

ON THE THEORY OF LIQUIDS—III.

BY T. S. WHEELER,
Royal Institute of Science, Bombay.

Received April 9, 1935.

1. Introduction.

IN 1922 Edser¹ discussed a theory in which liquids are regarded as consisting of attracting force centres (molecules), each of which keeps clear around it by its thermal motion, a spherical space of diameter σ . Edser assumed that σ is independent of temperature, and that the force coefficient μ varies with it. In previous papers² the present author has developed a modification of Edser's theory, which involves regarding μ as independent of, and σ as varying with temperature. The spherical spaces are considered as closely packed, and σ is therefore related to V by the equation,

$$N\sigma^3 = V \sqrt{2} \quad \dots \quad (1)$$

Introducing the relation given by (1) into Edser's equations, the following relations have been obtained for temperatures of low vapour pressure near the melting point:—

$$K = \frac{4\pi\mu}{3(m-4)\sigma^{m+2}} \quad \dots \quad (2)$$

$$\gamma = \frac{\pi\mu}{4(m-5)\sigma^{m+1}} \quad \dots \quad (3)$$

$$A_i = \frac{2\sqrt{2}\pi\mu N}{3(m-4)\sigma^{m-1}} \quad \dots \quad (4)$$

The following equations additional to Edser's have also been deduced:—

$$L_i = A_i \left[1 + \frac{T(m-4)\alpha}{3} \right] \quad \dots \quad (5)$$

$$-\left(\frac{\delta L_i}{\delta T} \right)_p = C_{pl} - C_{vg} = A_i \alpha \left[1 + \frac{T(m-4)\alpha}{3} \cdot \frac{m-1}{3} \right] \quad \dots \quad (6)$$

$$C_{pl} - C_{vl} = L_i \alpha \quad \dots \quad (7)^3$$

It will be noted that (3) and (1) give immediately,

$$\gamma \propto V^{-\frac{(m+1)}{3}} \quad \dots \quad (8)$$

which is a general parachor law.

¹ *Brit. Assoc. Fourth Report on Colloid Chem.*, 1922, 40.

² *Ind. J. Physics*, 1934, **8**, 521; *Proc. Ind. Acad. Sciences*, 1934, **1**, 105; *cf. Current Science*, 1934-35, **3**, 23, 347.

³ *Cf. Tyrer, Z. Phys. Chem.*, 1914, **87**, 178.

As the usual parachor law is,

$$\gamma = \frac{P^4}{V^4} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (9)$$

(8) indicates that for liquids obeying this parachor law,

$$m = 11 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (10)$$

For most liquids μ is not known, but we can express it in terms of γ from (3) and insert the values in (4) to obtain

$$A_i = \frac{8\sqrt{2}}{3} \cdot \frac{m-5}{m-4} N\gamma\sigma^2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (11)$$

This value of A_i can be inserted in (5), (6) and (7) to obtain equations which it has been found⁴ do reproduce the experimental results for temperatures of low vapour pressure near the melting point, if m be given the value, 10, approximately.

The equations can immediately be extended⁵ to include the effect of the repulsive forces, and the following expressions have been deduced:—

$$K = \frac{4\pi\mu}{3(m-4)\sigma^{m+2}} - \frac{4\pi\lambda}{3(n-4)\sigma^{n+2}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (12)$$

$$\gamma = \frac{\pi\mu}{4(m-5)\sigma^{m+1}} - \frac{\pi\lambda}{4(n-5)\sigma^{n+1}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (13)$$

$$A_i = \frac{2\sqrt{2}\pi\mu N}{3(m-4)\sigma^{m-1}} - \frac{2\sqrt{2}\pi\lambda N}{3(n-4)\sigma^{n-1}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (14)$$

$$L_i = \frac{2\sqrt{2}\pi\mu N}{3(m-4)\sigma^{m-1}} \left[1 + \frac{T(m-4)\alpha}{3} \right] - \frac{2\sqrt{2}\pi\lambda N}{3(n-4)\sigma^{n-1}} \left[1 + \frac{T(n-4)\alpha}{3} \right] \quad (15)$$

Corresponding expressions can be written for (6) and (7). It has been shown⁶ that if μ , λ , m and n be calculated from the second virial coefficient by the Lennard-Jones method for He, H₂, Ne, Ar and N₂, and the values inserted in (13) and (15), then these equations reproduce satisfactorily the experimental results. As a general rule the terms relating to the repulsive force can be neglected in comparison with those relating to the attractive force. It may be mentioned that for normal liquids μ is related to the parachor by the equation

$$\mu = \frac{96}{\pi} \cdot \frac{P^4}{N^4} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (16)$$

which is deduced from (9), (3) and (1), m being put equal to 11.

The equations so deduced require a knowledge of the mean distances of the molecules from one another, but do not involve their thermal motions. The present paper is concerned with these motions which are

⁴ *Ind. J. Physics, loc. cit.*

⁵ *Proc. Ind. Acad. Sciences, loc. cit.*

⁶ *Proc. Ind. Acad. Sciences, loc. cit.*

expressed with reference to a temperature-variable factor β involving the fractional amplitude of vibration of a molecular centre within its spherical space. It has been found possible to relate β to (a) frequency of vibration of a liquid molecule, (b) internal thermal pressure, (c) density, (d) internal latent heat, (e) surface tension, (f) viscosity, (g) vapour pressure. The equations so deduced on the whole express satisfactorily the experimental results. Semi-empirical equations for (h) the coefficient of thermal expansion, and (i) the compressibility, have also been obtained.

