202. *The Dependence of the Viscosity of Fluids on the Molecular Volume, and an Application of the Principle of the Continuity of State.*

By David T. Lewis.

The viscosities of gases are shown to depend on the molecular weight and the molecular cross-sectional area, as predicted mathematically by Chapman. The derived parachor equation is shown to account satisfactorily for the behaviour of fluids in general, and is applied to many liquids, a generalisation emphasising the importance of the principle of the continuity of state.

Andrade's equation for the variation of the viscosity of a simple substance with temperature is shown to follow directly from the general equation, and the connexion between the constants of this equation and the molecular weight and volume is demonstrated.

Part I. The Viscosity of Gases.

Chapman (*Proc. Roy. Soc.*, 1916, *A*, **93**, 1) has mathematically derived the following expression connecting the viscosity, η, with the gaseous density, σ (in g. per c.c.), the mean velocity of the molecules, ω, and the mean free path, L :

$$\eta = 0{\cdot}499\sigma\omega L/\sqrt{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It follows from the kinetic theory that ω is given by the expression

$$\omega = 0{\cdot}92\sqrt{3p/\sigma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where p is the pressure in dynes per sq. cm. Jeans (" Dynamical Theory of Gases," p. 37) has shown that L is related to the molecular diameter, S, and the number of molecules per c.c., n, by means of the equation

$$L = 1{\cdot}319/\pi S^2 n\sqrt{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Elimination of L and ω between (1), (2), and (3) yields the following expression for η :

$$\eta = \text{const.}\ \sqrt{p\sigma}/\pi S^2 n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

At constant temperature and pressure, n is the same for all gases, and since σ is directly proportional to the molecular weight, M, one obtains

$$\eta = \text{const.}\ \sqrt{M}/\pi S^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

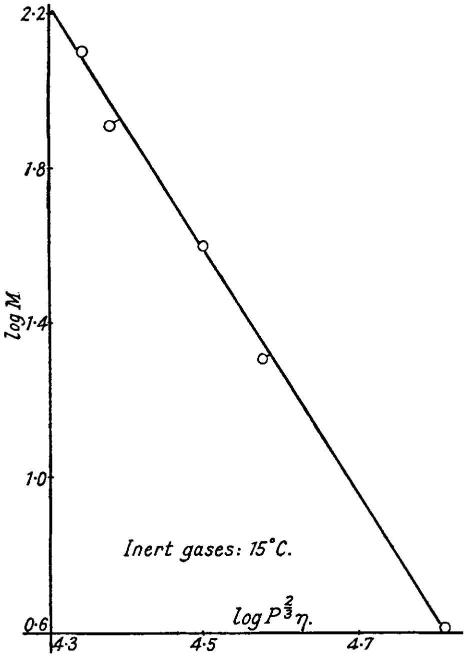
Now, Sugden (" The Parachor and Valency," 1930, p. 32) has shown that the parachor values, P, of various substances are connected with their molecular collisional areas, πR^2, by the relation $P^{\frac{2}{3}} = \text{constant} \times \pi R^2$. If the parachor yields a true comparative measure of the molecular volume, then the area function πS^2 is directly proportional to $P^{\frac{2}{3}}$, whence

$$\eta = \text{const.}\ \sqrt{M}/P^{\frac{2}{3}} \quad . \quad . \quad (6)$$

$$\text{or} \qquad \log P^{\frac{2}{3}}\eta = 0{\cdot}5 \log M - \lambda_c \quad . \quad (7)$$

where λ_c is a constant at one temperature and pressure.

FIG. 1.



