CALCULATION OF THE VISCOSITY OF REAL GASES

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A method of determining the constant a in Golubev's equation is given. The values determined in this way are found to be in good agreement with experimental values.

At present there is no rigorous theory of the viscosity of compressed gases. Hence, there are no theoretically based equations which give values in agreement with the experimental data in a wide range of parameters.

The available equations are empirical or semiempirical and experimental data are required for their use. The best of these equations is Golubev's equation, which was derived from simple molecular-kinetic considerations and predicts the experimental data at high pressures with a high degree of accuracy. This equation is

$$\eta_{pT} = \eta_T + a(p_T/T)^n. \quad (1)$$

The thermal pressure P_T is determined from the thermodynamic relationship

$$p_T = T\left(\frac{\partial p}{\partial T}\right)_V. \quad (2)$$

From Eqs. (1) and (2) we can write

$$\eta_{pT} = \eta_T + a\left(\frac{\partial p}{\partial T}\right)_V^n. \quad (3)$$

Introducing the reduced parameters

$$\pi = p/p_c, \quad \tau = T/T_c, \quad \omega = V_c/V,$$

we obtain

$$\eta_{pT} = \eta_T + a\left[\frac{p_c}{T_c}\left(\frac{\partial \pi}{\partial \tau}\right)_\omega\right]^n.$$

In the dimensionless coordinates π and τ the quantity $(\partial\pi/\partial\tau)_{\omega=1} = \alpha_c$ represents the slope of the pressure curve at the critical point or (on the basis of the fundamental Planck-Gibbs rule) the slope of the critical isochor.

Hence, the value of α_c can be determined from the equation of the equation of state, or from experimental data.

In view of the above we can determine the constant a by using the value $\Delta\eta_c = \eta_{(pT)c} - \eta_{Tc}$,

$$a = \Delta\eta_c \Big/ \left(\frac{p_c}{T_c}\alpha_c\right)^{1.115}. \quad (4)$$

The values of a for some gases were determined in such a way (Table 1). The values of $\Delta\eta_c$ were taken from [1] and those of α_c from [2].

As the table shows, from the viscosity at the critical point and the value of α_c we can determine farily accurately the constant a in Golubev's equation.

For little-investigated substances, however, we do not usually have experimental values of the viscosity at the critical point. Hence, in this case it is convenient to use the Grunberg-Nissan semiempirical equation [3], which has the form

$$\eta_{(pT)c} = K\rho_c^{2/3}T_c^{1/2}/M^{1/6} = K\varepsilon. \quad (5)$$

In [4] Swift et al. determined the constant K for methane, ethane, propane, and n-butane from experimental data and on averaging it for the class of saturated hydrocarbons obtained a value K = 570. The dimensionality of K is [$g^{1/2} \cdot cm/sec \cdot deg^{1/2} \cdot mole^{1/6}$].

We tested the applicability of the Grunberg-Nissan equation for other substances. The results of the test are summed up in Table 2, which shows that the equation can be effectively used to determine the critical viscosity of any substance with a relatively small error if K is taken as 594.1. The error does not usually exceed 5%.

In view of the difficulty of experimental determination of the viscosity at the critical point and the considerable disagreement of the data of different authors, such a result can be regarded as quite acceptable, particularly for uninvestigated substances.

An analysis of Eq. (1) shows that at low and moderate pressures the main contribution to the values of the viscosity coefficients is due to η_T, the values of which are usually known to within 1%.

Table 1

Experimental and Theoretical Values of a

Substance	p_c, atm	T_c, °K	α_c	$\Delta\eta_c$, 10^7 g/cm · sec	αcalc	αexpt	Error, %
Hydrogen	12.77	32.99	4.3	128.1	70.5	73	3.41
Methane	45.8	190.65	5.84	799	548	550	1.48
Carbon dioxide	75.28	304.19	6.91	1700	934	930	0.4
Ammonia	111.5	405.56	7.10	1155	548	550	0.36

Table 2

Determination of the Universal Constant K

Substance	Chemical formula	ε	$\eta^{expt}_{(pT)c}$	K	$\eta^{calc}_{(pT)c}$	Error, %
Hydrogen*	H_2	0.505	294	583	300.0	2
Deuterium*	D_2	0.810	484	597	481.2	0.6
Ammonia*	NH_3	4.640	2610	563	2756.6	5.5
Carbon monoxide*	CO	2.980	1836	616	1770.4	3.5
Nitrogen*	N_2	2.940	1810	616	1746.6	3.5
Air*	—	3.165	1960	618	1880.3	4.1
Oxygen*	O_2	3.990	2470	619	2370.5	4.0
Carbon dioxide*	CO_2	5.550	3220	580	3297.3	2.4
Methane*	CH_4	2.586	1580	610	1536.3	2.8
Methane**	CH_4	2.586	1500	580	1536.3	2.4
Ethane*	C_2H_6	3.420	2130	623	2031.8	4.6
Propane*	C_3H_8	3.795	2400	631	2254.6	6.0
Propane**	C_3H_8	3.795	2200	581	2254.6	2.5
n-Butane**	C_4H_{10}	3.910	2300	588	2322.9	1.0
n-Pentane**	C_5H_{12}	3.990	2300	577	2370.5	3.1
n-Hexane**	C_6H_{14}	4.070	2300	565	2418.0	5.1
n-Heptane**	C_7H_{16}	4.080	2400	588	2423.9	1.0
n-Octane**	C_8H_{18}	4.110	2300	559	2441.8	6.2
				K_{av}= =594.1		

*According to Golubev [1].

