

Viscosities of Gaseous Argon, Oxygen and Carbon Monoxide between 273 and 1300 K

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The viscosities of gaseous argon, oxygen and carbon monoxide have been measured at pressures below atmospheric and at nine temperatures from 273 to 1300 K. The viscosities of argon were obtained principally to test the apparatus. A comparative capillary-flow viscometer was used, nitrogen being used as the standard, and calibration runs were done at the same temperature as that used for the gas being studied. Viscosity values for nitrogen recommended by the National Engineering Laboratory, were used to convert corrected viscosity ratios to absolute values. Some implications from the results about the forms of the intermolecular potential functions are discussed.

Previous measurements of the viscosities of gases at high temperature fall into two groups. First, there is work mainly by Trautz and his coworkers and by Vasilescu covering a very wide range of gases. Secondly, a number of gases have been studied during the last 15 years by Kestin and coworkers using an oscillating-disc technique up to 1100 K, by Smith and coworkers using a capillary-flow method up to 1600 K and by Guevara and coworkers using a capillary-flow method at very high temperatures between 1100 and 2200 K. These data have been critically analysed in two recent reviews.^{1, 2} Both reviews and many of their sources reach one main conclusion: i.e. that the older measurements of Trautz and Vasilescu, which at high temperatures are lower than the new data by several percent, are incorrect.

Not all the important gases that are stable over 1000 K have been studied recently and only five gases (helium, neon, argon, krypton and nitrogen) have been studied by all three groups. The two gases oxygen and carbon monoxide are simple gases for which further study is appropriate. The viscosity of oxygen has been recently measured by Kestin *et al.*⁴ up to 770 K, but there are no results above this temperature. Carbon monoxide has not been measured recently and the only available data at elevated temperatures are those of Trautz *et al.*^{5,6} As a new apparatus was constructed, it was decided to make measurements also on a gas which had been thoroughly studied before. Argon was chosen for this purpose.

EXPERIMENTAL

The apparatus used is a capillary-flow viscometer very similar to that described by Dawe and Smith^{7, 8} and is shown in fig. 1. The experiment consists in allowing the gas to pass from the front vessel, V_f , to the back vessel, V_b , via the capillary, C , and measuring the time taken for mercury to pass between tungsten pointers in the manometer, M_f . A second manometer, M_b , also fitted with tungsten pointers is used to set the initial pressure in the back vessel.

The capillary, C , is a silica tube 1.5 m long and 0.5 mm internal diameter. The capillary is positioned centrally in the well of a Carbolite furnace operating in the temperature range 300 to 1300 K. For measurements at 273 K an ice bath is used. The temperature of the capillary is measured using chromel-alumel thermocouples. The temperature profile

across the furnace is found to be no more than 1 K below 1000 K, rising to 2 K at 1300 K. The overall temperature control and measurement is within the same limits.

The reservoirs and manometers are thermostatted to 303.6 ± 0.1 K. The front vessel is a 1 litre cylinder and the back vessel a 5 litre bulb. The front pressure range is 0.90 to 0.10 bar and the back pressure range zero to 0.40 bar. The average pressure can consequently be varied from 0.14 to 0.70 bar. A control circuit selects the tungsten pointers for setting the initial pressures in the front and back vessels and also selects the front manometer pointers which will activate a timer (Advance IT6054) and printer (Weyfringe 300).

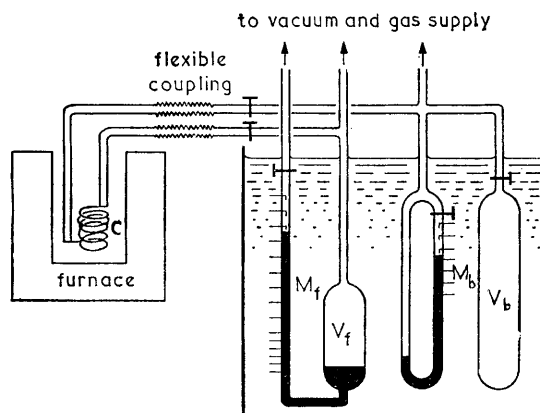


FIG. 1.—The viscosity apparatus.