The values for the viscosities of the inert gases vary in a chaotic fashion from helium to xenon when considered at the same temperature. This is to be expected, because according to the foregoing it is the product log $P^{\frac{2}{3}}\eta$ which should exhibit variations paralleled by those in M. That this variation does occur is indicated in Table I, which relates to 15°. Parachor values for the inert gases have been computed from the critical temperatures by Lewis (this vol., p. 261), the values being in excellent agreement with those tabulated by Pearson and Robinson (J., 1934, 740). Viscosities are expressed in c.g.s. units × 10^6 and are by Schultz and Rankine, the values for helium and argon at 15° being interpolated from the work of Schultz at various temperatures. Fig. 1 shows that the plot of log M against log $P^{\frac{2}{3}}\eta$ is approximately linear, but the coefficient of log M is 0·3 and not 0·5, the line being represented by

$$0{\cdot}3 \log M = \log P^{\frac{2}{3}}\eta + \lambda_T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\lambda_c \neq \lambda_T$.

In col. 6 are given calculated values for λ_c, which show a steady increase from helium to xenon, whereas λ_T in col. 7 does not fluctuate by more than 1% from the mean value, and the values show no definite trend as was the case with λ_c. Owing to lack of data, one cannot determine whether the constants of equation (8) are dependent on temperature,

TABLE I.

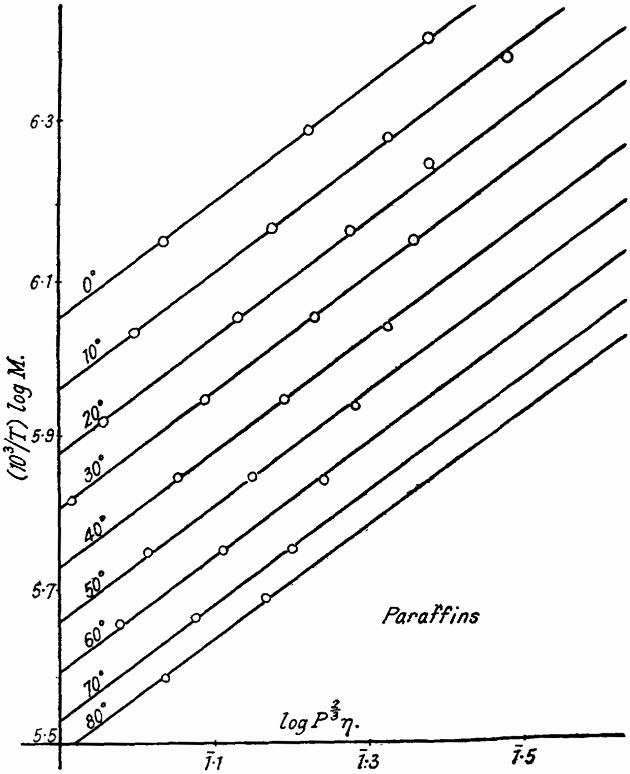
Gas.	P.	$\eta \times 10^6$.	M.	log $\eta P^{\frac{2}{3}}$.	λ_c.	λ_T.
He	21·9	196	4·00	−2·8141	3·1151	2·9947
Ne	25·0	312	20·2	−2·5739	3·2266	2·9655
A	53·78	221	39·91	−2·5019	3·3024	2·9822
Kr	69·72	246	82·90	−2·3803	3·3396	2·9560
Xe	91·22	222	130·2	−2·3469	3·4042	2·9812

as will be shown to be the case for liquids. Moreover, it has been observed that consistency in the values of λ_T for liquids is undoubtedly better for molecules of similar chemical type. This is to be expected, because similar molecules, owing to similar configurational and cohesive nature, may be expected to yield consistency amongst themselves because the factors producing anomalies affect them to the same degree. This has been shown to be the case with critical-temperature relations by Lewis (*loc. cit.*) and is probably true for viscosity relations also (cf. Table I).

PART II. THE VISCOSITY OF LIQUIDS.

Waller (*Phil. Mag.*, 1934, **18**, 579), from a study of the viscosity of liquids at the melting points and boiling points, has observed a rough periodic variation of this function. Such a variation seems to indicate that molecular constitution plays an important part in determining the magnitude of the coefficient of viscosity. Herzog and Kudar (*Z. physikal. Chem.*, 1933, **83**, 28) have developed various formulæ connecting the viscosity with stereochemical structure and atomic distances in molecules, and their conclusions also support the view that viscosity is probably closely connected with the molecular volume. Further, Dunstan and Thole (J., 1907, **91**, 23) have shown that the equation $\eta \times 10^6/V = 62$ (where V is the molecular volume) holds very approximately for 60 unassociated liquids, but this relation does not yield a constant result when the parachor is substituted for the molar volume.

