732. *The Viscosity and Intermolecular Potential of Silicon Tetrafluoride.*

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A modified form of transpiration apparatus, adapted for relative determinations involving only small volumes of gas, has been used to determine the viscosity of silicon tetrafluoride in the range 20—140°. The results are well represented by Sutherland's equation (with $C = 151°$ K), and the Lennard-Jones (12,6) potential parameters ($\varepsilon/k = 147°$ K; $\sigma = 5{\cdot}13$ Å) have been computed and compared with the values obtained from second virial coefficients.

The recent researches in these laboratories on the viscosity and intermolecular potential of boron trifluoride [1,2] led the authors to consider the gas silicon tetrafluoride whose properties are very similar. Although the second virial coefficient [3] has been determined and used to evaluate the intermolecular potential energy, the literature appears to lack data on the viscosity of silicon tetrafluoride.

Experimental

Preparation of Silicon Tetrafluoride.—This was prepared by heating barium hexafluorosilicate to about 500° in an electric furnace (Bairar *et al.*[4]). Purification by vacuum-distillation of the gas after it had passed from the reaction tube through an ethanol–carbon dioxide trap, was effected in an all-glass apparatus similar to that described by Germann and Booth.[5]

Viscometer.—In principle the apparatus is similar to Schultze's transpiration apparatus,[6] but a number of simplifying modifications have been introduced.

With the exception of rubber pressure tubing between the mercury reservoirs and the gas containers, it is made wholly from Pyrex glass. After the gas had been introduced, the levels in the multiplying manometers were adjusted at an equal height above and below the original level, so as to give a fixed pressure difference across the capillary tube. The taps isolating the capillary tube from the manometers and mercury reservoirs on either side were opened, and the gas was allowed to flow through a thin-walled spiral preheater and the capillary tube (length 33 cm., radius 0·01 cm.), both of which were contained in an oil-thermostat (±0·2°). The levels of the liquid in the multiplying manometers, and consequently the pressure differences, were kept unaltered throughout each determination. This was possible owing to the slow passage of the gas through the narrow-bore capillary. The time of flow of a fixed volume of gas (approx. 34 c.c.) was measured correct to 0·2 sec.

The multiplying manometers employed were of the type described by Higgins.[7] They increase the sensitivity of an ordinary mercury manometer approximately eight times.

The mercury reservoirs were operated manually through reduction gears situated close together at bench level to allow of their being turned by the operator whilst observing the levels of the liquid in the centrally placed multiplying manometers.

The use of a fixed volume of gas eliminated the necessity for withdrawing and weighing mercury after each determination. The maintenance of the manometer levels at a constant difference for all experiments obviated any error due to changes of atmospheric pressure.

Calculation of Results.—The apparatus was calibrated with pure dry air in the range 20—150°. By using the observed time of flow measurements in conjunction with the published mean results[8] for the viscosity of air at the same temperatures, a constant for the apparatus was obtained from the formula:

$$k' = (\eta - \eta_s)/(t - t_s) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k' is the constant for *differences* in temperature, η_s is the viscosity of air at a standard temperature (23°), t_s is the time of flow in seconds at a standard temperature, and η and t

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[1] Cooke and Mackenzie, *J. S. African Chem. Inst.*, 1951, **4**, 123.

[2] Raw, *ibid.*, 1954, **7**, 20.

[3] Hamann, McManamey, and Pearse, *Trans. Faraday Soc.*, 1953, **49**, 351.

[4] Bairar *et al.*, "Inorganic Syntheses," McGraw Hill, 1953, Vol. IV, p. 145.

[5] Germann and Booth, *J. Phys. Chem.*, 1917, **21**, 81.

[6] Schultze, *Ann. Physik*, 1901, **5**, 140.

[7] Higgins, M.Sc. Thesis, Natal.

[8] Landolt–Börnstein, "Physikalisch Chemische Tabellen."

represent the viscosity and time of flow at other temperatures. The value of k' was found experimentally to be 0·947 for this viscometer.