In this work, for each gas at each temperature, six runs were carried out at different initial back pressures, which were then repeated at least once, until consistent times were obtained. This gave between 13 and 21 flow times at different average pressures for each gas at each temperature. Measurements on the four gases (including the nitrogen standard) were completed at each temperature before moving on to the next temperature. Nitrogen was studied first and a further set of nitrogen runs were carried out as a check after measurements on the other gases had been completed.

The gases were supplied by the British Oxygen Company and were used without further purification. "White spot" nitrogen was used and argon, oxygen and carbon monoxide were taken from Grade X bottles. The specified purities are: nitrogen 99.999 %, argon 99.9995 %, oxygen 99.96 % and carbon monoxide 99.9 %.

CALCULATION OF RESULTS

A number of standard corrections must be applied to the times of flow through the capillary to bring them nearer to the values that would be obtained if the Poiseuille equation were exactly obeyed. The apparatus parameters, in particular the dimensions of the capillary, were chosen to minimise these corrections where possible. Further, since these corrections are often (and always in this work) in the same sense for the calibration gas and the test gases, the effect on time ratios will be reduced. These corrections are outlined below.

CURVED-PIPE FLOW.—Centrifugal effects in a coiled capillary cause increased resistance to flow and this is known to depend on the Dean number, D . In terms of the apparatus parameters,

$$D = \frac{r^3 M (\bar{P}_f^2 - \bar{P}_b^2)}{8 \eta^2 R T_c l} \left(\frac{r}{r_h} \right)^{\frac{1}{2}}$$

where r is the internal radius of the capillary, M is the molecular weight of the gas, \bar{P}_f and \bar{P}_b are the average front and back pressures respectively, η is the gas viscosity, T_c is the temperature of the capillary, l is the length of the capillary and r_h is the coil radius. Various authors

have suggested different critical values below which curved-pipe flow is negligible in capillary flow viscometers. In this work Dawe and Smith's conservative value of 3 has been used.⁷ The Dean number was calculated for all runs. Except for a few high-pressure runs at low temperatures, which were consequently rejected, it was found to be less than 3 in all experiments.

HAGENBACH CORRECTION.—The acceleration of gas into the capillary produces an increased resistance to flow. The standard correction⁹ has been used in this work. This correction is greatest for gases of high molecular weight and decreases as the temperature is raised. In most cases the correction was less than 0.1 % having a maximum of 0.5 % for argon at 321 K.

GAS IMPERFECTION.—The basic flow-rate equation is derived assuming ideal-gas behaviour and must be corrected to allow for gas imperfection.¹⁰ The correction depends on two terms, one dependent on the capillary temperature and one on the thermostat temperature. The two terms partially cancel and the correction was less than 0.5 % for all gases over the whole temperature range.

SLIP CORRECTION.—After making the last two corrections, ratios of times of flow with those for nitrogen at the same temperature were linearly extrapolated against the inverse of the mean pressure across the capillary.⁷ The value of the time ratio at the intercept was found using a least-squares method and was then taken as being equal to the viscosity ratio. The slip plots were made up of between 13 and 21 datum points. The gradients of the slip plots were very small for these similar gases.

RESULTS

Corrected ratios of the times of flow for argon, oxygen and carbon monoxide to those for nitrogen (at the same temperature) were obtained at nine temperatures between 273 and 1300 K. These ratios which are believed to be accurate to 0.3 % are given in table 1. Absolute viscosities for the three gases were then obtained using

TABLE 1.—CORRECTED RATIOS OF FLOW TIMES FOR ARGON, OXYGEN AND CARBON MONOXIDE TO THOSE FOR NITROGEN AT THE SAME TEMPERATURE

<i>T</i> /K	Ar	O ₂	CO
273	—	—	0.9855
321	1.2680	1.1564	—
417	1.3020	1.1569	1.0035
515	1.3089	1.1640	1.0056
612	1.3172	1.1725	1.0140
772	1.3253	1.1854	1.0275
911	1.3300	1.1790	1.0149
1060	1.3350	1.1810	1.0179
1211	1.3498	1.1902	1.0079
1300	1.3551	1.1890	1.0073

values for nitrogen recommended by the National Engineering Laboratory,² which are stated to be accurate to 0.25 % in the temperature range 250 to 600 K and to 0.5 % in the range 600 to 1300 K. The absolute viscosities are given in table 2. These viscosities were then fitted to the expression

$$\eta = \frac{T^{\frac{1}{2}}}{a + b/T + c/T^2 + d/T^3} \quad (1)$$

using the method of least squares refinement. The best estimates for the parameters, *a* to *d*, for each gas are given in table 3. Finally smoothed values of the viscosities at 100 degree intervals were then regenerated from these best estimates and are listed in

table 4. These smoothed viscosities are now compared with previous results, correlations and predictions.

