

# Theory of Surface Tension and Viscosity of Liquid

by

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## 액체의 표면장력과 점도에 관한 이론

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### 요 약

액체 분자는 고체, 천이상태 및 기체와 같은 자유도를 갖는다는 액체구조에 관한 천이상태이론을 적용하여 액체의 표면장력과 점도를 계산하여 측정치와 좋은 일치를 얻었다. 표면장력을 계산함에 있어서 표면 각층의 밀도는 이웃층 사이의 밀도를 주는 관계식으로부터 쉽게 얻었다. 그리고 액체가 점성흐름을 할 때 활성화된 분자는 흐르는 방향으로는 기체와 같은 자유도를 가지나, 이에 직교한 평면상에서는 천이상태 및 기체와 같은 자유도를 갖는다고 가정하였다.

### I. Introduction

There are several theories of liquid, the so-called cell theory<sup>(1)</sup>, hole theory<sup>(2)</sup>, radial distribution theory<sup>(3)</sup>, significant structure theory<sup>(4)</sup> and so on.

In actual application to the various liquids, significant structure theory is very powerful, although the theory has some theoretical defects. The theory has been applied not only to explain the thermodynamic properties, but also to explain surface tension and viscosity<sup>(5)</sup>. Some modification of the theory has been made by Chang et al<sup>(6)</sup>, and the modified theory has also been applied to various liquids.

And yet, no theory mentioned above was applied satisfactorily to surface tension and viscosity.

Recently, the theoretical defects of significant structure theory have been excluded by transient state theory proposed by H. Pak, W. Ahn, and S. Chang<sup>(7)</sup>. In

this paper, the respective theories of the surface tension and the viscosity of liquid are studied according to the transient state theory.

### II. Transient state theory of liquid

In the transient state theory, it is assumed that molecular-sized movable vacancies exist and that the liquid molecules are partitioned by three kinds of degrees of freedom, i. e., solid-like, transient, and gas-like,

by the fractions,  $\frac{V_s}{V}\alpha$ ,  $\frac{V_s}{V}(1-\alpha)$ , and  $\frac{V-V_s}{V}$ ,

respectively; where  $V_s$  is the molar volume of solid at the triple point,  $V$  is the molar volume of liquid and  $\alpha$  is a fractional number that can be determined by the thermodynamic equilibrium condition. According to the theory, the partition function of liquid is given as follow;

$$F = \left[ \frac{b_s e^{E_s/RT}}{(1-e^{-E_s/RT})^3} \left\{ 1 + n \frac{b_t(1-e^{-E_t/RT})^3}{b_s(1-e^{-E_t/RT})^3} \frac{V-V_s}{V_s} \exp \right. \right.$$

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$$\left( \frac{\epsilon}{n \frac{V-V_s}{V_s} RT} \right) \left] \right]^{V_s N} \left[ \frac{b_s (2\pi mkT)^{3/2}}{h^3} \frac{eV_s}{N} \right]^{V-V_s} \frac{V-V_s}{V} N \quad (1)$$

where  $b$  represents the partition function for the degrees of molecular rotation and interatomic vibration;  $\theta$ , the Einstein characteristic temperature;  $E_s$ , the ground state energy of the solid-like molecules; and  $\frac{\epsilon}{n \frac{V-V_s}{V_s}}$ , the

difference of the ground state energies between the solid-like and the transient molecule which is assumed to be inversely proportional to the neighboring vacancies,  $n \frac{V-V_s}{V_s}$ , around a molecule, where  $n$ , the nearest neighboring site, is equal to  $12 \frac{V_s}{V_t}$ ,  $V_t$  being the molar volume of liquid at the triple point; here, subscripts  $s$ ,  $t$ , and  $g$  indicate the states of the solid-like, the transient, and the gas-like, respectively.