The viscosity of air at 23° has been determined with particular accuracy, and a weighted mean viscosity of 1830×10^{-7} g. cm.$^{-1}$ sec.$^{-1}$ assigned to it.[9] This was consequently selected as the standard.

In these experiments the pressure difference was held constant for all readings, the same volume of gas was used throughout, the radius and length of the capillary also remained constant, hence Poiseuille's formula [10] reduces to

$$\eta_s = kt_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k is the apparatus constant for a particular temperature—in this case 23°. At 23° the average rate of flow for dry air was found to be 678·0 sec., whence $k = 2{\cdot}700 \times 10^{-7}$.

For the range of temperatures employed, the slip effect is less than the experimental accuracy of about 0·5% and it has been neglected in these experiments.

RESULTS and DISCUSSION

From results obtained in the case of silicon tetrafluoride the rate of flow at 23° was found to be 563·0 sec. Whence, by use of eqn. (2), $\eta_s = 1520 \times 10^{-7}$ g. cm.$^{-1}$ sec.$^{-1}$. The experimental results obtained are recorded in the Table, where η is calculated at the higher temperatures by using equation (1).

Variation of viscosity of silicon tetrafluoride with temperature.

Temp., T (°K)	$t - t_s$	$\eta - \eta_s$	$\eta \times 10^7$ (g. cm.$^{-1}$ sec.$^{-1}$)	$T^{3/2}/\eta$	Temp., T (°K)	$t - t_s$	$\eta - \eta_s$	$\eta \times 10^7$ (g. cm.$^{-1}$ sec.$^{-1}$)	$T^{3/2}/\eta$
296·0°	(t_s = 563)	—	1520	3·351	352·5°	239·6	226·9	1747	3·787
304·3	35·6	33·70	1554	3·416	362·8	285·6	270·4	1790	3·860
313·1	77·4	73·28	1593	3·477	373·1	327·5	310·1	1830	3·938
321·8	105·2	99·61	1620	3·563	383·5	371·8	352·1	1872	4·013
332·1	147·0	139·2	1695	3·647	394·1	417·5	395·3	1915	4·091
342·4	194·4	184·1	1704	3·718	406·8	477·0	451·6	1972	4·161

Sutherland's equation for the variation of the viscosity of a gas with temperature can be written [10] in the form, $T = (AT^{3/2}/\eta) - C$, where A and C are constants; C can be obtained as the negative intercept on the T-axis if T is plotted against $T^{3/2}/\eta$.

From a plot of the values given in the Table, C for silicon tetrafluoride is found to be 151° K.

The viscosity can be used, following Hirschfelder *et al.*,[11] to obtain the parameters in the empirical Lennard-Jones (12,6) form of the intermolecular potential energy. By trial-and-error values of these, potential parameters are chosen which on substitution in the theoretical equation for the viscosity give values in agreement with the experimental results. The potential parameters determined in this way have values $\varepsilon/k = 147°$ K and $\sigma = 5{\cdot}13$ Å, where ε is the depth of the potential well, σ is the collision diameter (the separation for which the potential energy is zero), and k is Boltzmann's constant.

The results obtained by Hamann *et al.*[3] from second virial coefficients are $\varepsilon/k = 147{\cdot}8°$ K and $\sigma = 5{\cdot}95$ Å. The discrepancy in the case of the collision diameter is no doubt due to the inadequacy of the Lennard-Jones model in describing different properties by using the same potential parameters.

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[9] Kaye and Laby, " Physical and Chemical Constants," Longmans Green and Co., London, 10th edn., 1948.

[10] Partington, " Advanced Treatise on Physical Chemistry," Longmans Green and Co., Vol. I, 1949.

[11] Hirschfelder, Curtiss, and Bird, " Molecular Theory of Gases and Liquids," Wiley, New York, 1954.