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New Methods for the Estimation of the Viscosity Coefficients of Pure Gases at Moderate Pressures (with Particular Reference to Organic Vapors)

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In an earlier communication (Reichenberg, 1973) it was shown that the frequently observed numerical indeterminacy of the potential parameters σ and ϵ/k is due to the fact that, under certain circumstances, these two parameters "collapse" together. When this occurs with a potential function involving only these two parameters, the predicted values of the physical property in question are effectively determined by a single parameter characteristic of the substance. The known fact that, even when this occurs, the predicted values continue to agree well with experimental values suggests that it may be possible to develop relationships which contain only a single parameter characteristic of the substance yet provide good estimates of the physical property over a wide range of temperatures.

In the particular case of the viscosity of pure gases at moderate pressures, analysis of the Lennard-Jones (12:6) potential function showed that one of the regions in which indeterminacy will occur is given by $0.4 \leqq kT/\epsilon \leqq 1.6$. Within this range, the Chapman-Enskog relation reduces to

$$\eta = aT \tag{1}$$

where η is the gas viscosity and a is a constant characteristic of the substance. Use may be made of the relation $k\,T_c/\epsilon \approx 1.3$ to convert these limits to $0.3 \leqq T_R \leqq 1.2$. Although the numerical value of kT_c/ϵ for the Lennard-Jones (12:6) function has not been completely finalized (see, for example, Barker et al., 1966), there can be no doubt that the critical temperature falls within this particular range of indeterminacy. If, therefore, within this range, Equation (1) were to hold exactly, then

$$a = \eta_c/T_c \tag{2}$$

Thus both $(\eta_c/T_c) - (\eta/T)$ and $d \log (T/\eta)/d \log T_R$ should be zero within this range. In Figure 1 it is shown that, on the contrary, a number of nonpolar gases exhibit the property that, at $T_R = 1$,

$$d \log (T/\eta)/d \log T_R = \alpha \tag{3}$$

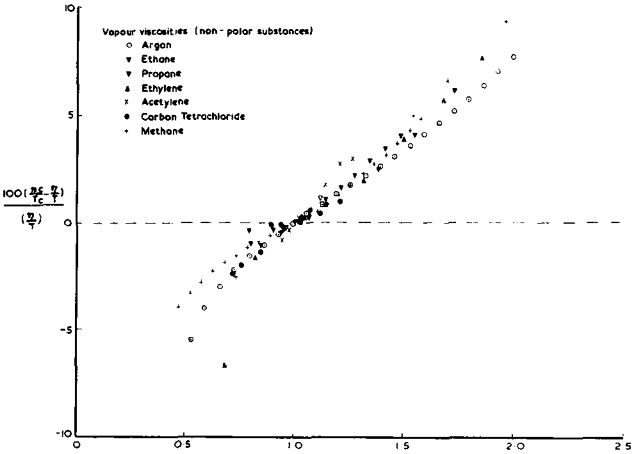

Fig. 1. Plot of 100 $(\eta_c/T_c - \eta/T)$ / (η/T) against T_R for nonpolar substances.

where the value of α is largely independent of the particular substance and lies within the range 0.06 to 0.08.

In view of the apparent failure of Equation (1), we abandon approaches based on the Chapman-Enskog treatment in favor of a more directly empirical approach.

An infinite number of one-parameter relationships may be devised to satisfy Equation (3). Two of the simpler are

$$\eta = aT/[1 + \alpha(T_R - 1)] \tag{4}$$

and

$$\eta = aT\,[1 - \alpha\,(T_R - 1)] \tag{5}$$

with a given by Equation (2) in both cases. Equation (4) fits the experimental data very well over a range of T_R values extending roughly from 0.7 to 1.5 (see Figure 1) but so does Equation (5). However, both relationships must fail at high temperatures because Equation (4) predicts that η will become independent of temperature and Equation (5) predicts that η will pass through a maximum and eventually become negative.

Polar organic compounds behave somewhat differently (Figure 2), but this difference, though probably beyond experimental error, is not very great. A single treatment will therefore be developed for polar and nonpolar substances (with the proviso that highly polar substances, like water or ammonia, may require separate consideration).