From the partition function the Helmholtz free energy,  $A$ , of liquid can be found as follows:

$$-\frac{A}{RT} (= \phi) = \frac{1}{x} [\sigma + y + (x-1)(g + \ln x)] \quad (2)$$

where  $x = \frac{V}{V_s}$ ,  $\sigma = \frac{E_s}{RT} - 3 \ln(1 - e^{-\theta_s/T}) + \ln b_s$ ,

$$g = \ln \left[ b_g \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV_s}{N} \right]$$

and  $y = \ln [1 + \lambda(x-1)e^{-\omega}]$ ;

here,  $\lambda = n \frac{b_s}{b_t} \frac{(1 - e^{-\theta_s/T})^3}{(1 - e^{-\theta_t/T})^3}$  and  $\omega = \frac{\epsilon}{n(x-1)RT}$ .

Using equation (2), the various thermodynamic properties such as the molar volume, the vapor pressure and the entropy can easily be determined.

### III. The theory of the surface tension of liquid

#### Review of previous theory

Various theories of liquid have been applied to the surface tension. Cell theory was applied by Lennard-Jones and Corner<sup>(8)</sup>, hole theory by Eyring et al<sup>(9)</sup>, radial distribution theory by Kirkwood and Buff<sup>(10)</sup> and modified radial distribution theory<sup>(11)</sup> by Reiss et al<sup>(12)</sup> and Mayer<sup>(13)</sup>. In addition to the above, several other approaches are made<sup>(14)</sup>. Although these theories are very approximate; they, nevertheless, give a vivid picture of the liquid-vapor transition layers.

Applying the significant structure theory, Chang et al<sup>(15)</sup> obtained the densities of the transition layers by an iteration method and calculated surface tension for simple liquids. The theory has been extended by Chang et al<sup>(16)</sup> to various liquids.

Ree et al<sup>(17)</sup> have proposed another theory of surface tension applying the modified significant structure theory by means of cell. They assumed that the transition region is one molecular layer and calculated surface tension for various liquids.

The monomolecular assumption of the transition region was further assumed by Lu et al<sup>(18)</sup>. They obtained a simple equation for surface tension applying the significant structure theory and calculated surface tension for various liquids.

The monomolecular assumption of the transition region is not realistic. Chang's theory may be exact; however, this theory includes an iteration process in calculating the layer densities.

The calculated surface tension by all the above methods according to the significant liquid structure deviate about 10 to 60% from the observed values.

#### Proposed theory

The surface of liquid consists of several molecular layers as stated by various authors<sup>(10)(14)(15)</sup>. They have shown that the transition of the density from the vapor does not occur abruptly but decreases gradually through the several layers.

Considering the above fact and in viewing the applicability of the transient state theory to both phases of liquid and vapor, the author assumes that surface consists of several molecular layers and that the transient state theory can be applied to the layers. The partition for the bulk liquid is applied without any modification.

By differentiating equation (2) with respect to  $x$ , equation of liquid state is obtained and the resulting equation can be transformed as follows:

$$\phi = \frac{\lambda e^{-\omega}(1+\omega)}{1+\lambda(x-1)e^{-\omega}} + g + \ln x + 1 - \frac{1}{x} - qx \quad (3)$$

where  $q = \frac{PV_s}{RT}$

Equation (3) is more convenient than equation (2) in calculating the free energies for the surface layers, since in equation (3)  $x$  is the only variable while in equation (2)  $x$  and  $E_s$  varies at a given temperature.

If the closest packing of the surface layer is assumed

as in the bulk liquid, the layer thickness,  $d$ , is equal to  $0.9165(V_s/N)^{1/3}$  cm.

Surface tension is, then given by definition as follows:

$$\begin{aligned} \gamma &= \sum_i \frac{(G_i - G_l)}{V_i/d} = d \frac{RT}{V_s} \sum_i \frac{1}{x_i} (\psi_l - \psi_i) \\ &= 0.9023 \frac{T}{V_s^{2/3}} \sum_i \left[ \frac{\lambda e^{-\omega_i}(1+\omega_l)}{1+\lambda(x_l-1)e^{-\omega_l}} - \frac{\lambda e^{-\omega_i}(1+\omega_i)}{1+\lambda(x_i-1)e^{-\omega_i}} \right. \\ &\quad \left. - \ln \frac{x_i}{x_l} - \frac{x_i - x_l}{x_i x_l} + 2q(x_i - x_l) \right] \quad (\text{dyne/cm}) \quad (4) \end{aligned}$$

where  $\psi = -\frac{G}{RT} = \phi - qx$  and subscripts  $i$  and  $l$  mean the  $i$ -th surface layer from the top surface layer and the bulk liquid, respectively.

