

PRESSURE IN A LIQUID

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ABSTRACT. Knowing the potential energy of a liquid, an idea is gained about the intermolecular forces. The pressure within the liquid at different temperatures is calculated by an application of the virial theorem. The virial function is seen to be a function of the volume of the liquid at that temperature; and hence an equation of state for the liquid is derived.

This paper is in continuation of a previous one by the author, (Bhatawdekar, 1951). From the virial theorem we know that

$$PV = RT + \frac{1}{3}\Sigma r.f(r).$$

where $f(r)$ is the intermolecular force at the average intermolecular distance r . Thus the total pressure in a fluid is due partly to molecular agitation and partly to intermolecular forces, which may be attractive or repulsive. In the deduction of the above expression, the force of repulsion is considered to be positive (Jeans, 1921). If $f(r)$ is known for any liquid at any temperature, the calculation of pressure is possible. When the molecules of a liquid are very close to each other there exists a force of repulsion between them which goes on decreasing as the average distance between two molecules goes on increasing; i.e., as the temperature increases. Beyond a certain limit the force of repulsion gives way to one of cohesion which also decreases with increase of temperature. If ξ denotes the potential energy of a liquid, $-d\xi/dr = f(r)$ will denote the force of attraction or repulsion between the molecules according to its sign.

In the previous paper (Bhatawdekar, 1951), the potential energy $\xi = \phi/2k$ for CCl_4 and NH_3 has already been calculated. If d denotes the density of the liquid, its specific volume will be $1/d$, and if N denotes the number of molecules in one

TABLE I

Substance	Temperature °C	$r \times N^{\frac{1}{3}}$	$\xi \times 10^{13}$ ergs	$\frac{d\xi}{dr} \times N^{-\frac{1}{3}}$ $\times 10^{12}$	$\Sigma r.f(r)$ $\times 10^{-10}$	$RT \times 10^{-8}$	V	P
							Atm $\times 10^{-4}$	
CCl_4	80	0.8780	3.16	12.0	4.12	1.91	0.6770	-1.98
	140	0.9059	5.93	10.0	3.54	2.23	0.7435	-1.54
	200	0.9439	8.96	6.0	2.22	2.56	0.8409	-0.837
	240	0.9858	11.39	4.0	1.54	2.78	0.9579	-0.398
	283	1.2140	17.55	2.0	0.95	3.01	1.739	-0.158
NH_3	-45	1.1280	0.582	6.0	23.9	11.1	1.4367	-5.39
	-20	1.1460	1.55	6.0	26.7	12.4	1.537	-5.77
	0	1.1610	2.37	5.5	22.6	13.3	1.5660	-4.66
	20	1.1790	3.26	5.0	20.8	14.3	1.6383	-4.01
	50	1.2120	4.68	3.0	8.60	15.8	1.7766	-1.44
	132.5	1.6240	12.1	1.0	5.74	19.8	4.2830	-0.418

gram of the liquid, $1/dN$ will be the volume per molecule. Hence, r can be taken to be equal to $(1/dN)^{1/3}$ to a first approximation. When a graph is plotted between ξ and r at various temperatures we get a continuous curve, the tangent at any point of which gives us the value of $d\xi/dr = f(r)$ for that value of r and the corresponding value of the temperature. Thus $N.r.d\xi/dr$ is calculated and this is taken to be equal to $\Sigma r.f(r)$. Knowing the temperature, the pressure is calculated. The results for CCl_4 and NH_3 are given in Table 1. If the calculated pressure is negative, it is an indication that at that intermolecular distance the pressure due to the cohesion between the molecules preponderates over the pressure due to the random motion of the molecules. Water tends to show an anomalous behaviour, the potential energy diminishing with temperature upto 70°C .

It is found that the virial function $N.r.d\xi/dr = \Sigma r.f(r)$ is a function of the volume of the liquid. From the graph it is seen that $N.r.d\xi/dr = K/V^{2.66}$ where K is a constant for the liquid. This relation fails near the critical temperature as then the molecules are under no attracting forces. Thus, an equation of state is obtained of the form

$$PV = RT - K/V^{2.66}$$

$$K = 4.5 \times 10^9 \text{ for } \text{CCl}_4 \text{ and } 3.8 \times 10^{11} \text{ for } \text{NH}_3$$

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