

## Significant Structure of Liquid Ethylene Chloride

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### 액체 염화에틸렌의 구조에 관하여

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요 약

고체상태에서 trans-form으로 존재하는 염화에틸렌은 액체로 되면서 그 일부가 gauche-form으로 변한다. H. Eyring 등에 의해서 제안된 액체구조에 관한 이론에 따라서 이 물질에 대한 분배함수를 정하고, 분배함수속에 들어 있는 parameters  $E_s$ ,  $\theta$ ,  $V_s$  및  $\alpha$ 를 정하였다. 이와 같이 해서 정한 분배함수를 써서 몰부피, 증기압, 한계점 성질, 증발엔트로피 및 표면장력 등을 계산하여 실험치와 비교하였다.

#### Abstract

Upon melting, a part of ethylene-chloride molecules in trans-form in the solid state changes into gauche-form. The partition function for the material was developed according to the significant structure theory of liquid proposed by H. Eyring and his co-workers, and the parameters  $E_s$ ,  $\theta$ ,  $V_s$ , and  $\alpha$ , therein, are determined by the manner developed by Chang, et al.

The molar volume, vapor pressure, vaporization entropy, critical point properties and surface tension of the liquid were calculated. The results are in good agreement with experimental values.

#### Introduction

Henry Eyring and his co-workers<sup>1,2,3</sup> assumed, in their significant structure theory of liquid, a liquid molecule to possess both the solid-like and the gas-like degrees of freedom. A molecule around the vacant hole in the liquid assumes the gas-like degree of freedom when it jumps into the hole. They liquid as a product of two partition functions for the liquid as a product of two partition functions, one for the portion having the solid-like degree of freedom and the other having the gas-like degree of freedom; where  $N$  is the Avogadro number and  $1/x$ , which

$$f = f_s \frac{N \frac{1}{x}}{f_g} \frac{N(1-\frac{1}{x})}{f_s}$$

represents contribution of the solid-like molecules, may be given by  $V_s/V$ ,  $V$  and  $V_g$  representing the molar volume of the liquid and of the molecules having the solid-like degree of freedom, respectively. The latter is one of the parameters involved in the partition function.

With the study of the Raman spectra of ethylene-chloride<sup>4,5</sup>, it was concluded that in the solid state all the molecules assume the trans-form( $C_{2h}$ ) in which the two chlorine atoms are at the farthest distance apart. In the gaseous or liquid state, however, the gauche-form( $C_2$ ) coexists under the thermal equi-

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brium due to the hindered internal rotation about the C-C bond as axis.

### Partition Function

From coexistence of the two isomeric forms in the liquid state, we assume the gas-like molecules in the liquid alone are under the thermal equilibrium between the two forms. The partition function for the ethylene-chloride, therefore, may be written as

$$f = f_s N \frac{1}{x} \left\{ f_{C_{2h}} \frac{N_{C_{2h}}}{N_{C_{2h}} + N_{C_2}} + f_{C_2} \frac{N_{C_2}}{N_{C_{2h}} + N_{C_2}} \right\} N \left( 1 - \frac{1}{x} \right),$$

where  $\frac{N_{C_{2h}}}{N_{C_{2h}} + N_{C_2}}$  and  $\frac{N_{C_2}}{N_{C_{2h}} + N_{C_2}}$  represent the fraction of the trans-form and the gauche-form, respectively. It can be determined at the various temperatures by the following equations<sup>6)</sup>:

$$\frac{N_{C_2}}{N_{C_{2h}}} = \frac{2f_{C_2}}{f_{C_{2h}}} e^{-\frac{\Delta E_s^0}{RT}}$$

$$\frac{f_{C_2}}{f_{C_{2h}}} = \left[ \frac{(I_A \cdot I_B \cdot I_C)_{C_2}}{(I_A \cdot I_B \cdot I_C)_{C_{2h}}} \right]^{\frac{1}{2}} \frac{\prod_{C_2}}{\prod_{C_{2h}}}$$

$$\prod_{C_{2h}} = \prod_{i=1}^{18} (1 - e^{-h\nu_i/kT})$$

$$\prod_{C_2} = \prod_{i=1}^{18} (1 - e^{-h\omega_i/kT})$$

where the 2 in the first equation comes from the two symmetric gauche-forms, the transition energy between the trans-form and gauche-form at the ground state,  $\Delta E_s^0$ , is known to be 1100 cal. through the spectroscopic study<sup>7)</sup>. The principal moment of inertias are calculated from the molecular configuration<sup>8) 9)</sup>.

$$\prod_{C_{2h}} = (I_A \cdot I_B \cdot I_C)_{C_{2h}}$$

$$= 335.729 \times 233.591 \times 558.114 \times 10^{-120}$$

$$\left[ \frac{\prod_{C_2}}{\prod_{C_{2h}}} \right]^{\frac{1}{2}} = 1.355$$

where the vibrational frequencies,  $\nu_i$  and  $\omega_i$ , are available from the literature<sup>7)</sup>.