TABLE 2.—UNSMOOTHED EXPERIMENTAL VISCOSITIES ($\eta/\mu\text{N s m}^{-2}$)

T/K	Ar	O ₂	CO
273	—	—	16.38
321	23.99	21.88	—
417	29.79	26.47	22.96
515	34.87	31.01	26.79
612	39.41	35.08	30.34
772	46.24	41.36	35.85
911	51.71	45.84	39.46
1060	57.30	50.69	43.69
1211	63.17	55.70	47.17
1300	66.40	58.26	49.36

TABLE 3.—BEST ESTIMATES OF THE PARAMETERS IN EQN (1)

	a	$b \times 10^{-2}$	$c \times 10^{-4}$	$d \times 10^{-6}$
Ar	0.41379	2.1856	—7.2069	11.639
O ₂	0.53130	1.2420	—1.0845	0.20782
CO	0.66872	0.70992	1.4880	—2.4377

TABLE 4.—SMOOTHED VISCOSITY VALUES ($\eta/\mu\text{N s m}^{-2}$)

T/K	Ar	O ₂	CO
300	22.80	20.81	17.80
400	28.92	25.73	22.36
500	34.10	30.30	26.34
600	38.77	34.54	29.94
700	43.17	38.50	33.26
800	47.37	42.22	36.34
900	51.40	45.72	39.24
1000	55.29	49.04	41.98
1100	59.05	52.20	44.58
1200	62.69	55.22	47.07
1300	66.21	58.11	49.44

ARGON

Good results are already available for argon over a wide range of temperatures from a number of sources. These have been correlated by Watson² and by Maitland and Smith¹ and recommended values given. The principal reason for measuring argon viscosities was therefore to test the apparatus. The recommended values from both sources are compared with our smoothed values in fig. 2. Agreement with Watson's recommended values is seen to be well within 0.5 % over the whole temperature range and with Maitland and Smith's recommended values to within 0.75 %. In both cases agreement is within the combined quoted uncertainties.

OXYGEN

Both the Watson² and Maitland and Smith¹ recommendations for oxygen are based on measurements available in 1971, which were all made below 300 K. Recently Kestin *et al.*⁴ have published data for oxygen at temperatures up to 770 K. The Watson recommendations, obtained by a corresponding-states calculation, and the

main experimental values are compared with our smoothed values in fig. 3. Agreement is within quoted uncertainties except that there is an unexplained difference of about 1.5 % between our data and the recently published data of Kestin *et al.*

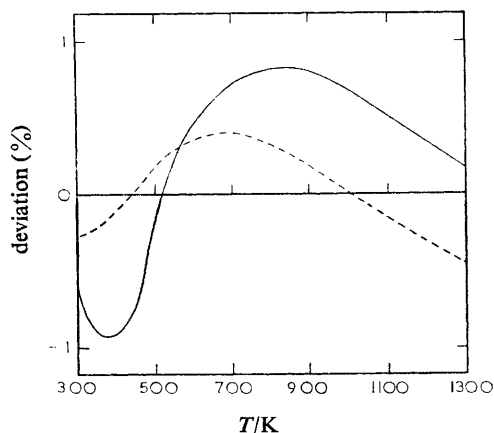


FIG. 2

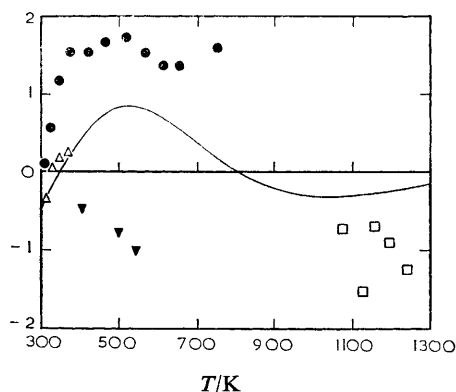


FIG. 3

FIG. 2.—Deviations of recommended argon viscosities from our smoothed values. ---, Watson's values; ² —, Maitland and Smith's values.¹