#### Recursion formula

The values of  $x_i$  in equation (4) can be determined from the following recursion formula for the molar volumes:

$$\rho = \frac{\Delta V_i}{V_i} / \frac{\Delta V_{i-1}}{V_{i-1}} = \left( \frac{V_l}{V_c} \right)^2 \exp\left(-\frac{E_s}{3nRT}\right) \quad (5)$$

where  $\Delta V_i = V_i - V_l$  is the excess molar volume of the  $i$ -th layer, and  $V_c$ , the critical molar volume.

Equation (5) is obtained from the following stepwise considerations:

(a) If a molecular-sized vacancy is introduced in the  $i$ -th layer, the layer has one more gas-like molecule than before the vacancy is not introduced.

(b)  $\frac{\Delta V_i}{V_i}$  corresponds to the excess gas-like molecules per unit volume of the  $i$ -th layer compared with the bulk liquid.

(c)  $\frac{\Delta V_i}{V_i} / \frac{\Delta V_{i-1}}{V_{i-1}}$  is the ratio of the excess gas-like molecules per unit volume between the two adjacent  $i-1$  and  $i$ -th layers.

(d) Since the gas-like molecules obey the Boltzmann distribution law, the ratio,  $\rho$ , should be proportional to  $\exp\left(-\frac{E_s}{3nRT}\right)$ , where  $E_s/n$  is the bond energy. The factor 1/3 is introduced because only one direction normal to the surface is considered.

(e) The neighboring probability of the sites for the two adjacent layers is proportional to  $V_l^2$ .

(f) Thus,  $\rho$  is proportional to  $V_l^2 \cdot \exp\left(-\frac{E_s}{3nRT}\right)$ , and the proportionality constant is  $1/V_c^2$  in order to satisfy the boundary condition  $\rho=1$  at the critical point.

The equation (5) can be rearranged as follows:

$$x_i = x_l \left[ 1 - \left( 1 - \frac{x_l}{x_{i-1}} \right) \left( \frac{x_l}{x_c} \right)^2 \tau \right]^{-1} \quad (6)$$

where  $\tau = \exp\left(-\frac{E_s}{3nRT}\right)$  and  $x_c = V_c/V_s$ . For the first layer, the equation (6) becomes,

$$x_1 = x_l \left[ 1 - (1 - q_{x1}) \left( \frac{x_l}{x_c} \right)^2 \tau \right]^{-1}$$

since  $1/x_{i-1} = 1/x_c = V_s/V_c = \frac{PV_s}{RT}$  where  $V_s$  is the molar volume of the vapor; from which  $x_1$  can easily be found. Introducing the value of  $x_1$  into the equation (6)  $x_2$  is found and so forth.

#### Orientation of the polar molecules

In addition to the energy difference  $E_s/3n$  between the two adjacent layers of the transition region, the polar molecule has some orientation energy,  $\mu X$ , where  $\mu$  is the dipole moment and  $X$ , the orientation field normal to the surface which is produced by the surrounding molecules. The field strength is assumed to be proportional to  $\mu/a^2$ , where  $a$ , the intermolecular distance, is equal to  $2^{1/3}(V_s/N)^{1/3}$  if the closest molecular packing is assumed.

Then, for the polar molecules,  $\tau$  in equation (6) is modified as follows:

$$\tau = \exp \left[ - \left( \frac{E_s}{3nRT} + \frac{\xi \mu^2 N^2}{\sqrt{2} V_s RT} \right) \right] \quad (7)$$

where  $\xi$  is the proportionality constant.