FIG. 2.



On the basis of Andrews's principle of the continuity of state (*Phil. Trans.*, 1876, **2**, 421), *viz.*, "that liquid and gaseous states are only distant stages in a long series of continuous physical changes," it was thought probable that equation (7) which was derived from considerations involving gases might apply equally well to liquids of similar chemical type. Experimental data for various hydrocarbon and halide homologous series have completely justified this conclusion. It was found that at constant temperature and for any homologous series, the plot of log M against log $P^{\frac{1}{4}}\eta$ was linear, showing that an equation similar to (8) was obeyed; then from a study of the values of the coefficient of log M at different temperatures, it was found that the product of this coefficient and the absolute temperature was constant. Hence one obtains

$$\log P^{\frac{1}{4}}\eta = (A/T) \log M - \lambda_T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where A is a constant independent of temperature. Fig. 2 gives the plot of log $P^{\frac{1}{4}}\eta$ against $(1/T)$ log M for the liquid paraffins at various temperatures, and the parallelism of the lines indicates the constancy of A for a distinct series. In Table II the values for the viscosities as calculated from the known molecular weights and parachors (with $A = 666$ for paraffins and $A = 1018$ for alkyl iodides) are compared with Prasad's experimental values (*J. Indian Chem. Soc.*, 1933, **10**, 143). The mean values of λ_T employed in the computation are given in the final column.

In view of the nature of the logarithmic terms involved, the agreement between the computed and the experimental values is all that can be expected. Moreover, it should be noted that λ_T is an extremely sensitive function, and small errors in the numerical estimation of the mean value of this term would considerably affect the calculated value for the viscosity.

It is seen from the graph that λ_T decreases steadily with increasing temperature, and the relation between this function and temperature was determined by a graphical

TABLE II.

Paraffins.

Temp.	$\eta \times 10^6$. Obs.	$\eta \times 10^6$. Calc.	log $P^{\frac{1}{4}}\eta$.	$(10^3/T)$ log M.	λ_T.
		Pentane ($M = 72$; $P = 229{\cdot}2$).			
0°	2894	2894	$\bar{1}$·0350	6·801	5·495
10	2624	2627	$\bar{2}$·9925	6·561	5·377
20	2396	2395	$\bar{2}$·9528	6·337	5·268
30	2200	2200	$\bar{2}$·9159	6·130	5·167
		Hexane ($M = 86$; $P = 268{\cdot}2$).			
0	4020	4037	$\bar{1}$·2231	7·087	5·495
10	3602	3607	$\bar{1}$·1754	6·837	5·377
20	3258	3252	$\bar{1}$·1319	6·606	5·268
30	2963	2939	$\bar{1}$·0906	6·387	5·167
40	2708	2717	$\bar{1}$·0516	6·183	5·066
50	2483	2478	$\bar{1}$·0139	5·991	4·977
60	2288	2303	$\bar{2}$·9783	5·812	4·892
		Heptane ($M = 100$; $P = 307{\cdot}2$).			
0	5236	5318	$\bar{1}$·3773	7·324	5·495
10	4653	4696	$\bar{1}$·3261	7·066	5·377
20	4163	4159	$\bar{1}$·2777	6·825	5·268
30	3754	3723	$\bar{1}$·2328	6·601	5·167
40	3410	3401	$\bar{1}$·1911	6·390	5·066
50	3105	3081	$\bar{1}$·1504	6·191	4·977
60	2841	2840	$\bar{1}$·1118	6·006	4·889
70	2617	2720	$\bar{1}$·0760	5·830	4·791
80	2413	2413	$\bar{1}$·0390	5·665	4·734
90	2239	2240	$\bar{1}$·0083	5·508	4·660
		Octane ($M = 114$; $P = 346{\cdot}2$).			
0	7060	6778	$\bar{1}$·5411	7·536	5·495
10	6154	5903	$\bar{1}$·4821	7·269	5·377
20	4828	5200	$\bar{1}$·3768	7·023	5·268
30	4628	4605	$\bar{1}$·3582	6·790	5·167
40	4328	4151	$\bar{1}$·3292	6·573	5·066
50	3907	3920	$\bar{1}$·2847	6·369	4·977
60	3551	3412	$\bar{1}$·2432	6·179	4·889
70	3241	3240	$\bar{1}$·2035	5·998	4·791
80	2971	2851	$\bar{1}$·1658	5·828	4·734
90	2730	2636	$\bar{1}$·1291	5·666	4·660