2. *Frequency of Vibration of a Liquid Molecule.*

We assume with Andrade⁷ that a theory on simple classical lines is initially more profitable than one involving the introduction of quantum conditions. Further we follow Andrade in regarding the molecular centres of a liquid near the melting point as vibrating for the most part about a mean position of equilibrium; the progressive motion through the liquid is slow compared with the vibratory motion. There is a good deal of evidence for this quasi-crystalline character of a liquid near its melting point.⁸ We look on each molecule then as confined in its thermal motions inside the spherical space of diameter σ , which we have associated with each attractive force centre and we assume that, at a given temperature, the average amplitude of the displacement of the centre of a molecule from the centre of its spherical space is given by $\frac{\beta\sigma}{2}$. As the index of the repulsive force is large, a molecule in repulsion behaves very much as rigid body, and can be considered as a rigid core moving within its own sphere. If a molecule has an average velocity u normal to a plane during a vibration, the associated frequency of vibration will be

$$\nu = \frac{u}{2\beta\sigma} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (17)$$

Assuming the usual distribution law, the mean frequency will be given by

$$\nu = 2 \int_0^\infty \frac{1}{b\sqrt{\pi}} \cdot \frac{u}{2\beta\sigma} e^{-u^2/b^2} du \quad \dots \quad \dots \quad \dots \quad \dots \quad (18)$$

where

$$b = \sqrt{\frac{2kT}{m}} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (19)$$

Hence

$$\nu = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{kT}{m}} \cdot \frac{1}{\beta\sigma} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (20)$$

⁷ *Phil. Mag.*, 1934, 17, 497.

⁸ Cf. Bradley, *J. Chem. Soc.*, 1934, 1910.

and inserting (1) and the values of the constants,

$$\nu = \frac{2.76 \times 10^{11}}{\beta} \cdot \frac{T^{1/2}}{M^{1/2} V^{1/3}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (21)$$

Lindemann's formula for the frequency at the melting-point may be written

$$\nu_{m.p.} = (2-3) \times 10^{12} \frac{T_{m.p.}^{1/2}}{M^{1/2} V_{m.p.}^{1/3}} \quad \dots \quad \dots \quad \dots \quad (22)$$

depending on whether ν is deduced from specific heats, elastic constants, and so on. If we equate (21) and (22), we find

$$\beta_{m.p.} = 0.1 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (23)$$

This value is of the same order as the value obtained for $\beta_{m.p.}$ in solids from specific heat and other data.⁹

3. Internal Thermal Pressure.

The internal thermal pressure at low external pressures will balance the cohesive pressure (2), if it be assumed that the repulsive force term in (12) can be neglected. This internal thermal pressure can be calculated as follows:—

We consider a unit plane in the liquid, and suppose that all the molecules with the centres of their spherical spaces on one side of the plane are removed, and that the plane itself generates all the forces due to the molecules removed. It is further assumed that where a spherical space, belonging to a molecule not removed is cut by the plane, the vibration of the molecule is not affected, that is, the molecule passes through the plane to the limit of its usual amplitude, and returns, being throughout under the forces generated by the plane which substitutes the molecules removed. The thermal pressure on the plane will be the product of the number of molecules in contact with it, the frequency of vibration of these molecules, and the change of momentum in each vibration towards the plane, due to the repulsive force generated by the plane.

The number of molecules per unit area in contact with the plane is given by the close-packing formula,

$$n' = \frac{2}{\sqrt{3} \sigma^2} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (24)$$

The fraction of these molecules which will have an average velocity lying between u and $u + du$ perpendicular to the plane during a vibration is given by

$$dn' = \frac{2}{b \sqrt{\pi}} e^{-u^2/b^2} du \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (25)$$

⁹ Gruneisen, *Ann. d. Phys.*, 1912, **39**, 298.

The frequency of each of these molecules will be $\frac{u}{2\beta\sigma}$, and the change of momentum when sent back by the plane is $2\bar{m}u$.

Hence the thermal pressure generated by the molecules with velocities lying between u and $u + du$ will be,

$$dp_T = \frac{2}{\sqrt{3}\sigma^2} \cdot \frac{u}{2\beta\sigma} \cdot 2\bar{m}u \cdot \frac{2}{b\sqrt{\pi}} e^{-u^2/b^2} du \quad \dots \quad (26)$$

and the total internal thermal pressure will be

$$p_T = \frac{4}{\sqrt{3}\pi} \cdot \frac{\bar{m}}{\beta\sigma^3} \cdot \frac{1}{b} \int_0^\infty u^2 e^{-u^2/b^2} du \quad \dots \quad (27)$$

Integrating and inserting (19),

$$p_T = \frac{2}{\sqrt{3}} \cdot \frac{kT}{\beta\sigma^3} \quad \dots \quad (28)$$

or combining (1),

$$p_T = \sqrt{\frac{2}{3}} \cdot \frac{1}{\beta} \cdot \frac{RT}{V} \quad \dots \quad (29)$$

6. Density.

Under equilibrium conditions,

$$p_T = K, \quad \dots \quad (30)$$

and therefore from (2) and (28),

$$\frac{4\pi\mu}{3(m-4)\sigma^{m+2}} = \frac{2}{\sqrt{3}} \cdot \frac{kT}{\beta\sigma^3} \quad \dots \quad (31)$$

whence

$$\beta = \frac{\sqrt{3}(m-4)\sigma^{m-1}kT}{2\pi\mu} \quad \dots \quad (32)$$

Inserting the values of the constants

$$\beta = \frac{3.77 \times 10^{-17} (m-4)\sigma^{m-1}T}{\mu} \quad \dots \quad (33)$$

From (32),

$$\sigma = \left[\frac{2\pi\mu\beta}{\sqrt{3}k(m-4)T} \right]^{\frac{1}{m-1}} \quad \dots \quad (34)$$

and inserting the values of the constants,

$$\sigma = \left[\frac{2.65 \times 10^{16} \beta\mu}{(m-4)T} \right]^{\frac{1}{m-1}} \quad \dots \quad (35)$$

If β is put equal to 0.1, we have,

$$\sigma_{m.p.} \doteq \left[\frac{2.65 \times 10^{15} \mu}{(m-4)T_{m.p.}} \right]^{\frac{1}{m-1}} \quad \dots \quad (36)$$