The mean orientation angle subtended between the polar axis and the normal to the surface can be found from the following Langevin function:

$$\begin{aligned} \frac{1}{\cos \theta} &= \frac{\int_0^\pi \cos \theta \cdot e^{\frac{\mu X \cos \theta}{kT}} \sin \theta d\theta}{\int_0^\pi e^{\frac{\mu X \cos \theta}{kT}} \sin \theta \cdot d\theta} = L\left(\frac{\mu X}{kT}\right) \\ &= L\left(\frac{\xi \mu^2 N^2}{\sqrt{2} V_s RT}\right) \quad (8) \end{aligned}$$

If the value of  $\xi$  is assigned by trial and error method, the orientation angles can be calculated from the equation (8). In Table 1 the observed dipole moment  $\mu^{(19)}$ , the assigned parameter  $\xi$  and the calculated

Table 1.  $\mu$ ,  $\xi$  and  $\theta$  of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$

CH <sub>3</sub>		H <sub>2</sub> O		CH <sub>3</sub> OH	
$\mu=2.3\text{D}$ , T°K	$\xi=0.2446$ $\theta^\circ$	$\mu=1.87\text{D}$ , T°K	$\xi=0.3330$ $\theta^\circ$	$\mu=1.70\text{D}$ , T°K	$\xi=1.3526$ $\theta^\circ$
213.15	84.47	273.15	74.87	273.15	68.10
239.75	85.08	293.15	75.85	303.15	70.03
253.15	85.33	333.15	77.47	337.85	71.90
273.15	85.68	373.15	78.77	363.15	73.07

mean orientation angles at various temperatures are shown.

### Parameters for the bulk liquids

The necessary values for the calculation of surface tension such as the parameters included in the liquid partition function and the critical molar volume<sup>(20)</sup> are listed in Table 2.

Table 2. The parameters for the bulk liquids

	$E_s$ , cal/mole	$\theta_s$ , °K	$\theta_t$ , °K	$\epsilon$ , cal/mole	$n$	$V_s$ , cc	$V_t$ , cc
A <sup>(7)</sup>	1771	47.65	47.33	10.90	10.69	24.98	75.26
N <sub>2</sub> <sup>(7)</sup>	1507	54.18	50.05	31.13	11.01	29.31	90.1
O <sub>2</sub> <sup>(21)</sup>	1818	58.62	52.06	10.31	11.68	24.0	78.0
C <sub>6</sub> H <sub>6</sub> <sup>*</sup>	10350	56.52	49.04	468.3	10.59	77.0	260.5
C <sub>6</sub> H <sub>12</sub> <sup>(22)</sup>	8823	76.27	75.15	281.2	11.30	100.2	308.3
CCl <sub>4</sub> <sup>**</sup>	8743	57.30	54.54	179.0	11.48	87.9	275.7
CHCl <sub>3</sub> <sup>(7)</sup>	10036	38.20	31.00	504.1	11.07	67.0	238.8
CS <sub>2</sub> <sup>(7)</sup>	8919	58.94	40.53	613.5	11.23	49.0	173.1
H <sub>2</sub> O <sup>(23)</sup>	10940	234.6	224.0	286.4	11.76	≅	56.3
NH <sub>3</sub> <sup>***</sup>	6850	196.4	15.3	407.3	10.64	20.57	72.5
CH <sub>3</sub> OH <sup>*</sup>	10952	118.03	98.96	143.3	11.37	36.0	117.8

\* Calculated by H. Lee et al; \*\* by D. Choi et al;

\*\*\* by Y. Sung et al (to be published).

≅  $V_s$  for water is given by  $V_s = V_{s0}\alpha + V_t(1-\alpha)$  where  $V_{s0}$  (=18.018 cc) and  $V_t$  (=16.095 cc) are the molar volumes of the solid-like and the transient molecules, respectively; and  $\alpha$  is a fractional number given in section II.

### Result

The calculated in comparison with the observed values of surface tensions for various liquids are shown in Table 3 and the contribution percentages to each layer are also listed in the Table 3.

### Discussion

The agreements of the surface tensions between the calculated and the observed values are excellent for all the above liquids.

In the temperature range between the normal boiling point, the contribution to each layer of the surface tension are about 90%, 10% and 1% for the 1st, the 2nd and the 3rd, respectively. As the temperature is raised, the higher layer contributions increase gradually. This result agrees with the data calculated by means of the radial distribution function<sup>(14d)</sup>.

