameters.

7) T : 53.54°K	E_s : 1752.1 cal/mole
7) 8) P : 0.002182 atm.	θ : 52.504 °K
V_s : 21.94 c.c.	n : 11.851
9) V_m : 22.215 c.c.	a : 0.0011770
8) S_l : 14.586 e.u.	

(a) **Molar volume and vapor pressure.** Calculations are made from this partition function for molar volumes and vapor pressures for temperatures between the melting and boiling points. The results obtained are shown in Table 2 and compared with observed values.

Table 2. Molar volume and vapor pressure.

Volume (c.c.)			Vapor pressure (atm.)		
Temp. (°K)	$V_{cal.}$	$V_{obs.}^{9)}$	% error	$P_{cal.}$	$P_{obs.}^{9)}$
53.54	22.215	22.215	0.00	0.002182	0.002182
66.03	23.089	23.270	-0.777	0.05131
77.22	24.047	24.328	-1.15	0.3402	0.3689
85.02	24.849	25.157	-1.22	0.9200	1.0000

The difference between calculated values and observed values are less than 1.22% for the molar volume and less than 8% for the vapor pressure. The agreements are good even for the vapor pressure. For a liquid with a very low vapor pressure at the low melting point, such as liquid fluorine, accurate measurement of vapor pressure is extremely difficult and a slight error in the observed value can significantly affect the magnitude of parameters in the partition function.

(b) **Critical point properties and entropy of vaporization.** A further check on the accuracy of the function was made for the vaporization entropy at the boiling point and for the critical point properties. The results are given in Table 3. Again, good agreements can be observed with observed values for the vaporization entropy.

Table 3. Critical point properties and entropy of vaporization.

	T_c (°K)	P_c (atm)	V_c (c.c.)	S_l (at m. p., e.u.)	S_v (at b. p., e.u.)
Calculated	156.59	64.1	72.40	14.586	18.894
Observed	144 ¹⁰⁾	55 ¹⁰⁾	...	14.586 ⁹⁾	18.378 ⁹⁾
% error	8.74	16.55	...	0.00	2.81

Surface tensions of liquid fluorine at various temperatures are calculated in a similar manner as proposed by Chang and his coworkers¹⁾. The calculated values are compared with the experimental values as shown in Table 4.

Table 4. Surface tension of liquid fluorine.

Temp. °K	% of 1st.	contribution of 2nd.	layers 3rd.	cal. (dyne/cm)	obs. (dyne/cm)	% error
53.54	94.80	5.20	...	22.52
66.03	92.30	7.70	...	19.48	18.8	3.62
77.22	88.88	10.40	0.72	16.73	15.7	6.15
85.02	85.47	13.22	1.31	14.52

Summary

Parameters in the partition function for liquid fluorine are determined, thermodynamic properties and surface tension are calculated in a manner similar to that was proposed by Chang *et al.*

The agreements between the calculated and observed values are good for molar volumes, and the entropy of vaporization at the boiling point. Somewhat less, but reasonably good agreements are observed for surface tensions and vapor pressures.

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