TABLE II (continued).

Alkyl Iodides.

Temp.	$\eta \times 10^6$. Obs.	$\eta \times 10^6$. Calc.	$\log P^{\frac{2}{3}}\eta$.	$(10^3/T)\log M$.	λ_T.
Methyl iodide (M = 141·9; P = 186·5).					
0°	6055	6052	$\bar{1}$·2953	7·881	8·728
10	5481	5481	$\bar{1}$·2520	7·603	8·487
20	5001	4989	$\bar{1}$·2122	7·343	8·263
30	4601	4601	$\bar{1}$·1761	7·103	8·054
40	4240	4240	$\bar{1}$·1405	6·877	7·858
Ethyl iodide (M = 155·9; P = 225·5).					
0	7269	7551	$\bar{1}$·4302	8·032	8·728
10	6537	6764	$\bar{1}$·3841	7·749	8·487
20	5925	6095	$\bar{1}$·3415	7·484	8·263
30	5403	5575	$\bar{1}$·3014	7·238	8·054
40	4951	5072	$\bar{1}$·2640	7·006	7·858
50	4558	4521	$\bar{1}$·2276	6·789	7·686
60	4217	4327	$\bar{1}$·1938	6·586	7·499
70	3914	4018	$\bar{1}$·1614	6·393	7·334
Propyl iodide (M = 169·9; P = 264·5).					
0	9435	9397	$\bar{1}$·5896	8·170	8·728
10	8332	8302	$\bar{1}$·5356	7·879	8·487
20	7432	7432	$\bar{1}$·4860	7·612	8·263
30	6687	6653	$\bar{1}$·4402	7·360	8·054
40	6067	6013	$\bar{1}$·3972	7·125	7·858
50	5527	5310	$\bar{1}$·3573	6·904	7·686
60	5065	5065	$\bar{1}$·3195	6·697	7·499
70	4662	4662	$\bar{1}$·2845	6·501	7·334
Butyl iodide (M = 183·9; P = 303·5).					
10	10,320	10,130	$\bar{1}$·6684	8·007	8·487
20	9,166	8,857	$\bar{1}$·6169	7·727	8·263
30	8,189	7,970	$\bar{1}$·5680	7·476	8·054
40	7,298	7,152	$\bar{1}$·5179	7·238	7·858
50	6,762	6,300	$\bar{1}$·4847	7·013	7·686

investigation involving various functions of T. It was found that the plot of λ_T against $1/T$ was linear and that an equation of the type $\lambda_T = B/T + C$ gave λ_T with an accuracy of within 1%. The manner in which this relation is obeyed is indicated below, the equations used for the various series being given.

Paraffins : $\lambda_T = 915/T + 2{\cdot}143$.

Temp., ° K.	273	283	293	303	313	323	333	343	353	363
λ_T, exptl.	5·495	5·377	5·268	5·167	5·066	4·977	4·889	4·791	4·734	4·660
λ_T, calc.	5·495	5·375	5·266	5·163	5·066	4·975	4·891	4·811	4·735	4·663

Alkyl iodides : $\lambda_T = 1862/T + 1{\cdot}906$.

