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C.J. Smith B.Sc. A.R.C.S. D.I.C.

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XLVII. *On the Viscosity and Molecular Dimensions of Sulphur Dioxide.* By C. J. SMITH, B.Sc., A.R.C.S., D.I.C., Research Student, Imperial College of Science and Technology, London*.

RECENT work on the viscous properties of compounds which are ordinarily gaseous having been successful in elucidating the molecular structure of these compounds, it was thought that it would be interesting to apply similar methods in the case of sulphur dioxide, especially as Langmuir† has already suggested a possible arrangement of the atoms which constitute this particular molecule. This paper describes the necessary viscosity measurements for sulphur dioxide. Previously the data regarding the viscosity of this gas were very scanty and did not extend over a sufficient range of temperature to determine Sutherland's constant—a factor of almost as great an importance as that of the viscosity itself in determining the mean collision area of a molecule.

Apparatus and Method of Observation.

The apparatus and method of observation which have been used for the purpose of measuring the viscosity of sulphur dioxide have recently been fully described‡.

Method of Experiment.

The mercury pellet, which was used to drive the gas through a capillary tube which forms part of a complete circuit consisting of this tube and a fall tube in which the pellet moves between specified marks, is the same as that which was used by the author in his experiments on carbon oxysulphide§. The time of fall for air proved to be 105.53 secs. at 18.0° C. With this time of fall the corresponding time of fall for sulphur dioxide has been compared, and, with appropriate corrections, this gives the relative viscosity of air and sulphur dioxide. From this relative value the absolute viscosity has been obtained by assuming that the viscosity of air at 18.0° C. is 1.814×10^{-4} C.G.S. units. In addition, the variation of viscosity with temperature has been derived from comparisons of the corrected times of fall at atmospheric and steam temperatures.

* Communicated by Prof. Rankine.

† Langmuir, Journ. Amer. Chem. Soc. vol. xli. p. 868 (1919).

‡ A. O. Rankine and C. J. Smith, Phil. Mag. vol. xlii. p. 601 (1921); and C. J. Smith, Proc. Phys. Soc. vol. xxxiv. p. 155, June 1922.

§ C. J. Smith, Phil. Mag. vol. xlv. p. 289 (1922).

Preparation and Purification of the Sulphur Dioxide.

The sulphur dioxide was generated by the action of dilute sulphuric acid on sodium sulphite. It was dried by being passed through several wash bottles containing concentrated sulphuric acid, and then solidified in a U-tube surrounded by liquid air. The U-tube was then cut off from the generating apparatus, and all permanent gases removed by means of a pump. The gas was made to evaporate by removing the liquid air, and samples were collected over mercury. The chief difficulty in using this gas is to dry it sufficiently well that the motion of the pellet of mercury in the fall tube shall be smooth. It is difficult because sulphur dioxide boils at $-10^{\circ}\text{C}.$, and at this temperature water has a small vapour-pressure. It was finally purified and dried in the following way, before introduction into the viscometer:—The gas was solidified in a tube maintained at $-80^{\circ}\text{C}.$ by means of a mixture of solid carbon dioxide and alcohol, and all permanent gases and possible traces of carbon dioxide removed by means of a Toepler pump. Sufficient alcohol was then added to the carbon dioxide mixture to raise the temperature to $-60^{\circ}\text{C}.$ At this temperature water has a negligible vapour-pressure, while sulphur dioxide is liquid and has an appreciable vapour-pressure. This enabled successive small quantities of the dry gas to be pumped off and introduced into the viscometer, which was previously exhausted, until the pressure therein was atmospheric.

Experimental Results.

TABLE I.

Each time recorded in this table is the mean of four observations in each direction for the whole pellet, and of three when the pellet is divided into two segments. The letters in parentheses indicate the order in which observations were made.

Temp. (deg. C.).	Time of fall (secs.).		Capillary correction. (x).	Corrected time (t).	Time at	
	Whole pellet.	Two segments.			$18^{\circ}\text{C}.$	$100^{\circ}\text{C}.$
(a) 17.72	76.16	79.67	0.0422	72.95	73.03	
(b) 17.80	76.48	80.38	0.0463	72.95	73.01	
(c) 17.85	76.82	81.00	0.0491	73.05	73.09	
(f) 17.38	76.40	80.37	0.0471	72.80	72.97	
				Mean	73.03	
(d) 100.0	97.10	99.32	0.0219	94.97	...	94.97
(e) 99.96	97.13	99.37	0.0220	94.99	...	95.00
					Mean	94.99

We have $t_{18}=73\cdot03$ sec., and $t_{100}=94\cdot99$ sec.