An extension of the treatment leads to the relationship

$$\eta = aT/[1 + 0.36(1 + 4/T_c)T_R(T_R - 1)]^{1/6} \tag{6}$$

The following points may be noted:

Equation (6) conforms to Equation (3) with $\alpha = 0.06\,(1 + 4/T_c)$. This last quantity is almost, but not quite, independent of the substance in question. The factor $(1 + 4/T_c)$ was introduced because it was found that helium and, to a lesser extent, hydrogen, exhibit a value of α appreciably greater than other substances. This is almost certainly due to quantum effects and is most simply (and most crudely) represented empirically by means of a term inversely proportional to T_c;

Equation (6) predicts that, at high temperatures, η will become proportional to $T^{2/3}$ instead of $T^{1/2}$, as usually assumed (Reid and Sherwood, 1966, p. 410). Liley (1959) has argued strongly that, for most purposes, a two-thirds law is preferable and plots of log η vs. log T for data on helium and hydrogen at temperatures up to 1000 K supported this viewpoint. [This applied equally to the older data of Trautz and Zink (1930) and the more recent values of Guevara et al. (1969)];

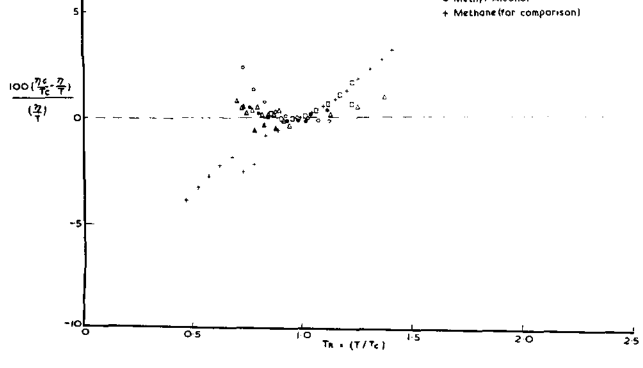

Fig. 2. Plot of 100 $(\eta_c/T_c - \eta/T)\,/\,(\eta/T)$ against T_R for polar substances.

Equation (6) was adopted rather than the simpler expression

$$\eta = aT/[1 + 0.18(1 + 4/T_c)\,(T_R - 1)]^{1/3} \tag{7}$$

because it fitted data on helium down to the lowest temperature while Equation (7) failed increasingly below about 170 K.

Equation (6) was tested using data on a large number of substances. a was determined by linear least-squares fitting so as to minimize the quantity $\Sigma[(\eta_{\text{calc}} - \eta_{\text{exp}})/\eta_{\text{exp}}]^2$. Where more than one set of data was available for the same substance, all data regarded as acceptable were included in a single least-squares fitting operation. As a result, in many cases the observed deviations reflected the degree of disagreement between different sets of data rather than any inadequacy of Equation (6).

To test Equation (6) for a given substance, it is necessary that experimental viscosity data be available at more than one temperature. This condition was found to be satisfied for 79 organic compounds tested. Of these, 23 gave mean deviations within 0.5%, 51 within 1.0%, 61 within 1.5%, and 72 within 2.0%. The maximum deviations were 22 within 1%, 46 within 2%, 63 within 3%, and 69 within 4%. Of the 10 substances showing maximum deviations greater than 4%, the three which gave the highest deviations could be accounted for by disagreement of experimental data (as described above). The same three were the only ones (of the 79 compounds) to show mean deviations greater than 2.4%.

With helium, hydrogen, neon, argon, and methane, it was possible to test Equation (6) over wide temperature ranges. The agreement was very satisfactory. In the case of neon (16.5 to 1100 K), the mean deviation was 1.35%. Apart from deviations of − 8.7%, − 6.5%, and − 5.0% at temperatures of 16.5 K, 17.8 K, and 19.0 K (where experimental accuracy might be expected to be low), all deviations were within 3.7% over the whole of this large temperature range despite the use of data from different sources. [These sources are those quoted for neon in a paper by Stiel and Thodos (1961).]

It is concluded that the accuracy of Equation (6) is satisfactory in all cases tested so far. Among the organic compounds tested were a number with large dipole moments though the most suitable criterion of polarity is not the dipole moment itself but some dimensionless quantity related to it (Mason and Monchick, 1962). Equation (6) has not yet been tested with compounds (such as water and ammonia) that are highly polar by any criterion.

Since we have now a satisfactory one-parameter relationship, it is of interest to examine the way in which this parameter varies with molecular structure. It was found that a decreases with increasing molecular size and complexity. Some rather crude theoretical arguments (Reichenberg, 1971) suggested that the quantity $y \equiv M^{1/2}/a$ might be expected to be proportional (or nearly proportional) to the volume of the molecule and hence an additive function of the constituents of the molecule. We therefore write

$$y = M^{1/2}/a = \sum_i n_i\,C_i \tag{8a}$$

and, of course,

$$a = M^{1/2} \Big/ \sum_i n_i\,C_i \tag{8b}$$

where n_i is the number of times that a particular entity (atom, bond, or grouping) occurs in the molecule and C_i is the contribution to y of that entity.

