

Structure and Properties of Liquid Carbon Tetrachloride (Part I)

by

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액체 사염화탄소의 구조와 성질 (제 1 보)

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요 약

H. Eyring 등의 액체의 구조에 관한 이론에 따라서 액체 사염화탄소의 Partition function을 정하였다. 이 Partition function에 쓰인 Parameter E_s , a , θ , V_s 등은 액체 안의 고체와 같은 분자의 고유한 값으로 새로운 방법 (4)으로 그 값들을 정하였다.

이렇게 정해진 Partition function을 써서 액체 사염화탄소의 몰부피, 증기압, 한계점, 증발엔트로피 및 표면 장력등을 계산하였다. 계산치와 실험치를 비교한 결과 몰부피와 증기압, 엔트로피의 값은 거의 일치하였다. 표면 장력 또한 실험치와 좋은 일치를 보여주는 값을 얻었다.

According to the "significant structure theory of liquids" of Henry Eyring and others (1) (2) (3), a liquid molecule possesses both solid-like and gas-like degrees of freedom.

A molecule around the hole assumes gas-like degrees of freedom when it jumps into the vacancy. The relative contributions of the two types are given by $\frac{V_s}{V}$ and $\frac{V-V_s}{V}$, respectively, where V_s is the molar volume of the solid-like molecules in the liquid (4), and V is the molar volume of the liquid at the various temperatures.

Hence the partition function of a liquid is written as a product of solid partition function f_s and gas partition function f_g ;

$$f = (f_s)^{N \frac{V_s}{V}} (f_g)^{N \frac{V-V_s}{V}}$$

Carbon tetrachloride has tetrahedral molecules rotating freely in the liquid phase as well as in the gaseous and solid phases. And the partition function for this

liquid compound is given as follows;

$$f = \left[\frac{e^{-\frac{E_s}{RT}}}{(1-e^{-\theta/RT})^3} \left\{ 1 + n \left(\frac{V-V_s}{V_s} \right) e^{\frac{-aE_s V_s}{n(V-V_s)RT}} \right\} \right]^{N \frac{V_s}{V}} \left[\frac{(2m\pi kT)^{3/2}}{h^3} \frac{eV}{N} \right]^{N \frac{V-V_s}{V}} \times \left[\frac{\pi^{1/2} (8\pi^2 h kT)^{3/2}}{12h^3} \prod_{i=1}^0 \right] \left[\frac{1}{1-e^{-h\nu_i/RT}} \right]^N$$

where E_s , θ , V_s are parameters corresponding to the heat of sublimation, Einstein characteristic temperature and molar volume of the solid-like molecules, respectively. And a is a proportionality constant, $\frac{aE_s \cdot V_s}{n(V-V_s)}$ giving the strain energy stored in the system as the molecule shifts to one of the neighboring available sites. And n is the number of nearest neighboring sites around a molecule accommodated by other molecules. The number n is given by the relation $n = Z \times \frac{V_s}{V_m}$, where Z is the number of all the accessible neighboring sites nearest to a molecule. For

a close-packed structure as in the present case of CCl_4 , $Z=12$. And V_m is the molar volume of the liquid at the melting point under its own vapor pressure.

In the previous works (1) (2) (3) (9) (10) (11), the parameters E_s , θ , V_s are taken to be the same as the respective values for solid.

But the values of these parameters may be different from those of solid because the environment of a molecule in the liquid phase is somewhat different from that in the solid phase. The parameters E_s , θ , V_s , and a for this liquid are determined in a manner developed by Chang et al. (6), using the equilibrium conditions between the liquid and vapor at the melting point.

The melting point data needed and the parameters determined are listed in tables 1 and 2.

Table 1. Melting point data (5) (6) (7).

$V = 92.12 \text{cc}$	$P = 8.45 \text{mmHg}$
$T = 250.22^\circ\text{K}$	$\Delta H_{vap} = 8240 \text{cal}$

Table 2. Parameters

$V_s = 89.39 \text{cc}$	$\theta = 53.53^\circ\text{K}$
$E_s = 4334.3 \cdot R$	$a = 0.003758$

Calculations are made from this partition function for molar volumes and vapor pressures at various temperatures. The results are shown in Table 3 and Figs 1 and 2, with comparisons to experimental findings (5) (8).

Table 3. Molar volume and vapor pressure.

Temp. $^\circ\text{C}$	Volume, cc			Vapor pressure, mm-Hg		
	Vcalc.	Vobs. (8)	% error	Pcalc.	Pobs. (5)	% error
0	94.01	94.25	-0.25	32.73	33.1	-1.12
20	95.78	96.53	-0.78	89.72	91	-1.43
50	98.79	100.20	-1.43	314.04		
76.75 (bp)	102.02	103.89	-1.83	784.07	760.	3.17