Temp., ° K.	273	283	293	303	313	323	333	343
λ_T, exptl.	8·728	8·487	8·263	8·054	7·858	7·686	7·499	7·334
λ_T, calc.	8·728	8·487	8·261	8·058	7·857	7·686	7·500	7·336

These considerations lead to a general formula for the variation of the viscosity of liquids in homologous series which has the form

$$\log P^{\frac{2}{3}}\eta = (A \log M - B)/T - C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where A, B, and C are independent of temperature and are probably configurational or cohesive functions characterising a particular type of molecule. Table III demonstrates the application of the general equation in the case of the alkyl bromides, viscosities being calculated from the relation

$$\log P^{\frac{2}{3}}\eta = (988 \log M - 1680)/T - 2{\cdot}0585$$

The agreement is exceptionally good, the calculated results being within 1% of the experimental values. The *iso*-derivatives of the paraffins, which form a distinct homologous family, have also been found to yield results in excellent agreement with the general equation.

TABLE III.

	$\eta \times 10^6$.					$\eta \times 10^6$.			
Temp.	Obs.	Calc.	$\log P^{\frac{1}{4}}\eta$.	$(10^3/T) \log M$.	Temp.	Obs.	Calc.	$\log P^{\frac{1}{4}}\eta$.	$(10^3/T) \log M$.
Ethyl bromide ($M = 108{\cdot}9$; $P = 163{\cdot}1$).									
0°	4866	4860	$\bar{1}{\cdot}1621$	7·461	20°	4020	4004	$\bar{1}{\cdot}0792$	6·952
10	4407	4390	$\bar{1}{\cdot}1192$	7·197	30	3678	3677	$\bar{1}{\cdot}0407$	6·725
Propyl bromide ($M = 122{\cdot}9$; $P = 202{\cdot}1$).									
0	6509	6522	$\bar{1}{\cdot}3506$	7·652	40	4338	4309	$\bar{1}{\cdot}1744$	6·676
10	5815	5813	$\bar{1}{\cdot}3017$	7·382	50	3966	3949	$\bar{1}{\cdot}1355$	6·469
20	5241	5230	$\bar{1}{\cdot}2565$	7·131	60	3563	3634	$\bar{1}{\cdot}0889$	6·275
30	4748	4736	$\bar{1}{\cdot}2136$	6·896	70	3374	3368	$\bar{1}{\cdot}0652$	6·091

For any one substance, *M* and *P* are fixed, and the general equation takes the form $\eta = \alpha e^{\beta/T}$, which is identical with Andrade's well-known equation for the variation of the viscosity of a simple substance with temperature. The Andrade equation has been applied to certain non-associated halogen and hydrocarbon derivatives by Prasad (*loc. cit.*; *Phil. Mag.*, 1933, **16**, 263), who demonstrated the excellence of its application but could find no general relation between α, β, and configuration. From the general equation it is obvious that $\beta = A \log M - B$, and thus β should depend on the molecular weight. In Table IV values of β as determined numerically by Prasad are compared with those calculated from the molecular weights of the various liquids.

TABLE IV.

Substance	C_5H_{12}.	C_6H_{14}.	C_7H_{16}.	C_8H_{18}.	CH_3I.	C_2H_5I.	C_3H_7I.	C_4H_9I.	C_2H_5Br.	C_3H_7Br.
β (Prasad)	328	370	406	456	330	358	409	445	335	380
β (calc.)	322	374	417	455	329	370	408	442	333	385

Similarly, it is observed that the constant term α of Andrade's equation is a function of the parachor and hence of the molecular cross-sectional area. Since *A*, *B*, and *C* remain unchanged for members of one distinct series, many simplifications occur in dealing with the question of mixtures of the same series. For such mixtures it is probable that the viscosity will depend on a mean molecular weight and a mean parachor value for the particular mixture. When liquids of different series are mixed, the problem becomes extremely complicated owing to the variation of the constants concerned. It is probable that this variation accounts for the fact that no expression has yet been derived that satisfactorily accounts for the behaviour of mixed liquids.

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