

## MOLECULAR DIAMETER OF A LIQUID

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*(Received for publication, August 25, 1952)*

**ABSTRACT.** Knowing the potential energy of a liquid, an idea is gained about the molecular diameter. The pressure within liquid carbon dioxide and ethyl alcohol at different temperatures is calculated ; for the former, change in free energy and internal energy is also calculated.

This paper is in continuation of the previous ones by the author (Bhatawdekar, 1951 and 1952). As explained (Bhatawdekar 1951), the free energy  $H$ , internal energy  $E$ , and  $\frac{dH}{dT}$  are determined for carbon dioxide with the help of  $\beta$  (Tables I and II) Applying Virial theorem (Bhatawdekar, 1952), the pressure within carbon dioxide and ethyl alcohol is also calculated at different temperatures (Table III).

TABLE I

Temperature °C	Log $km$	No of maxima	$I$	$F$	$r - d/D$
-30	9.0405	70	715	$2.1 \times 10^3$	$3.4 \times 10^{-2}$
-20	9.0230	75	800	$8.6 \times 10^3$	$5.1 \times 10^{-2}$
-10	9.0061	75	875	$4.7 \times 10^4$	$7.4 \times 10^{-2}$
0	10.9899	80	890	$1.5 \times 10^5$	$1.1 \times 10^{-1}$
10	10.9743	85	1135	$9.9 \times 10^5$	$1.5 \times 10^{-1}$
20	10.9592	90	1335	$8.5 \times 10^6$	$2.5 \times 10^{-1}$
31.1°C	10.9431	95	2800	$3.9 \times 10^9$	$1.0 \times 10^0$

A general study of the variation of potential energy of a liquid with temperature shows that the author's earlier observation that water tends to show an anomalous behaviour is wrong. It is of general application. It is general occurrence with a liquid that its potential energy diminishes with diminishing temperature, becomes zero, and then reverses its sign. This change of sign is noted in the case of water and ethyl alcohol at temperatures between 70°C and 100°C, and 80°C and 120°C respectively. Similar observations are also possible in other liquids only if calculations can be carried at still

TABLE II

Temperature °C	$\beta \times 10^{-10}$ ergs per gm.	$H \times 10^{-10}$ ergs	$P(V_2 - V_1)$ $\times 10^8$ ergs	$(H - E)$ $\times 10^{10}$ ergs	$\frac{(H - E)}{T}$ $\times 10^{-7}$ ergs per deg.	$dH/dT$ from graph	$\phi$ $k$ $\times 10^{13}$ ergs	$2\phi R$ $\times 10^{15}$ ergs per deg
-30	1.01	1.10	3.75	0.81	3.46	$3.0 \times 10^7$ ergs per degree	7.35	3.03
-20	1.18	1.13	3.50	0.89	3.51		8.36	3.42
-10	1.27	1.15	3.39	0.91	3.57		9.32	3.55
0	1.45	1.19	3.20	0.99	3.62		10.63	3.90
10	1.66	1.22	2.88	1.06	3.73		12.15	4.30
20	1.21	1.25	2.37	1.12	3.84		13.93	4.76
31.1	2.52	1.26	0.00	1.26	4.14		18.43	6.06

TABLE III

Sub- stance	Temper- ature °C	$\nu \times N^{1/3}$	$\xi \times 10^{13}$ ergs.	$\frac{d\xi}{dr} \times N^{-1/3}$ $\times 10^{12}$	$\Sigma r f(r)$ $\times 10^{-10}$	$RT \times 10^{-8}$	$V$ cc. per gm.	$P$ Atm $\times 10^{-4}$
C <sub>2</sub> H <sub>5</sub> OH	80	1.100	-0.68	?	?	6.37	1.361	?
	120	1.131	2.08	15.0	22.14	7.10	1.444	-4.098
	160	1.164	4.58	10.0	15.20	7.82	1.579	-3.082
	200	1.215	9.87	5.5	8.73	8.54	1.796	-1.539
	213	1.537	10.20	2.5	5.02	9.32	3.629	-0.430
CO <sub>2</sub>	-30	0.9761	3.68	5.8	7.70	4.59	0.9392	-2.075
	-20	0.9900	4.33	4.2	5.64	4.78	0.9699	-1.863
	-10	1.0070	4.66	3.3	4.48	4.97	1.0194	-1.396
	0	1.270	5.32	2.6	3.69	5.16	1.0811	-1.077
	10	1.0520	6.08	1.8	2.57	5.35	1.1628	-0.679

lower temperatures. The potential energy is assumed to be due to the existence of intermolecular forces. The change in the sign of the potential energy is interpreted as due to the change in the nature of the intermolecular forces which are known to depend on the intermolecular distances. Due to the dipole character of the molecule, they exert an attractive force  $F_s$  on each other which varies as  $1/r^8$ . When at lower temperatures, the two molecules approach very close to each other and due to the similar electronic shell charges they repel each other with a force  $F_r$  varying as  $1/r^1$ . Therefore, the resultant molecular force  $F = F_s - F_r = A/r^8 = B/r^1$ .