The mean orientation angle of the polar molecules increases as the temperature is raised, because the higher the temperature, the randomness of the molecular states increases. In the case of chloroform, the

Table 3. Surface tensions and their contribution percentages to each layers

T°K	Contribution percentage to the layer			$\gamma$ calc.	$\gamma$ obs.	$\Delta$ %
	1 st	2 nd	3 rd			
<b>Argon</b>						
84.25	85.29	13.31	1.40	13.19	13.3 <sup>(15)</sup>	-0.8
86.90	84.85	13.66	1.49	12.40	12.7	-2.4
90.00	84.31	14.09	1.60	11.51	11.9	-3.3
120.00	75.03	21.17	3.80	4.75	...	...
<b>Nitrogen</b>						
63.14	86.80	12.08	1.12	12.41	12.1 <sup>(16)</sup>	2.6
70.00	85.41	13.23	1.36	10.51	10.53	-0.2
80.00	83.27	14.93	1.80	8.02	8.27	-3.0
90.00	80.38	17.09	2.53	5.93	6.16	-3.7
<b>Oxygen</b>						
56.36	90.70	8.75	0.55	24.34	22.3 <sup>(30)</sup>	9.1
70.00	88.58	10.59	0.83	19.00	18.3	3.8
80.00	87.43	11.54	1.03	15.49	15.7	-1.3
90.00	86.17	12.57	1.26	12.49	13.2	-5.4
<b>Benzene</b>						
283.15	91.60	7.89	0.51	28.58	30.35 <sup>(30)</sup>	-5.8
303.15	90.67	8.72	0.61	26.22	27.70	-5.3
323.15	89.85	9.44	0.71	23.65	25.08	-5.7
343.15	89.03	10.15	0.82	21.07	22.52	-6.4
<b>Cyclohexane</b>						
298.15	89.43	9.76	0.81	24.69	24.5 <sup>(30)</sup>	0.8
313.15	88.15	10.89	0.96	23.23	22.1	5.1
343.15	86.33	12.43	1.24	19.52	17.3	12.8
353.90	85.74	12.91	1.35	18.16	15.6	16.4
<b>Carbon tetrachloride</b>						
273.15	90.29	9.06	0.65	31.34	29.49 <sup>(30)</sup>	6.3
298.15	88.59	10.54	0.87	28.03	26.32	6.5
313.15	87.88	11.15	0.97	25.75	24.45	5.3
343.15	86.72	12.09	1.19	21.23	20.79	2.1
<b>Chloroform</b>						
243.15	92.83	6.80	0.37	32.43	33.8 <sup>(31)</sup>	-4.1
273.15	91.63	7.90	0.47	28.49	29.8	-4.4
303.15	90.55	8.84	0.61	24.16	25.9	-6.7
334.35	89.39	9.83	0.78	19.84	21.9	-9.4
<b>Carbon disulfide</b>						
223.15	91.88	7.68	0.44	42.62	43.0 <sup>(30)</sup>	-0.9
273.15	89.92	9.39	0.69	34.62	35.3	-1.9
319.40	88.28	10.80	0.92	27.10	28.5	-4.9
373.15	86.04	12.65	1.31	19.44	20.7	-6.1
<b>Water</b>						
273.15	97.82	2.18	0.00	77.98	75.64 <sup>(30)</sup>	3.1
293.15	97.24	2.76	0.00	77.09	72.75	6.0
333.15	96.45	3.55	0.00	68.30	66.18	3.2
373.15	95.80	4.20	0.00	58.48	58.85	-0.6
<b>Ammonia</b>						
213.15	93.95	5.80	0.25	38.80	40.4 <sup>(31)</sup>	-4.0
239.75	92.63	6.99	0.38	33.92	34.1	-0.5
253.15	91.98	7.55	0.47	31.12	31.0	0.4
273.15	91.00	8.41	0.59	26.91	26.6	1.2
<b>Methanol</b>						
273.15	98.01	1.99	0.00	24.18	24.49 <sup>(30)</sup>	-1.3
303.15	97.40	2.60	0.00	22.12	21.75	1.7
337.85	96.64	3.36	0.00	18.94	18.88	0.3
363.15	96.06	3.94	0.00	16.43	16.65	-1.3

orientation effect can be neglected since the dipole moment and the orientation field strength are relatively small.