The ratio of the viscosities at 18° C. and 100° C. is given by the ratio of these times ; thus

$$\frac{\eta_{100}}{\eta_{18}} = \frac{t_{100}}{t_{18}} = \frac{94\cdot99}{73\cdot03} = 1\cdot301.$$

Assuming Sutherland's law to hold over the range of temperature used in these experiments, the value of Sutherland's constant is 416. The validity of Sutherland's law for this gas over the range of temperature investigated cannot be expected to be great on account of the probable large deviations from Boyle's law which this gas may exhibit, since the temperatures at which measurements have been made are not very far removed from the boiling-point of liquid sulphur dioxide. The value of C given, and subsequent deductions depending thereon, should therefore be accepted with some reserve.

$$\text{Also at } 18^{\circ}\text{C.}, \quad \frac{t_{\text{SO}_2}}{t_{\text{air}}} = \frac{73\cdot03}{105\cdot53} = 0\cdot6923.$$

Correcting for slip in the usual way, we obtain

$$\frac{\eta_{\text{SO}_2}}{\eta_{\text{air}}} = 0\cdot6908.$$

Assuming that the viscosity of air at 18° C. is $1\cdot814 \times 10^{-4}$ C.G.S. units, the values for SO_2 are

$$\eta_{18} = 1\cdot253 \times 10^{-4} \text{ C.G.S. units,}$$

$$\eta_{100} = 1\cdot630 \times 10^{-4} \text{ C.G.S. units,}$$

and by extrapolation, using Sutherland's law,

$$\eta_0 = 1\cdot168 \times 10^{-4} \text{ C.G.S. units.}$$

According to the usual works of reference and published papers, Vogel* is the only modern worker on this subject, and he found that $\eta_0 = 1\cdot183 \times 10^{-4}$ C.G.S. units.

Calculation of Molecular Dimensions.

The above results enable us to calculate for sulphur dioxide that mean area which is interpreted by Professor Rankine† as the area which the molecule presents in mutual collision with others. Chapman's‡ formula, modified in its interpretation, as indicated above, is the basis of this calculation. The

* H. Vogel, *Berlin Diss.* p. 46, 1914.

† Proc. Faraday Soc. vol. xvii. part 3 (1922).

‡ Chapman, Phil. Trans. A. vol. ccxvi. p. 347.

value obtained is $\bar{A} = 0.94 \times 10^{-15} \text{ cm.}^2$, which may be subject to an experimental error of 2 or 3 per cent. It is difficult to estimate the degree of precision with which this figure represents the real dimensions of the molecule. The measurements of viscosity, owing to the comparatively small temperature range over which they extend, provide no proof that, for this gas, Sutherland's law holds. Indeed, as mentioned earlier, it is improbable that the sulphur dioxide in the circumstances of the experiments was sufficiently superheated to give the true value of Sutherland's constant. It is not unlikely that the actual mean collision area differs from that calculated by an amount appreciably greater than that attributable to experimental error.

Summary of Results.

TABLE II.

Viscosity in C.G.S. units $\times 10^{-4}$.			Sutherland's constant.	Mean col- lision area ($\text{cm.}^2 \times 10^{-15}$).
18° 0 C.	100° 0 C.	0° 0 C.		
1.253	1.630	1.168	416	0.94

In conclusion, the author would like to record his appreciation of the continued help and advice received from Professor Rankine, and also to thank the Government Grant Committee of the Royal Society for a grant which enabled the research to be undertaken.

Imperial College of Science
and Technology, London, S.W.7.
10th June, 1922.

XLVIII. *On a Simple Model to Illustrate Elastic Hysteresis.*
By S. LEES, M.A., *St. John's College, Cambridge* *.

§ 1. *Introduction.*

MUCH material has accumulated† in recent years concerning the behaviour of metals when taken through either a series of cycles of alternate compressions and tensions, or a series of periodic shear stresses. In the main, the experimental results here utilized are those of

* Communicated by the Author.

† See *e. g.* 'Dictionary of Applied Physics,' vol. i. p. 178.