Again,

$$d = \frac{M}{V} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (37)$$

which combined with (1) gives,

$$d = \frac{M \sqrt{2}}{N \sigma^3} \dots \dots \dots \dots \dots \dots \dots \dots \dots (38)$$

so that from (35) we have

$$d = \frac{M \sqrt{2}}{N} \left[\frac{2.65 \times 10^{16} \beta \mu}{(m-4)T} \right]^{\frac{-3}{m-1}} \dots \dots \dots \dots (39)$$

(36) is approximate since β is only approximately equal to 0.1 at the melting-point. Table I shows the application of (33) to calculate values of

TABLE I.

$$(33) \beta = \frac{3.77 \times 10^{-17} (m-4) \sigma^{m-1} T}{\mu} \quad (36) \sigma_{m.p.} = \left[\frac{2.65 \times 10^{15} \mu}{(m-4) T_{m.p.}} \right]^{\frac{1}{m-1}}$$

Substance	T	$\sigma \times 10^8$ obs.	m	σ^{m-1}	μ	β calc. (33)	$\sigma \times 10^8$ calc. (36)
He ..	1.0	4.02	7	4.22×10^{-45}	5.77×10^{-60}	0.083	4.15
H ₂ ..	13.9	3.92	8	1.42×10^{-52}	2.33×10^{-66}	0.128	3.78
Ne ..	24.5	3.35	7	1.41×10^{-45}	2.55×10^{-59}	0.153	3.12
Ar ..	83.1	4.02	8	1.70×10^{-52}	1.41×10^{-65}	0.151	3.79
N ₂ ..	63.1	4.23	8	2.42×10^{-52}	2.02×10^{-65}	0.114	4.16

β for some liquefied gases near the melting-point. The values of μ and m are those derived from the gaseous second virial coefficients.¹⁰ The values of β are of the expected order. The application of (36) to calculate approximate values of $\sigma_{m.p.}$ is also shown. The agreement between σ (calc.) from (36) and σ (obs.) calculated by means of (1) from the observed density* at the melting-point is satisfactory.

7. Internal Latent Heat.

It is desirable to obtain an equation for β which does not involve μ , as the force coefficient has only been derived, from the virial coefficient, for

¹⁰ See *Proc. Ind. Acad. Sciences, loc. cit.*, p. 110.

* The experimental results used in this paper have been taken from Landolt-Bornstein, and from the International Critical Tables.

the substances given in Table I. We therefore proceed as follows:—from (4) we have,

$$\frac{(m-4) \sigma^{m-1}}{\mu} = \frac{2 \sqrt{2} \pi N}{3 A_i} \dots \dots \dots (40)$$

and hence from (40) and (32),

$$\beta = \sqrt{\frac{2}{3}} \cdot \frac{RT}{A_i} \dots \dots \dots (41)$$

and inserting (5),

$$\beta = \frac{\sqrt{2} RT \left[1 + \frac{T(m-4) \alpha}{3} \right]}{\sqrt{3} L_i} \dots \dots \dots (42)$$

$$= \frac{2 \sqrt{2} T \left[1 + \frac{T(m-4) \alpha}{3} \right]}{\sqrt{3} L_{i(\text{cal.})}} \dots \dots \dots (43)$$

$$= \frac{1.63 T \left[1 + \frac{T(m-4) \alpha}{3} \right]}{L_{i(\text{cal.})}} \dots \dots \dots (44)$$

Table II shows the application of (44) to a few normal liquids. It will be seen that in each case β has a value of the order of 0.1. (44) when

TABLE II.

$$(44) \beta = \frac{1.63 T \left[1 + \frac{T(m-4) \alpha}{3} \right]}{L_{i(\text{cal.})}}$$

Substance	$T_{m.p.}$	m^*	T_1	† $L_{i(\text{cal.})}$	α	$\beta(T_1)$ calc. (44)	T_2	‡ $L_{i(\text{cal.})}$	α	$\beta(T_2)$ calc. (44)
(C ₂ H ₅) ₂ O ..	156	10.5	233	7200	0.0014	0.09	273	6280	0.0015	0.13
(CH ₃) ₂ CO..	179	11.5	213	8500	0.0013	0.07	293	7060	0.0014	0.14
C ₆ H ₁₄ (n) ..	179	10	203	8400	0.0010	0.06	273	7110	0.0014	0.11
CHCl ₃ ..	210	10	213	8400	0.0012	0.06	288	6980	0.0012	0.11
CCl ₄ ..	250	9	250	7900	0.0012	0.08	273	7450	0.0012	0.09
C ₆ H ₆ ..	279	9.5	279	7700	0.0012	0.09

* *Ind. Journal Physics, loc. cit.*, p. 532.

† From vapour-pressure curves.

‡ Observed.

applied to the substances given in Table I will yield the same values of β as (33), because the equation obtained by combining (4) and (5),

$$L_i = \frac{2\sqrt{2}\pi\mu N}{3(m-4)\sigma^{m-1}} \left[1 + \frac{T(m-4)\alpha}{3} \right] \quad \dots \quad \dots \quad \dots \quad (45)$$

that is

$$L_{i(\text{cal.})} = \frac{4.31 \times 10^{16} \mu}{(m-4)\sigma^{m-1}} \left[1 + \frac{T(m-4)\alpha}{3} \right] \quad \dots \quad \dots \quad \dots \quad (46)$$

has been shown to apply to these substances¹¹ and (46) and (44) give (33).