### IV. The theory of the viscosity of liquid

#### Introduction

Although there are several kinetic approaches<sup>(24), (25), (26)</sup> to the viscosity of liquid, the problem of the viscosity is remain unsolved.

Eyring et al<sup>(27)</sup> have approached to the viscosity of liquid by means of the theory of rate process. They have assumed that the viscous flow occurs through an activated state. For the ordinary viscous flow, i. e., the shear force is relatively small, the viscosity of liquid was given by

$$\eta = \frac{hN}{V} \frac{1}{K^*} \quad (9)$$

where  $K^*$  is an equilibrium constant between the initial state of the flow and the activate state. The theory has been modified and applied to various flow<sup>(28)</sup>. The actual calculation of the viscosity of liquid, however, is still difficult since no partition functions for the states have been given completely.

Recently, Eyring et al<sup>(29)</sup> have proposed a theory of the viscosity according to the significant structure theory of liquid. They have calculated the viscosity of liquid by adding the viscosities correspond to the solid-like and the gas-like molecules. This is a crude approximation.

The transient state theory of liquid may suggest that the viscosity of liquid can be treated easily, since in the theory the transient state is assumed which may be related to the activated state of the viscous flow.

#### The partition function for the activated state

In formulation the partition function for the activated state of the viscous flow according to the transient state theory, the following assumptions are made: The molecules in the activated state have gas-like degrees of freedom in the direction of the flow as given by the theory of rate process. In the normal direction of the flow, the molecules are partitioned by two kinds of degrees of freedom, i. e., the transient and the gas-like. According to the transient state theory liquid molecules in the normal state are partitioned by the solid-like, the transient and the gas-like. In the activated state, however, the solid like molecules may not

exist, since the activated molecules are in the higher energy state than the normal liquid molecules for the viscous flow.

Then, the partition function for the activated state is given as follows;

$$F^* = \left[ b_s \frac{n}{Z} \frac{V - V_s}{V_s} e^{-\frac{E_s - E_0}{RT}} \right] \frac{V_s}{V} N$$

$$\left[ b_s \frac{2\pi mkT}{h^2} \frac{V - V_s}{\delta} \right] \frac{V - V_s}{V} N \frac{1}{\left( \frac{V - V_s}{V} N \right)!} \quad (10)$$

where  $\delta$  is the distance of the activated molecules which can move in the direction of the flow, and  $E_0$  is the molar activation energy. The number of the nearest neighboring site in the normal plane of the flow is assumed to be a half of that for the bulk liquid.

#### The viscosity of liquid

The equilibrium constant in equation (9) is related to the partition functions for the normal liquid and the activated state as follows:

$$K^* = \exp \left( -\frac{\Delta G^*}{RT} \right) = \exp \left( \frac{\partial \ln F^*}{\partial N} - \frac{\partial \ln F}{\partial N} \right) \quad (11)$$

Introducing equations (1) and (10) into the equation (11), and the resulting equation into the equation (9), viscosity of liquid can be obtained as follows:

$$\eta = \frac{hN}{V_s} \left[ \frac{2e^{-\frac{E_0}{RT}}}{1 - e^{\delta u/T}} \frac{1 + \lambda(x-1)e^{-u}}{\lambda(x-1)e^{-u}} \right]^{\frac{1}{x}}$$

$$\left[ \frac{(2\pi mkT)^{1/2}}{h} \delta \right]^{1 - \frac{1}{x}} \quad (12)$$

In equation (12),  $V_s$  is taken instead of  $V$  in equation (9), since the equilibrium distance between the neighboring sites is held constant according to the transient state theory.

If  $x$  is large as in the vapor, equation (12) gives the viscosity for the vapor:

$$\eta_{x \rightarrow \infty} = \frac{N}{V_s} (2\pi mkT)^{1/2} \delta \quad (13)$$

The parameter  $\delta$  can be found from equation (13) using the observed viscosity of the vapor, and then  $E_0$ , from equation (12) using the observed viscosity of the liquid at a temperature. The parameters obtained for the various liquids are listed in Table 4.