**According to Swift et al. [4].

Table 3

Dynamic Viscosity of Trichloromonofluoromethane (Freon-11)

p, bar	η, 10^7 g/cm · sec at t, °C							
	120	140	160	180	190	210	220	240
1	1399.5	1447.2	1495.3	1539.2	1561.4	1606.8	1630.1	1673.2
10	1493.0	1530.2	1569.8	1607.0	1626.5	1667.1	1688.3	1727.7
20			1727.6	1763.6	1744.1	1768.9	1783.8	1813.2
30				2006.5	1966.3	1937.3	1934.9	1938.7
40						2258.0	2194.0	2130.16
50						3431.7	2756.8	2439.4
60						4690.2	4036.5	2857.7
70						7003.3	5499.4	3910.7
80						8482.8	6494.3	4850.9
90						9943.9	7445.1	5520.5
100						11412.3	8384.9	6082.2
110						12884.4	9306.4	6592.5
120						14356.5	10227.8	7066.0

p, bar	η, 10^7 g/cm · sec at t, °C							
	260	280	300	320	340	360	380	400
1	1716.0	1754.9	1795.0	1835.8	1877.8	1912.0	1949.9	1983.8
10	1767.3	1803.4	1841.1	1879.7	1919.7	1952.1	1988.4	2020.8
20	1845.0	1873.5	1907.2	1941.2	1977.6	2006.8	2040.1	2070.1
30	1954.0	1971.2	1994.0	2020.5	2050.6	2074.5	2103.5	2129.6
40	2107.3	2100.3	2106.0	2120.0	2140.2	2156.3	2179.4	2199.6
50	2327.2	2274.0	2250.2	2243.3	2248.6	2253.7	2267.4	2280.6
60	2649.6	2506.7	2433.8	2395.6	2379.3	2406.1	2369.9	2372.9
70	3127.2	2818.1	2665.0	2580.3	2533.1	2501.2	2487.3	2478.3
80	3773.3	3221.5	2951.8	2801.7	2713.7	2655.9	2619.5	2595.0
90	4504.2	3717.8	3269.8	3061.9	2921.9	2826.8	2767.5	2724.6
100	5113.6	4282.5	3699.9	3365.9	3157.5	3020.7	2931.6	2867.4
110	5574.3	4830.2	4152.2	3702.2	3423.0	3235.1	3111.8	3022.7
120	5934.1	5278.4	4619.2	4077.0	3716.3	3472.2	3308.9	3191.2

At high pressures the contribution of $a(p_T/T)^n$ becomes greater and the error in determining the viscosity coefficients begins to depend on the accuracy in determining the constant a.

We can postulate from an examination of Tables 1 and 2 that the error in the determination of the constant a and, hence, of the viscosity coefficients at high pressures will not exceed 5%.

Proceeding from the above, we determined the viscosity of $CFCl_3$ (Freon-11) at the critical point from Eq. (5),

$$\eta_{(pT)_c} = 3780 \cdot 10^{-7} \text{ g/cm} \cdot \text{sec}.$$

The value of η_{T_c}, i.e., the viscosity at atmospheric pressure and the critical temperature, was determined by extrapolation of the available experimental data [5] to the critical temperature (198° C) by means of Sutherland's equation. In this case we obtained

$$\eta_{T_c} = 1563 \cdot 10^{-7} \text{ g/cm} \cdot \text{sec}.$$

The constant a for Freon-11, calculated from Eq. (4), was 3671.1. In this case we took p_c = 43.73 bar and T_c = 471° K. The average value of 1.115 was taken as the index of the power n.

The value of $\partial p/\partial T)_V$ in Eq. (2) and the value of α_c in Eq. (4) were calculated from the equation of state, which was derived from the correlation of the law of corresponding states [6] and has the form

$$\sigma = \alpha_0 + \alpha_1\tau + \beta\psi + \gamma\varphi.$$

A comparison of the theoretical value α_c = 6.85 with the data given in [2] showed good agreement (according to [2], α_c = 6.72). Finally, the equation for calculation of the coefficients of dynamic viscosity of Freon-11 takes the form

$$\eta_{pT} = \eta_T + 3671.7 \left\{ 0.342938\omega \left[0.84969\omega - 0.23550\omega^2 - \right.\right.$$
$$- 0.111735\omega^4 + 1.029986\omega^6 - 0.481076\omega^8 + 1.000 - \frac{3}{\tau^4} \times$$
$$\times (0.213680\omega - 0.040869\omega^2 + 0.39755\omega^4 - 0.523211\omega^6 +$$
$$\left.\left. + 0.262237\omega^8) + \frac{5}{\tau^6}(0.020481\omega - 0.022775\omega^2 + \right.\right.$$
$$\left.\left. + 0.02460\omega^4 + 0.00628\omega^6) \right] \right\}^{1.115}. \quad (6)$$

From Eq. (6) we calculated the values of the viscosity coefficients of Freon-11 is the pressure range 1–120 bar and the temperature range 0°–400° C. These values are given in Table 3.

NOTATION

η_{pT} is the viscosity of compressed gas at temperature T and pressure p; η_T is the viscosity of gas at temperature T and atmospheric pressure; p_c is the critical pressure; T_c is the critical temperature; V_c is the critical specific volume; ρ_c is the critical density; M is the molecular weight; K is the universal constant in Grunberg-Nissan equation; α_0, α_1, β, γ are the polynomials in powers of dimensional density ω in equation of state; ψ, φ are the diminishing functions of reduced temperature τ in equation of state; $\sigma = pV/RT$ is the dimensionless group in equation of state.

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3 May 1966

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