8. Surface Tension.

From (5) and (11) we have,

$$L_i = \left[\frac{8\sqrt{2}}{3} \cdot \frac{m-5}{m-4} N\gamma\sigma^2 \right] \left[1 + \frac{T(m-4)\alpha}{3} \right] \quad \dots \quad \dots \quad \dots \quad (47)$$

which we can combine with (42) to yield,

$$\beta = \frac{\sqrt{3}}{8} \cdot \frac{m-4}{m-5} \cdot \frac{kT}{\gamma\sigma^2} \quad \dots \quad \dots \quad \dots \quad \dots \quad (48)$$

Now if we insert (1) in (47) we get,

$$L_i = \frac{2^{23i6}}{3} \cdot \frac{m-5}{m-4} \gamma N^{\frac{1}{3}} V^{\frac{2}{3}} \left[1 + \frac{T(m-4)\alpha}{3} \right] \quad \dots \quad \dots \quad \dots \quad (49)$$

which reduces to

$$L_{i(\text{cal.})} = 9.61 \frac{m-5}{m-4} \gamma V^{\frac{2}{3}} \left[1 + \frac{T(m-4)\alpha}{3} \right] \quad \dots \quad \dots \quad \dots \quad (50)$$

Since (50) has been shown to hold for normal liquids,¹² (47) also applies, and hence (48) will give the same values of β as (42).

We can also deduce from (3) and (32) that,

$$\beta = \frac{\sqrt{3}(m-4)kT}{2} (\pi\mu)^{\frac{-2}{m+1}} [4\gamma(m-5)]^{-\frac{(m-1)}{m+1}} \quad \dots \quad \dots \quad (51)$$

Since (3) has been found to apply to the substances given in Table I,¹³ (51) will give the same values of β for these substances as (32).

9. Viscosity.

We apply the method of Andrade.¹⁴ He assumes that communication of translational momentum from one layer of a liquid to the next takes place at each extreme libration. If we regard each layer as moving as a whole with one unit of momentum faster than one neighbouring layer, and one unit slower than the other, then at each extreme libration, a molecule is in contact with molecules with one unit of translational velocity more or

¹¹ *Proc. Ind. Acad. Sciences, loc. cit.*, p. 112.

¹² *Ind. Jour. Physics, loc. cit.*, p. 532.

¹³ *Proc. Ind. Acad. Sciences, loc. cit.*, p. 110.

¹⁴ *Phil. Mag.*, 1934, 17, 497.

less than its average translational velocity. Hence two units of momentum are transferred for each half period of vibration, that is, four units for each period.

The transfer of momentum per unit of area per unit time is given by $\eta \frac{dv}{dz}$ where η is the viscosity, and $\frac{dv}{dz}$ is the translational velocity gradient. We can write, therefore,

$$\eta \frac{dv}{dz} = (4) \left(\frac{m}{m} \frac{dv}{dz} \cdot \frac{\sqrt{2}\sigma}{\sqrt{3}} \right) \left(\frac{2}{\sqrt{3}\sigma^2} \right) \left(\frac{1}{\sqrt{2\pi}} \cdot \sqrt{\frac{kT}{m}} \cdot \frac{1}{\beta\sigma} \right) \dots (52)$$

The factor 4 is explained above; $\frac{\sqrt{2}\sigma}{\sqrt{3}}$ is the perpendicular distance between two adjacent layers, so that $\frac{m}{m} \frac{dv}{dz} \cdot \frac{\sqrt{2}\sigma}{\sqrt{3}}$ is the difference in translational momentum per molecule between two adjacent layers, $\frac{2}{\sqrt{3}\sigma^2}$ is the number of molecules per unit area, and $\frac{1}{\sqrt{2\pi}} \cdot \sqrt{\frac{kT}{m}} \cdot \frac{1}{\beta\sigma}$ is the frequency [See (20)]. (52) then reduces to

$$\eta = \frac{8R^{\frac{1}{2}}}{3\sqrt{\pi}N} \cdot \frac{M^{\frac{1}{2}}T^{\frac{1}{2}}}{\beta\sigma^2} \dots \dots \dots (53)$$

We can substitute any of the equations deduced for β ; (48), however, appears to be most suitable, and with (53) gives

$$\eta = \frac{64R^{\frac{1}{2}}}{3\sqrt{3}\pi} \cdot \frac{m-5}{m-4} \cdot \frac{\gamma M^{\frac{1}{2}}}{T^{\frac{1}{2}}} \dots \dots \dots (54)$$

$$= 7.61 \times 10^{-4} \cdot \frac{m-5}{m-4} \cdot \frac{\gamma M^{\frac{1}{2}}}{T^{\frac{1}{2}}} \dots \dots \dots (55)$$

Table III shows that (55) applies to a variety of liquids with a fair degree of accuracy, particularly when allowance is made for the fact that for some of the liquids, data near the melting-point are not available.

10. Vapour Pressure.

The method at present used for the calculation of the vapour pressure of a liquid from kinetic considerations¹⁵ is open to objection, since it involves the assumption that a molecule is displaced through a liquid at the same rate as it is through a gas. The surface of the liquid is considered as being bombarded from the interior with molecules, and it is assumed that all molecules with a velocity u , normal to and towards the surface, contained within a prism of height u and unit base, will strike unit area of the surface each second. These assumptions neglect the finite size of the molecules.

¹⁵ See, for example, Eucken, *Lehrbuch Chem. Physik*, 1931, p. 241.