#### Result

The calculated and the observed viscosity for various liquids are listed in Table 5

### Discussion

The calculated viscosity for various liquids are in good agreements with the observed values except the

Table 4. The parameters for viscosity

	$E_a$ cal/mole	$\delta$ Å°
A	192.1	0.219
C <sub>6</sub> H <sub>12</sub>	1654	0.187
CHCl <sub>3</sub>	1253	0.153
H <sub>2</sub> O	768.5	0.0907
Hg	1021	0.0923
Zn	2562	0.139
C <sub>6</sub> H <sub>6</sub>	1493	0.166
CCl <sub>4</sub>	1440	0.323
CS <sub>2</sub>	1055	0.135
CH <sub>3</sub> OH	1359	0.204
Cd	2411	0.160

Table 5. The viscosity of liquid at various temperatures

T°K	$\eta$ calc. poise	$\eta$ obs. poise	$\Delta$ %
<b>Argon</b>			
84.25	0.00282	0.00282 <sup>(33)</sup>	0.0
86.90	0.00259	0.00256	1.2
90.00	0.00236	0.00232	1.7
120.00	0.00118	0.00116	1.7
149.00	0.00051	0.00050	2.0
<b>Benzene</b>			
283.15	0.00757	0.00757 <sup>(30)</sup>	0.0
303.15	0.00586	0.00561	4.5
323.15	0.00474	0.00436	8.7
343.15	0.00394	0.00350	12.6
353.25	0.00361	0.00317	13.9
<b>Cyclohexane</b>			
298.15	0.0089	0.0089 <sup>(30)</sup>	0.0
313.15	0.00652	0.0069	-5.5
343.15	0.00413	0.0041	0.7
353.90	0.00360	0.0033	9.1
<b>Carbon tetrachloride</b>			
273.15	0.01346	0.01346 <sup>(30)</sup>	0.0
298.15	0.00838	0.00903	-7.2
313.15	0.00680	0.00738	-7.9
343.15	0.00477	0.00523	-8.8
<b>Chloroform</b>			
243.15	0.00995	0.01021 <sup>(30)</sup>	-2.5
273.15	0.00699	0.00699	0.0
303.15	0.00533	0.00510	4.5
334.35	0.00421	0.00383	9.9
373.15	0.00323	0.0029*	11.4
<b>Carbon disulfide</b>			
223.15	0.00663	0.00688 <sup>(30)</sup>	-3.6
273.15	0.00429	0.00429	0.0
319.40	0.00324	0.00305	6.2
373.15	0.00246	0.00221	11.3
423.15	0.00193	0.00172*	12.2

cases for water and methanol. The polar molecules may be oriented in the flow process. Neglecting the orientation effect in the polar molecules, viscous flow shows some deviations of the viscosities of water and methanol.

Equation (13) is analogous to the result of the kinetic theory for the viscosity of gas, that is, the viscosity of gas is proportional to the square root of the absolute temperature. The viscosity of the vapor can be easily calculated by equation (13).

Assuming the activated molecules for the viscous flow to have the degrees of freedom as shown in this theory, the other transport properties such as self-diffusion coefficient and thermal conductivity can be

T°K	$\eta$ calc. poise	$\eta$ obs. poise	$\Delta$ %
<b>Water</b>			
273.15	0.017921	0.017921 <sup>(26)</sup>	0.0
293.15	0.010191	0.010050	1.4
333.15	0.005669	0.004688	20.9
373.15	0.003958	0.002838	39.5
<b>Methanol</b>			
253.15	0.01144	0.01144 <sup>(30)</sup>	0.0
303.15	0.00621	0.00515	20.6
337.85	0.00455	0.00330	37.9
363.15	0.00373	0.00248	50.4
<b>Mercury</b>			
234.27	0.02301	0.021 <sup>(32)</sup>	9.6
273.15	0.01685	0.01685	0.0
373.15	0.01183	0.01240	-4.6
473.15	0.01042	0.01052	-1.0
573.15	0.00997	0.00950	4.9
<b>Cadmium</b>			
594.15	0.0255	0.0252 <sup>(32)</sup>	1.2
623.15	0.0237	0.0237	0.0
673.15	0.0214	0.0216	0.9
773.15	0.0185	0.0184	0.5
873.15	0.0169	0.0154	9.7
<b>Zinc</b>			
992.65	0.0416	0.037 <sup>(32)</sup>	12.4
773.15	0.0278	0.0278	0.0
873.15	0.0224	0.0224	0.0
973.15	0.0197	0.0188	4.8
1073.15	0.0181	0.016*	13.1