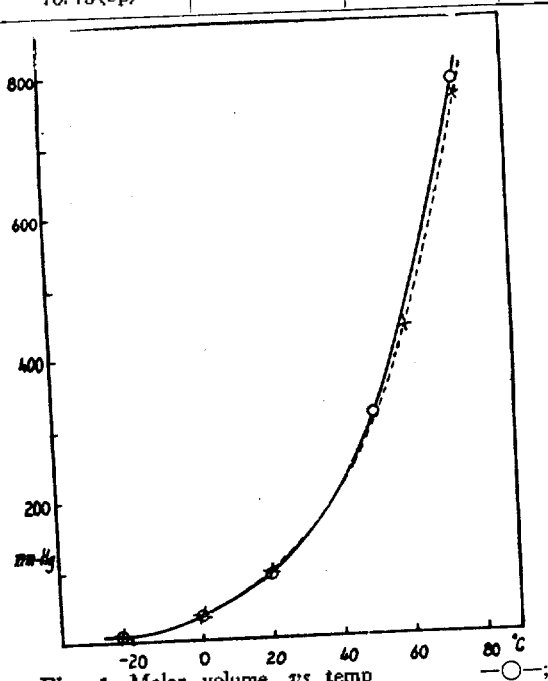


Fig 1. Molar volume vs temp. —○— calculated, ...×... experimental.

The departures from the experimental values are less than 1.83 percent for the molar volumes and less than 3.17 percent for the vapor pressures in the temperature

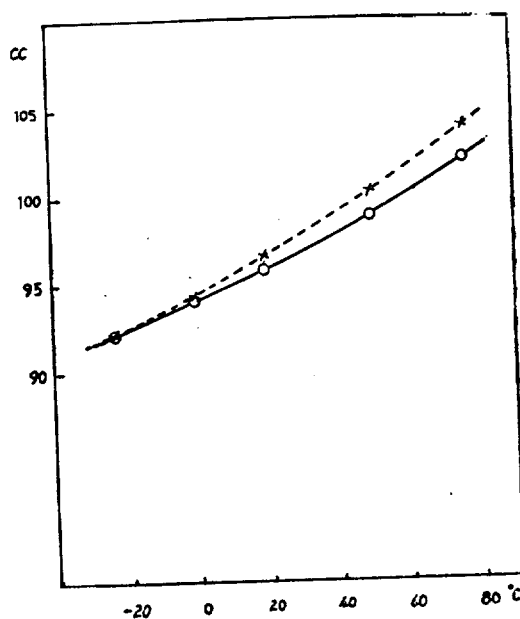


Fig 2. Vapor press. vs temp. —○— calculated, ...×... experimental.

range from the melting point up to the boiling point.

Also the vaporization entropy at the boiling point and the critical point properties are calculated, the

results are given in table 4. where again good agreements with observed data are shown.

Table 4. Entropy of vaporization and critical point properties.

	Svapn. at bp.	T _c , °K	P _c , atm.	V _c , cc.
Calculated	21.22eu	567.3	56.85	295.0
Observed (5)	20.41eu	556.3	45	275.7
% error	3.79	1.98	26.3	7.00

Surface tensions of CCl₄ at various temperatures are

Table 5. Surface tension of CCl₄.

Temp. °C	% Contribution of				Γ calc. dyne/cm	Γ obs(4) dyne/cm	% error
	1st layer	2nd layer	3rd layer	4th layer			
0	90.16	9.27	0.57	—	37.167	29.55	25.8
20	88.43	10.76	0.81	—	43.396	26.95	27.6
50	84.97	13.93	1.10	—	30.109	23.22	29.7
76.75 (bp)	85.58	16.41	1.81	0.21	26.158	20.00	30.8

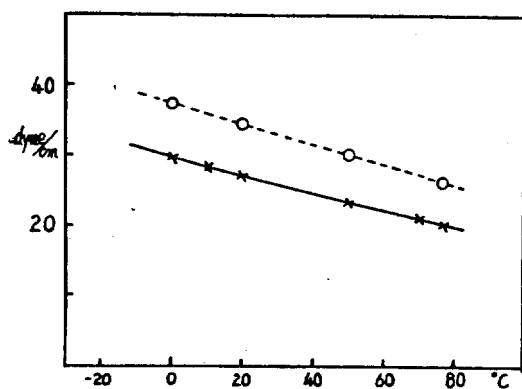


Fig. 3. Surface tension vs Temp.

Summary

The four parameters E_s , θ , a , and V_s are determined for this liquid in a manner developed by Chang et al. (6).

The agreements between the calculated and observed values are excellent for the molar volumes, vapor pressures and the boiling entropy.

Also the calculation for the surface tension has given reasonably good agreements. The tendency of variation of surface tension with temperature is nearly the same for the computed and observed values as shown by the slopes in the figure, an indication of a good agreement for surface entropy.

calculated by a method similar to that used by Chang and his coworkers for other liquids (9) (10) (11), where the surface tension is taken to be the excess free energy per unit surface area over that of the bulk liquid. For this calculation, however, E_{s1} is used in place of E_s in the expression of $\frac{p_0}{p_1}$ for the first layer. That is;

$$\frac{p_0}{p_1} = \text{Exp} \left[-\frac{E_{s1}}{2RT} \left(1 - \frac{T}{T_c} \right) \right]$$

The calculated values are compared to the experimental values as shown in table 5 and Fig. 3.

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