TABLE III.

$$(55) \quad \eta = 7.61 \times 10^{-4} \cdot \frac{m-5}{m-4} \cdot \frac{\gamma M^{\frac{1}{2}}}{T^{\frac{1}{2}}}$$

Substance	$T_{m.p.}$	M	$M^{\frac{1}{2}}$	T	$T^{\frac{1}{2}}$	m	$\frac{m-5}{m-4}$	γ obs.	η calc. (55)	η obs.
$(C_2H_5)_2O$..	156	74	8.59	198	14.1	10.5	0.845	28.5	0.011	0.009
$(CH_3)_2CO$	179	58	7.61	200	14.1	11.5	0.867	35.6	0.013	0.013
$C_6H_{14}(n)$..	179	86	9.27	273	16.5	10	0.833	20.5	0.007	0.004
$CHCl_3$..	210	119.5	10.92	263	16.2	10	0.833	31.0	0.013	0.008
CCl_4 ..	250	154	12.40	273	16.5	9	0.800	28.5	0.013	0.013
C_6H_6 ..	279	78	8.82	279	16.7	9.5	0.818	30.8	0.010	0.008
Cl_2 ..	172	71	8.42	201	14.1	8*	0.75	33.0	0.011	0.007
HCl ..	163	36.5	6.03	163	12.8	8*	0.75	27.9	0.008	0.006
HBr ..	187	81	9.0	187	13.7	8*	0.75	28.9	0.011	0.009
HI ..	222	128	11.3	225	15.0	8*	0.75	29.1	0.013	0.014
H_2S ..	190	34	5.83	190	13.8	8*	0.75	33.2	0.008	0.005
He† ..	1.0	4	2.0	2.5	1.58	7	0.67	0.30	0.0002	0.0003

* From analogy with the liquefied gases given in Table I.

† Burton, *Nature*, 16-2-1935, p. 265.

In the following method of treatment, we adhere to the considerations already advanced, and we consider the surface molecules of the liquid as vibrating in the surface layer until a molecule acquires a velocity normal to the surface greater than a critical velocity, when it passes into the vapour phase.

Frequency of a surface molecule.—It is necessary first to examine the frequency of the molecules in the surface layer. We may neglect the somewhat looser packing of the surface molecules discussed by Edser¹⁶ and assume that in the downward portion of a vibration normal to the surface, a molecule is displaced the usual distance. The average upward displacement from the mean position can be calculated as follows:—Edser¹⁷ has shown that the work W done in removing a molecule a distance x measured upward from and normal to the surface is given by,

$$W = \frac{\pi\mu N}{\sigma^{m-4} V} \left[\frac{x}{(m-3)\sigma} - \frac{x^3}{3(m-1)\sigma^3} \right] \quad \dots \quad (56)$$

¹⁶ *Loc. cit.*, p. 51.

¹⁷ *Loc. cit.*, p. 96.

As a first approximation we assume that at temperature of low vapour pressure, $\frac{x}{\sigma}$ is small, and that $\left(\frac{x}{\sigma}\right)^3$ can be neglected. Hence

$$W = \frac{\pi\mu Nx}{(m-3)V\sigma^{m-3}} \dots \dots \dots \dots \dots \dots (57)$$

and inserting (1),

$$W = \frac{\sqrt{2}\pi\mu x}{(m-3)\sigma^m} \dots \dots \dots \dots \dots \dots (58)$$

The average kinetic energy of an escaping molecule normal to the surface will be $\frac{kT}{2}$, and hence,

$$\frac{\sqrt{2}\pi\mu x}{(m-3)\sigma^m} = \frac{kT}{2} \dots \dots \dots \dots \dots \dots (59)$$

so that,

$$\frac{x}{\sigma/2} = \frac{(m-3)\sigma^{m-1}kT}{\sqrt{2}\pi\mu} \dots \dots \dots \dots \dots \dots (60)$$

and inserting (32),

$$\frac{x}{\sigma/2} = \frac{(m-3)}{(m-4)} \sqrt{\frac{2}{3}} \beta \dots \dots \dots \dots \dots \dots (61)$$

For values of m within the range considered, $\frac{m-3}{m-4} \sqrt{\frac{2}{3}}$ is approximately equal to unity, so that

$$x \doteq \frac{\beta\sigma}{2} \dots \dots \dots \dots \dots \dots (62)$$

and the upward displacement of a surface molecule in its average state is approximately equal to the normal displacement. Hence the frequency of the surface molecules is approximately the same as that of molecules within the liquid.

Number of molecules leaving unit area of the surface per second.—We assume that the number of molecules in unit area of the surface is constant, that is to say, as soon as a molecule leaves the surface, its place is taken by a molecule arriving from the vapour phase. The number of molecular places per unit area is given by (24), the frequency associated with each place is given by (20), and the fractional number of vibrations normal to the surface associated with a velocity greater than u_0 is given by

$$\frac{2}{b\sqrt{\pi}} \int_{u_0}^{\infty} e^{-u^2/b^2} du$$

Hence if u_0 is the critical velocity for return, the number of molecules leaving the surface per unit area per second is

$$N_l = \frac{2}{\sqrt{3}\sigma^2} \cdot \frac{1}{\sqrt{2\pi}} \sqrt{\frac{kT}{m}} \cdot \frac{1}{\beta\sigma} \cdot \frac{2}{b\sqrt{\pi}} \int_{u_0}^{\infty} e^{-u^2/b^2} du \dots \dots (63)$$

$$= \sqrt{\frac{2kT}{3\pi m}} \cdot \frac{1}{\beta\sigma^3} \cdot \frac{2}{b\sqrt{\pi}} \int_{u_0}^{\infty} e^{-u^2/b^2} du \dots \dots (64)$$

$$\text{Now } \frac{2}{b\sqrt{\pi}} \int_{u_0}^{\infty} e^{-u^2/b^2} du = \frac{2}{b\sqrt{\pi}} \int_0^{\infty} e^{-u^2/b^2} du - \frac{2}{\sqrt{\pi}} \int_0^{u_0/b} e^{-u^2/b^2} d\left(\frac{u}{b}\right) \dots (65)$$

$$= (1-A) \dots \dots \dots (66)$$

$$\text{where } A = \frac{2}{\sqrt{\pi}} \int_0^{u_0/b} e^{-u^2/b^2} d\left(\frac{u}{b}\right) \dots \dots (67)$$