\* extrapolated value

likewise studied.

The degeneracy of the transient molecules for metals

is given by  $n \frac{V - \frac{1}{3} V_s}{V_s}$  assuming the size of the ion

to be about one third of the atomic size. The partition function of metal may be justified in view of the fact that the calculated thermodynamic properties agree well with observed values as shown in Table 6.

Table 5. Thermodynamic properties of Hg, Cd and Zn

T°K	Molar volume(cc)			Vapor pressure(atm)			Entropy of vaporization(e. u.)		
	calc.	obs. (32)	Δ%	calc.	obs. (32)	Δ%	calc.	obs. (32)	Δ%
Mercury									
234.27	14.70	14.65	0.36	$2.59 \times 10^{-9}$	...	...	63.65	63.18	0.75
273.15	14.76	14.76	0.00	$2.43 \times 10^{-7}$	$2.43 \times 10^{-7}$	0.00	54.22	53.94	0.52
373.15	14.83	15.02	-1.27	$3.51 \times 10^{-4}$	$3.59 \times 10^{-4}$	-2.31	39.26	39.04	0.55
473.15	14.89	15.30	-2.63	0.02245	0.02275	-1.32	30.70	33.45	0.82
573.15	14.95	15.57	-4.01	0.3296	0.3247	1.51	25.15	24.87	1.11
629.73	14.98	15.74	-4.79	1.0266	1.0000	2.66	22.78	22.49	1.29
Cadmium									
594.15	14.14	14.02	0.86	$1.37 \times 10^{-4}$	$1.32 \times 10^{-4}$	3.71	41.76	42.49	-1.72
623.15	14.16	14.07	0.64	$3.64 \times 10^{-4}$	$3.57 \times 10^{-4}$	1.99	39.74	40.35	-1.51
673.15	14.18	14.18	0.00	$1.60 \times 10^{-3}$	$1.60 \times 10^{-3}$	0.00	36.67	37.09	-1.13
773.15	14.22	14.37	-1.04	0.01733	0.01762	-1.65	31.75	31.83	-0.25
873.15	14.26	14.56	-2.06	0.1075	0.1089	-1.29	27.97	27.77	0.72
1038.15	14.32	14.89	-3.83	1.0005	1.0000	0.05	23.34	22.79	2.41
Zinc									
692.65	9.422	9.448	-0.28	$1.93 \times 10^{-4}$	$1.95 \times 10^{-4}$	-1.03	42.40	41.86	1.29
773.15	9.531	9.503	0.29	$1.73 \times 10^{-3}$	$1.73 \times 10^{-3}$	0.00	37.28	37.25	0.08
873.15	9.601	9.601	0.00	0.01468	0.01468	0.00	32.64	32.71	-0.21
973.15	9.646	9.758	-1.15	0.07883	0.07917	-0.43	29.06	29.10	-0.14
1073.15	9.685	9.951	-2.67	0.3066	0.3083	-0.55	26.18	26.17	0.04
1179.15	9.722	10.20	-4.69	0.9998	1.0000	-0.02	23.70	23.60	0.42

Parameters	$E_s$ , cal/mole	$\epsilon$ , cal/mole	$\theta^{\circ}K^*$	$V_s^{(32)}$ , cc	$n^{(32)}$
Hg	15963	367.9	86	14.13	11.574
Cd	27335	888.8	136.1	13.39	11.461
Zn	32772	2415.8	195.7	8.838	11.225

\*  $\theta_s = \theta_s$

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