FIG. 3.—Deviations of experimental and recommended oxygen viscosities from our smoothed values. —, Watson's recommended values; ² ●, Kestin *et al.*; ⁴ ▼, Trautz *et al.*; ⁶ △, Wobser and Mueller; ¹¹ □, Raw *et al.*¹³

CARBON MONOXIDE

Only older data are available for carbon monoxide above room temperature and these values are compared with our smoothed values in fig. 4. The measurements of Trautz *et al.* are up to 3 % lower than our data, which is in line with comparisons of Trautz's data for other gases with more recent data. In fact the ratios of the viscosities

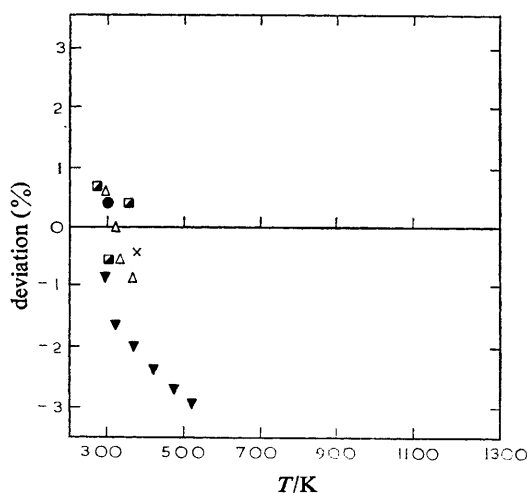


FIG. 4.—Deviations of other experimental carbon monoxide viscosities from our smoothed values. ●, Kestin *et al.*; ¹⁴ ▼, Trautz *et al.*; ^{5, 6} △, Wobser and Mueller; ¹¹ □, Barua *et al.*; ¹² ×, Smith.¹⁵

of carbon monoxide and nitrogen obtained in this work are very similar to those obtained by Trautz *et al.* Agreement with the other lower-temperature values is as good as would be expected from the probable uncertainties.

DISCUSSION

Nitrogen (the standard gas), oxygen and carbon monoxide are all molecules of similar size, shape and mass and, despite the small dipole moment of carbon monoxide, a corresponding-states analysis might be expected to work well for them. The second virial coefficients for these gases certainly conform well to the principle of corresponding states. Fig. 5 shows second virial coefficients,¹⁷ $B(T)$, for these three gases reduced by $B_0 (= -B \text{ at } 0.7T_B)$ ¹⁶ plotted against the temperature reduced by the Boyle temperature, T_B . The reducing parameters used are given in table 5.

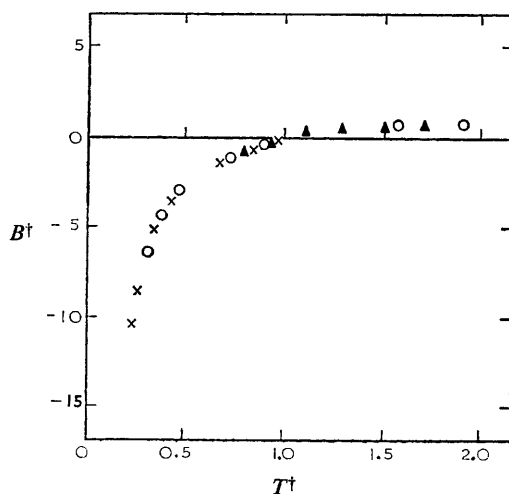


FIG. 5.—Reduced second virial coefficients for: \circ , nitrogen; \times , oxygen; \blacktriangle , carbon monoxide. $T^\dagger = T/T_B$ and $B^\dagger = B/B_0$. Values for $B(T)$ are taken from ref. (17) and the values for T_B and B_0 used are shown in table 5.