For values of $u_0/b \ll 3$, the corresponding value of A may be found from Tables.¹⁸ For larger values of u_0/b we can use the approximation,¹⁹

$$1 - A = \frac{e^{-u_0^2/b^2}}{\sqrt{\pi} u_0/b} \dots \dots (68)$$

From (64) and (66) we have

$$N_l = \sqrt{\frac{2kT}{3\pi m}} \cdot \frac{1}{\beta\sigma^3} \cdot (1-A) \dots \dots (69)$$

which on insertion of (19) gives,

$$N_l = \frac{b}{\sqrt{3}\pi} \cdot \frac{1}{\beta\sigma^3} \cdot (1-A) \dots \dots (70)$$

The number of molecules from the vapour phase which strike unit area of the surface of the liquid per second is given by

$$N_g = \frac{N}{V_g} \cdot \frac{b}{2\sqrt{\pi}} \dots \dots (71)$$

where V_g is the molecular volume of the vapour. If the dilute vapour is considered to be a perfect gas, we can write,

$$p = \frac{NkT}{V_g} \dots \dots (72)$$

where p is the vapour pressure.

¹⁸ See Jeans, *Dynamical Theory of Gases*, 1916, Appendix B.

¹⁹ See Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, 1929, p. 11.

Hence from (71) and (72),

$$N_g = \frac{p}{kT} \cdot \frac{b}{2\sqrt{\pi}} \dots \dots \dots (73)$$

At equilibrium we can put,

$$N_l = N_g \dots \dots \dots (74)$$

so that from (70), (73) and (74),

$$\frac{b}{\sqrt{3}\pi} \cdot \frac{1}{\beta\sigma^3} \cdot (1-A) = \frac{p}{kT} \cdot \frac{b}{2\sqrt{\pi}} \dots \dots \dots (75)$$

that is, $p = \frac{2(1-A)kT}{\sqrt{3}\beta\sigma^3} \dots \dots \dots (76)$

Inserting (1), we have

$$p = \sqrt{\frac{2}{3}} \cdot \frac{(1-A)RT}{\beta V} \dots \dots \dots (77)$$

which with (41) gives,

$$p = \frac{A_i(1-A)}{V} \dots \dots \dots (78)$$

Now as u_0 is the critical velocity for escape,

$$A_i = \frac{1}{2} N\bar{m} u_0^2 \dots \dots \dots (79)$$

and from (19)

$$RT = \frac{1}{2} N\bar{m} b^2 \dots \dots \dots (80)$$

so that from (79) and (80),

$$\frac{u_0}{b} = \sqrt{\frac{A_i}{RT}} \dots \dots \dots (81)$$

$$= \sqrt{\frac{A_i(\text{cal.})}{2T}} \dots \dots \dots (82)$$

when A_i is expressed in cals. Thus A can be determined from $\frac{A_i(\text{cal.})}{2T}$.

If we express p in *mm.* of mercury, and A_i in cals., (78) becomes,

$$p_{mm} = \frac{3 \cdot 15 \times 10^4 A_i(\text{cal.})(1-A)}{V} \dots \dots \dots (83)$$

As the value of A is very sensitive to small changes in the value of A_i , it is preferable for comparison between theory and experiment, to calculate A_i and thence L_i from the observed value of p , and compare the calculated and observed values of L_i .

Taking logarithms (83) gives,

$$\log A_i(\text{cal.}) + \log (1-A) = \log p_{mm} \pm \log V - 4.498 \dots \dots (84)$$

It is convenient to write

$$\log \frac{A_i(\text{cal.})}{RT} + \log (1-A) = \log p_{mm} + \log V - \log RT - 4.498 \dots (85)$$

that is,

$$\log \frac{A_i(\text{cal.})}{2T} + \log (1-A) = \log p_{mm} + \log V - \log T - 4.799 \quad \dots (86)$$

and to determine $\frac{A_i(\text{cal.})}{2T}$.

For the substances given in Table IV, $\sqrt{\frac{A_i(\text{cal.})}{2T}}$ is found to lie between 2 and 3. In this range it has been found empirically by the use of Tables for A, that

$$\frac{A_i(\text{cal.})}{2T} = -2.61 X - .53 \quad \dots \dots \dots (87)$$

$$\text{where } X = \log \frac{A_i(\text{cal.})}{2T} + \log (1-A) \quad \dots \dots \dots (88)$$

Hence from (86) and (87),

$$\frac{A_i(\text{cal.})}{2T} = -2.61 (\log p_{mm} + \log V - \log T) + 12.00 \quad \dots \dots (89)$$

and from (5) and (89),

$$L_i(\text{cal.}) = T \left[1 + \frac{T(m-4)\alpha}{3} \right] [24 - 5.22 (\log p_{mm} + \log V - \log T)] \quad (90)$$

As Table IV shows, (90) gives moderately good results.

TABLE IV.

$$(90) \quad L_i(\text{cal.}) = T \left[1 + \frac{T(m-4)\alpha}{3} \right] [24 - 5.22 (\log p_{mm} + \log V - \log T)]$$

Substance	T	α	m	$1 + \frac{T(m-4)\alpha}{3}$	p_{mm}	V	L_i obs.	L_i calc. (90)
He ..	1.75	0	7	1.0	12	27.5	18.6	21.2
H ₂ ..	15.0	0.012	8	1.240	108	26.3	189	225
Ar ..	87.1	0.0046	8	1.534	740	28.4	1326	1540
N ₂ ..	63.1	0.0048	8	1.403	91	31.9	1330	1360

For the normal liquids given in Table V, $\sqrt{\frac{A_i}{2T}}$ lies between 3 and 3.2. From (68), (82) and (83) we then have

$$p_{mm} = \frac{3.15 \times 10^4 A_i(\text{cal.})}{V} \cdot \frac{e^{-\frac{A_i(\text{cal.})}{2T}}}{\sqrt{\pi} \sqrt{\frac{A_i(\text{cal.})}{2T}}} \quad \dots \dots \dots (91)$$

which gives,

$$\frac{1}{2} \log \frac{A_i(\text{cal.})}{2T} - \frac{.434 A_i(\text{cal.})}{2T} = \log p_{mm} + \log V - \log T - 4.550 \quad (92)$$