We have assumed the free molecular rotation in the gaseous phase alone and write the partition function in detail as follows;

$$f_s = \frac{e^{E_s/RT}}{(1 - e^{-\theta/RT})^6} \left\{ 1 + n(x-1)e^{-\frac{aE_s}{n(x-1)RT}} \right\} \frac{1}{\prod_{C_{2h}}}$$

$$f_{C_{2h}} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \cdot \frac{eV}{N} \cdot \frac{\sqrt{\pi}(8\pi^2 kT)^{\frac{3}{2}} (\prod_{C_{2h}})^{\frac{1}{2}}}{2h^3} \cdot \frac{1}{\prod_{C_{2h}}}$$

$$f_{C_2} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \cdot \frac{eV}{N} \cdot \frac{\sqrt{\pi}(8\pi^2 kT)^{\frac{3}{2}} (\prod_{C_2})^{\frac{1}{2}}}{h^3} \cdot \frac{1}{\prod_{C_2}}$$

where  $E_s$  and  $\theta$  are parameters corresponding to the heat of sublimation and the Einstein characteristic temperature of the solid-like molecules, respectively. Values of  $E_s$  and  $\theta$  do not coincide with those of the solid due to the different environment in the solid and liquid states. And  $a$  is also a parameter involved in the strain energy term  $\frac{aE_s V_s}{n(V - V_s)}$  for a molecule shifting to one of the available neighboring sites. The  $n$  is a number of the nearest neighboring sites around a molecule. It is given by the relation  $n = Z \times \frac{V_s}{V_m}$ , where  $V_m$  is the molar volume of the liquid at the melting point and  $Z$  is the number of all the accessible neighboring sites nearest to a molecule.  $Z$  is taken 12, assuming a close-packed model. The parameters  $E_s$ ,  $V_s$ ,  $\theta$  and  $a$  are determined at the melting point in a similar way as developed by Chang, *et al.*<sup>10)</sup>

### Results

Owing to the low vapor pressure and low melting point, the vapor pressure and molar volume are extrapolated<sup>11) 12)</sup>. The heat of vaporization was taken as 8565 cal/mole. The melting point data and the parameters determined are listed in Table 1.

Table 1. Melting Point Data and Parameters.

$V = 74.20$ cc	$V_s = 73.22$ cc
$P = 2.4$ mm Hg	$E_s = 9405.94$ cal/mole
$T = 237.85^\circ\text{K}$	$\theta = 23.38^\circ\text{K}$
$\Delta H_{vap} = 8565$ cal/mole	$a = 1.6958 \times 10^{-3}$

Calculations are made from this partition function for molar volumes and vapor pressures at the various temperatures between the melting and the boiling points. The results are shown in Table 2 with an observed values. Relative error of 15% for the vapor pressure near the melting point is not so serious, since the observed value may also has 2 or 3 mm Hg. error which may amount up to 20% relative error.

Table 2. Molar Volume and Vapor Pressure.

Temp. ( $^\circ\text{K}$ )	Molar volume(cc)			Vapor pressure(atm)		
	Vcalc.	Vobs.	% error	Pcalc.	Pobs.	% error
237.85	74.20	74.20	0.0	0.0031	0.0031	0.0
270.75	76.08	76.96	-1.1	0.0275	0.0239	15.0
302.55	78.06	79.82	-2.2	0.1353	0.1277	5.9
323.14	79.52	81.84	-2.8	0.3136	0.3070	2.1
337.15	80.62	83.28	-3.2	0.5162	0.5189	0.5
357.15	82.45	85.35	-3.4	0.9814	1.0000	1.9

The vaporization entropy at the boiling point and critical point properties are calculated. Except the critical pressure, the results are in good agreement with observed values as shown in Table 3.

Table 3. Critical Point Properties and Entropy of Vaporization.

	Tc(°K)	Pc(atm)	Vc(cc)	$\Delta St$ (at b. p., e. u.)
Calculated	645.54	79.17	241.63	20.87
Observed <sup>12)</sup>	561.55	53.0	224.93	21.63 <sup>11)</sup>
% error	15.0	49.4	7.4	-3.7

Surface tensions are calculated in a similar way as proposed by Chang, *et al.*<sup>13) 14) 15)</sup> The calculated values exceed those of experimental values<sup>12)</sup> by more than 40 per cent. The deviation may be attributed to the assumption that the ethylene-chloride molecule is an ideal one, with non-polar and spherical structure. However, the tendency of variation with the temperature is close to the experiments.

Table 4. Surface Tension.

Temp (°K)	% contribution of layers			$\gamma_{calc.}$ (dyn e/cm)	$\gamma_{obs.}$	% error
	1st	2nd	3rd			
237.85	92.63	6.98	0.39	53.08		
270.75	89.81	9.24	0.95	48.54	34.55	40.5
302.55	87.94	11.25	0.81	43.32	30.10	43.9
337.15	84.34	14.21	1.45	37.34	25.40	46.9

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