There are various ways in which the entities might be defined. The Lydersen scheme (Lydersen, 1955; Reid and Sherwood, 1966, pp. 8-10) was finally adopted mainly because it or similar schemes are recommended for use in computer programs for the estimation of physical properties (Reid, 1968).

The method of testing Equation (8a) was to determine, by linear-least squares, those values of C_i which would minimize the quantity $\Sigma[(y_{\text{calc}} - y_{\text{exp}})/y_{\text{exp}}]^2$. In all, 99 compounds were fitted: the 79 used in testing Equation (6), minus methane (which cannot be coded on the Lydersen scheme), plus 21 where viscosity values were available at only one temperature and so could not be used to test Equation (6). Of these, 8 (including methylacetylene) gave zero residuals because they each contained a grouping not contained in any of the other compounds; and in addition, acetylene gave a zero residual because it contained a grouping found only in itself and methylacetylene. Of the remaining 90 compounds, 78 showed deviations (in y) of less than 4%. A detailed discussion (Reichenberg, 1971) suggests that with 11 of the remaining 12 compounds a large part of the deviation may be due to experimental error. However, in the case of cyclopropane (where two independent sets of data agreed to within 1%), there is reason to think that the deviation (− 6%) is real and that some additional effect (probably connected with molecular geometry or ring strain) is superimposed on simple additivity. The group contributions C_i and their standard deviations are given in Table 1.

In summary, given a value of a, Equation (6) may be used to calculate the viscosity of a gas or vapor at any temperature. The value of a may be obtained either from Equation (6) if η is known at one or more temperatures, or, in the case of organic compounds, from the combined use of Table 1 and Equation (8b).

Reid (1973) has calculated values of η from the combination of Table 1, Equation (8b) and (6) and has tested these values against smoothed experimental data on 13 nonpolar and 11 polar organic compounds. For the nonpolar compounds, 48 data points gave a mean deviation of 1.9% and for the polar compounds, 45 data points gave a mean deviation of 2.0%.

TABLE 1. VALUES OF THE GROUP CONTRIBUTIONS

Group	Contribution $C_i \times 10^{-8}$ kg^{-1} m s K	Standard deviation $\Delta C_i \times 10^{-8}$ kg^{-1} m s K
$-CH_3$	0.904	0.012
$>CH_2$ (non-ring)	0.647	0.012
$>CH-$ (non-ring)	0.267	0.031
$>C<$ (non-ring)	−0.153	0.037
$=CH_2$	0.768	0.019
$=CH-$ (non-ring)	0.553	0.022
$>C=$ (non-ring)	0.178	0.033
$\equiv CH$	0.741	0.022
$\equiv C-$ (non-ring)	0.524	0.070
$>CH_2$ (ring)	0.691	0.012
$>CH-$ (ring)	0.116	0.125
$>C<$ (ring)	0.023	0.038
$=CH-$ (ring)	0.590	0.012
$>C=$ (ring)	0.359	0.053
$-F$	0.446	0.013
$-Cl$	1.006	0.014
$-Br$	1.283	0.034
$-OH$ (alcohols)	0.796	0.035
$>O$ (non-ring)	0.359	0.038
$>C=O$ (non-ring)	1.202	0.094
$-CHO$ (aldehydes)	1.402	0.071
$-COOH$ (acids)	1.865	0.084
$-COO-$ (esters) or $HCOO-$ (formates)	1.341	0.050
$-NH_2$	0.971	0.084
$>NH$ (non-ring)	0.368	0.108
$=N-$ (ring)	0.497	0.088
$-CN$	1.813	0.083
$>S$ (ring)	0.886	0.071

NOTATION

a = constant characteristic of the substance
C_i = contribution of ith entity to the value of y
ΔC_i = standard deviation of C_i
k = Boltzmann constant
M = relative molecular mass of the substance
n_i = number of times the ith entity occurs in the molecule
T = absolute temperature
T_c = critical temperature of the substance
T_R = reduced temperature = T/T_c
y = $M^{1/2}/a$
y_{calc} = value of y calculated from Equation (8a)
y_{exp} = value of y obtained using an experimentally determined value for a

Greek Letters

α = dimensionless quantity defined by Equation (3)
ϵ = depth of the potential well [defined more fully in Reichenberg (1973)]
η = gas viscosity at temperature T and moderate pressures
η_c = gas viscosity at the critical temperature and moderate pressures (*not* at the critical point!)
η_{calc} = value of η calculated from Equation (6)
η_{exp} = value of η determined experimentally
σ = collision diameter [defined more fully in Reichenberg (1973)]

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