For values of $\sqrt{\frac{A_i(\text{cal.})}{2T}}$ within the range under consideration it has been found empirically that

$$\frac{A_i(\text{cal.})}{2T} = -2.44 \left(\frac{1}{2} \log \frac{A_i(\text{cal.})}{2T} - \frac{.434 A_i(\text{cal.})}{2T} \right) + 0.65 \quad \dots (93)$$

Hence from (92) and (93)

$$\frac{A_i(\text{cal.})}{2T} = -2.44 (\log p_{mm} + \log V - \log T) + 11.77 \quad \dots (94)$$

and from (5) and (94)

$$L_{i(\text{cal.})} = T \left[1 + \frac{T(m-4)\alpha}{3} \right] [23.54 - 4.88 (\log p_{mm} + \log V - \log T)] \quad (95)$$

As Table V shows the calculated values of L_i are higher than those observed. Better agreement is scarcely to be expected in view of the nature of the assumptions.

TABLE V.

$$(95) \quad L_{i(\text{cal.})} = T \left[1 + \frac{T(m-4)\alpha}{3} \right] [23.54 - 4.88 (\log p_{mm} + \log V - \log T)]$$

Substance	T	α	m	$1 + \frac{T(m-4)\alpha}{3}$	p_{mm}	V	L_i obs.	L_i calc. (95)
C_6H_6 ..	279	0.0012	9.5	1.615	37	87.3	7700	8250
$CHCl_3$..	253	0.0012	10	1.609	20	76.3	7600	8000
CCl_4 ..	253	0.0012	9	1.508	10	92.0	7800	7900
$C_6H_{14}(n)$..	253	0.0013	10	1.659	14	124	7500	8100

11. Coefficient of Thermal Expansion.

There still remain for consideration the coefficient of thermal expansion and the compressibility of a liquid. To derive formulæ for these properties, it is necessary to examine the equations for the actual vibration of the molecular centre in its spherical space under the action of both the attractive and repulsive forces set up by the other molecules. It is hoped to do this in a subsequent paper. Meanwhile the following approximate semi-empirical treatment may be of interest :—

As an empirical fact it is assumed that α is independent of temperature, and that we can write,

$$\sigma = \sigma_0 \left(1 + \frac{\alpha T}{3} \right) \quad \dots \quad (96)$$

where σ_0 can be regarded as the diameter of the rigid core of the molecule, that is of the space within which the repulsive force increases very rapidly.²⁰ We may also, if we regard the molecule as having a rigid core vibrating within a spherical space, put

$$\sigma_0 = \sigma (1 - \beta) \quad \dots \quad (97)$$

whence eliminating σ_0 ,

$$\beta = \frac{\alpha T}{3} / (1 + \alpha T/3) \quad \dots \quad (98)$$

$$\doteq \frac{\alpha T}{3} \quad \dots \quad (99)$$

$$\text{and } \alpha = \frac{3\beta}{T(1-\beta)} \quad \dots \quad (100)$$

$$\doteq 3\beta/T \quad \dots \quad (101)$$

It should be emphasised that (98) to (101) are very approximate; (101) for example indicates that β is directly proportional to temperature which is not so. The equations cannot be applied to the liquefied gases given in Table I since with these the value of α varies rapidly with temperature. Table VI shows the application of (100) using values of β taken from Table II.

TABLE VI.

$$(100) \quad \alpha = \frac{3\beta}{T(1-\beta)}$$

Substance	T	β Table II	α obs.	α calc. (100)	T	β Table II	α obs.	α calc. (100)
(C ₂ H ₅) ₂ O ..	233	0.09	0.0014	0.0013	273	0.13	0.0015	0.0016
(CH ₃) ₂ CO ..	213	0.07	0.0013	0.0011	293	0.13	0.0014	0.0015
C ₆ H ₁₄ (n) ..	203	0.06	0.0010	0.0009	273	0.11	0.0014	0.0014
CHCl ₃ ..	213	0.06	0.0012	0.0009	288	0.11	0.0012	0.0013
CCl ₄ ..	250	0.08	0.0012	0.0010	273	0.09	0.0012	0.0011
C ₆ H ₆	279	0.09	0.0012	0.0011

The agreement between the calculated and observed values of α is satisfactory.

²⁰ Cf. Bradley, *Jour. Chem. Soc.*, 1934, 1911.

We can insert the equations relating a and β in the equations previously obtained and deduce some interesting results. Thus from (5) and (99) we have

$$L_i = A_i [1 + \beta (m - 4)] \quad \dots \quad (102)$$

which with (41) gives

$$L_i = A_i + \sqrt{\frac{2}{3}} (m - 4) RT \quad \dots \quad (103)$$

This equation is interesting as it expresses L_i in terms of A_i without the introduction of a . Again (41) and (103) give

$$L_i = \sqrt{\frac{2}{3}} RT \left[\frac{1}{\beta} + (m - 4) \right] \quad \dots \quad (104)$$

Again from (104) and (99) we have

$$L_i = \frac{(\sqrt{6}) R}{a} + \sqrt{\frac{2}{3}} (m - 4) RT \quad \dots \quad (105)$$

whence $\alpha = \frac{\sqrt{6} R}{L_i - \sqrt{\frac{2}{3}} (m - 4) RT} \quad \dots \quad (106)$

$$= \frac{4.89}{L_{i(\text{cal.})} - 1.63(m - 4)T} \quad \dots \quad (107)$$

Equations (102) to (107) must hold approximately as the equations on which they are based do so. As a matter of interest the application of (107) is shown in Table VII.