The value of  $r = r_0$  for which the resultant force becomes zero gives the equilibrium distance between the centres of two molecules and is equivalent to the molecular diameter  $\sigma$  (Saha and Shrivastava, 1935).

For a distance greater than  $r_0$ , (i.e. at higher temperatures) the resultant force will be the force of attraction and hence, the potential energy has plus sign, at smaller distances (i.e. at lower temperatures), the repulsive force will preponderate giving us the negative potential energy. When the resultant molecular force is zero the potential energy will also be zero. So, a graph is plotted between  $r$  [ $r = (\tau/d_v)^{1/3}$ , where  $d$  is the density of a liquid and  $N$  denotes the number of molecules in one gram of the liquid] and the potential energy. By extrapolation,  $r_0$  corresponding to zero potential energy and hence molecular diameter are known. The values of  $\sigma$  so determined are shown in Table IV, second column, while in the third and fourth columns are shown values calculated with the help of viscosity and Vander waals' constant data.

TABLE IV

Substance	From potential energy $\sigma p \times 10^8 \text{cm}$	From viscosity data $\sigma v \times 10^8 \text{cm}$	From Vander Waals constant $\sigma_v \times 10^8 \text{cm}$
$\text{CCl}_4$	5.50	5.09	4.64
$\text{NH}_3$	3.41	2.64	3.05
$\text{C}_2\text{H}_5\text{OH}$	4.67	3.90	4.05
$\text{CO}_2$	3.84	3.44	3.40
$\text{H}_2\text{O}$	3.14	2.53	2.75

The accuracy of  $\sigma$  will depend on the accuracy of the calculation of  $\beta$  and extrapolation in graph. The error is of the order of  $\pm 0.06 \times 10^{-8} \text{cm}$ .

In the case of  $\text{NH}_3$  and  $\text{CCl}_4$ , by plotting a graph between  $d\xi/dr$  and  $r$ , it is observed that  $d\xi/dr \propto 1/r^m$ , where  $m$  lies between 9 and 9.5. It is a matter of chance that the value of  $m$  comes out to be approximately the same for  $\text{NH}_3$  and  $\text{CCl}_4$ . It was, therefore, possible to get an equation of state where virial function is the same function of the specific volume of a liquid.  $S$  and  $t$  never have same values for all substances (Saha and Shrivastava, 1950) and hence the value of  $m$  will be different. Therefore, virial function will be a different function of volume of a liquid giving us different equations of state for different liquids. Further studies are under progress in this direction.

*Explanation, of the symbols used.*

$K = 1/2RT$  where  $R$  is the gas constant and  $T$  is the absolute temperature  
 $m$  = the mass of the particle

$$I = \int_0^\infty \frac{e^{-Kmu^2} x^3 dx}{px^2 \sqrt{x^2 + b} \cos^2 gx - \sqrt{x^2 + b} + \frac{x^2}{\sqrt{x^2 + b}}}$$

where

$$u^2 - b = x^2$$

$$p = \frac{16\pi^2 m^2}{1.2}$$

$$b = \frac{2U_1}{h} = \frac{4mL}{h} = 4L$$

$$g = \frac{a}{2} \sqrt{p}$$

$a$  = thickness of potential barrier

$L$  = latent heat

$h$  = Planck's constant

$F$  = the total probability of a molecule crossing the boundary

$d$  = density of saturated vapour

$D$  = density of liquid

$\beta$  = the correction term

$$\phi/k = m\beta = \phi/2k = \xi$$

$\xi$  = potential energy of a liquid

$V_1, V_2$  = Volumes in liquid and gas phase respectively

#### A C N O W L E D G M E N T

The author wishes to express his thanks to Prof. M. F. Soonawala, Maharaja's college, Jaipur, for his help and guidance.

#### R E F E R E N C E S

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