If the viscosity is reduced appropriately by the same parameters, the data for the three gases do not lie on the same curve (see fig. 6). This is in accord with previous observations⁸ that reducing parameters cannot be satisfactorily transferred from equilibrium data to transport property data for non-spherical molecules. It appears

TABLE 5.—REDUCING PARAMETERS OBTAINED FROM VIRIAL COEFFICIENTS¹⁷
USED IN FIG. 5 AND 6

	T_B/K	$B_0/\text{cm}^3 \text{ mol}^{-1}$
N_2	326	23.2
O_2	408	17.7
CO	343	23.0

that the effective spherical potentials for transport properties on the one hand and equilibrium properties on the other are different averages of the actual non-spherical potential; and that the differences vary even for such similar gases as nitrogen, oxygen and carbon monoxide.

If, however, the reducing parameters are adjusted, the three curves can be brought

to coincide within experimental error as shown in fig. 7. In this figure, reducing parameters, ϵ^* and σ^* , relative to nitrogen, are used; i.e. $\epsilon^* = \sigma^* = 1$ for nitrogen. For the other two gases ϵ^* and σ^* were obtained graphically using log-log plots in the standard procedure and are shown in table 6. They are compared with the

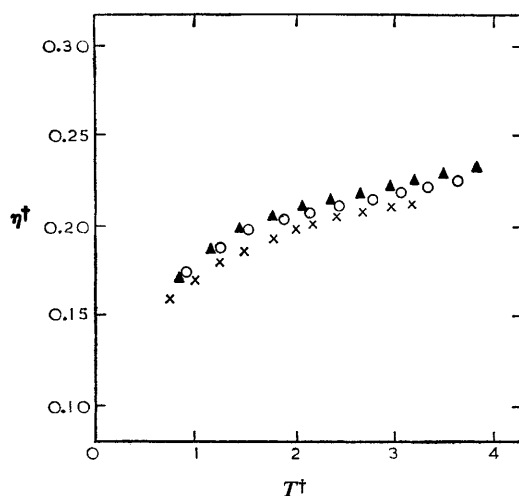


FIG. 6.—Smoothed experimental viscosities reduced by virial coefficient parameters for: ○, nitrogen; ×, oxygen; ▲, carbon monoxide. $T^\dagger = T/T_B$ and $\eta^\dagger = \eta B_0^\dagger / (MRT)^\frac{1}{2}$. Values for B_0 and T_B used are given in table 5.

relative reducing parameters published by Kestin *et al.* for oxygen (obtained from viscosity data) and the ratios of the Lennard-Jones parameters from Johnson and McCloskey¹⁸ (obtained from viscosity data at lower temperatures) and from Trautz *et al.*⁶ The agreement between the parameters for carbon monoxide obtained here and those of Trautz *et al.* arises because of the similarity in the viscosity ratios for carbon monoxide and nitrogen between the two sets of measurements.

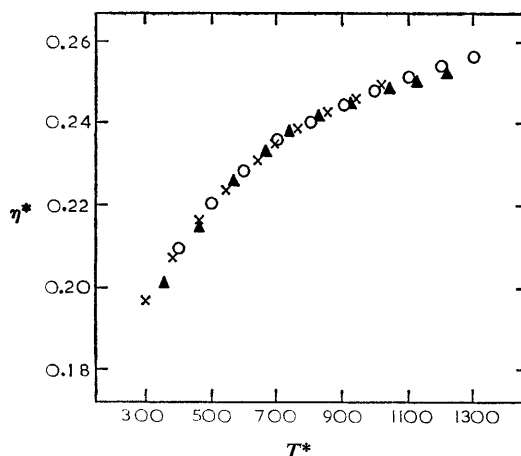


FIG. 7.—Smoothed experimental viscosities reduced by adjusted parameters for: ○, nitrogen; ×, oxygen; ▲, carbon monoxide. $T^* = T/\epsilon^*$ and $\eta^* = \eta(\sigma^*)^2 / (MRT)^\frac{1}{2}$. Values of ϵ^* and σ^* used are unity for nitrogen and for oxygen and carbon monoxide are given in table 6.

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TABLE 6.—ADJUSTED REDUCING PARAMETERS, RELATIVE TO NITROGEN, USED IN FIG. 7, COMPARED WITH PREVIOUS RESULTS

	present work	Kestin <i>et al.</i> ⁴	Johnson & McCloskey ¹⁸	Trautz <i>et al.</i> ⁶
O ₂	ε^*	1.29	1.21	1.23
	σ^*	0.932	0.931	0.933
CO	ε^*	1.08	—	1.20
	σ^*	0.986	—	0.975

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