TABLE VII.

$$(107) \quad \alpha = \frac{4.89}{L_{i(\text{cal.})} - 1.63(m - 4)T}$$

Substance	T	m	$L_i(\text{cal.})$ obs.	α calc. (107)	α obs.
$(C_2H_5)_2O$	273	10.5	6280	0.0014	0.0015
$(CH_3)_2CO$	293	11.5	7060	0.0014	0.0014
$C_6H_{14}(\mu)$	273	10	7110	0.0011	0.0014
$CHCl_3$	288	10	6980	0.0012	0.0012
CCl_4	273	9	7450	0.0009	0.0012
C_6H_6	279	9.5	7700	0.0009	0.0012

12. Compressibility.

The compressibility of a liquid is given by the equation,²¹

$$\epsilon = \frac{T\alpha^2 V}{C_{pl} - C_{vl}} \quad \dots \quad (108)$$

²¹ Cf. Tyrer, *loc. cit.*, p. 170.

This combined with (7) gives²²

$$c = \frac{T\alpha V}{L_i} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (109)$$

From (99) and (109) we have

$$c = \frac{3\beta V}{L_i} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (110)$$

The application of (110) is shown in Table VIII. The agreement between the calculated and observed values is not unsatisfactory.

TABLE VIII.

$$(110) \quad c = \frac{3\beta V}{L_i}$$

Substance	T	V	L_i ergs.	β Table II	c calc. (110)	c obs.
$(C_2H_5)_2O$..	273	100.5	2.63×10^{11}	0.13	14.9×10^{-11}	15.0×10^{-11}
$(CH_3)_2CO$..	293	73.3	2.96×10^{11}	0.14	10.4×10^{-11}	12.4×10^{-11}
$C_6H_{14}(n)$..	273	127.0	2.98×10^{11}	0.11	14.0×10^{-11}	12.5×10^{-11}
$CHCl_3$..	288	79.8	2.92×10^{11}	0.11	9.0×10^{-11}	9.7×10^{-11}
CCl_4 ..	273	94.2	3.12×10^{11}	0.09	8.1×10^{-11}	9.0×10^{-11}
C_6H_6 ..	279	87.3	3.23×10^{11}	0.09	7.3×10^{-11}	8.2×10^{-11}

Summary.

The theory which has been discussed in this and preceding papers regards a liquid as being composed of a number of force centres or molecules each vibrating within an associated spherical space kept free from other molecules by the thermal motion of the occupying molecule. The transitional motion of the molecules through the liquid is assumed to be small compared with the vibratory motion. Each molecule attracts and repels the others with forces varying as inverse powers of the distance. The diameter of a spherical space is calculated, assuming that these spaces are closely packed, so that it is taken to vary with temperature. In the calculation of properties, such as L_i and γ , it can be assumed that each molecule is on an average at the centre of its spherical space, and there need only be considered the attractive force since the repulsive force comes into play at distances much smaller than the diameter.

²² Cf. Edser, *loc. cit.*, p. 80; Lewis, *Zeit. phys. Chem.*, 1911, 78, 24.

In the present paper an attempt has been made to consider the vibratory motion of the molecules, and the amplitude of vibration β has been linked with the density, internal latent heat of vapourisation, surface tension, viscosity and vapour pressure. Formulæ relating viscosity with surface tension, and vapour pressure with internal latent heat have also been obtained. Equations for the coefficient of thermal expansion and compressibility have also been derived, but only on the assumption that the coefficient of thermal expansion does not vary with temperature.

The formulæ given above, on the whole, reproduce satisfactorily the experimental results for a number of properties. In order, however, that the theory should be completely satisfactory, it is necessary that formulæ should be obtained which will give β in terms of the force coefficients, the force indices, and the temperature. If this can be done, then from the equations given above a number of properties of liquids can be calculated from the fundamental properties of a molecule, the forces which it generates.

NOTATION ADOPTED.

- A See (67).
 A_i Internal work of evaporation. Work done against van der Waals forces in evaporating isothermally 1 g.-mol. of a liquid to the state of infinitely dilute vapour.
 $A_{i(\text{cal})}$ A_i expressed in cal.
b See (19).
c Compressibility.
 C_{pl} Molecular heat of the liquid at constant pressure.
 C_{vl} Molecular heat of the liquid at constant volume.
 C_{vg} Molecular heat of the liquid vapour at constant volume.
d Density of the liquid.
K Internal pressure.
k Boltzmann's constant.
 L_i Internal latent heat of vapourisation.
 $L_{i(\text{cal.})}$ L_i expressed in cal.
m Index of the power of the inverse distance expressing the variation of the attractive force between two molecules.
m.p. Melting point.
M Molecular weight.
 \bar{m} Mass of a molecule.
n Index for the repulsive force.
n' Number of molecules per unit area of a liquid layer or surface.
N Number of molecules in 1 g.-mol.
 N_g Number of molecules from the vapour phase which strike unit area of the liquid surface per second.
 N_l Number of molecules leaving the liquid surface per unit area per second.

- P Parachor constant.
 p Vapour pressure of a liquid.
 p_{mm} p expressed in mms.
 p_T Internal thermal pressure.
R Gas constant.
T Absolute temperature.
 u Velocity of a gas molecule normal to a plane.
 u_0 Critical velocity normal to the surface for escape of a molecule.
V Volume of 1 g.-mol. of the liquid in the normal state at T.
 V_g Molecular volume of the liquid vapour.
 v Layer velocity of the liquid.
W Work done in removing a liquid molecule from the surface.
 x Distance a molecule is removed from the surface of the liquid.
 z Distance measured normal to the translational motion of the liquid layers.
 α Coefficient of thermal expansion of a liquid.
 β Fractional amplitude of vibration of a molecular centre within its spherical space.
 η Viscosity.
 γ Surface tension.
 λ Repulsive force coefficient.
 μ Attractive force coefficient.
 ν Frequency of vibration.
 σ Diameter of spherical space which a molecule keeps clear around it by its thermal motion.