EUCKEN FACTOR AND THE ROLE OF INTERNAL DEGREES OF FREEDOM IN POLYATOMIC HYDROCARBON MOLECULE TRANSFER EFFECTS

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The dependence of the Eucken factor and the Prandtl criterion on the number of degrees of freedom and thermal capacity is investigated for complex molecules on the basis of systematic experimental data on the viscosity and thermal conductivity of alkane and alkene homologs [1, 2].

It is interesting to compare the latest theoretical and experimental results describing the transfer of momentum and the kinetic energy of the translational movement of molecules. For simple particles, for example, inert gas atoms, which do not have any degrees of freedom other than the translational, this theory leads to the well-known Maxwell formula

$$\lambda M=\frac{5}{2}\,\eta c_v, \tag{1}$$

where λ is the coefficient of thermal conductivity of the rarefied gas, M is the molecular mass, η is the coefficient of dynamic viscosity of the rarefied gas, and c_V is the molar thermal conductivity of the gas at constant volume.

For inert gases formula (1) is satisfied with experimental data accuracy throughout the temperature range under investigation from 100 to 2000°K.

The molecules of polyatomic gases may have a large number of internal degrees of freedom apart from the three translational ones [12]. The excitation and attenuation of the internal degrees of freedom of the molecule conform to complex quantum patterns and are dependent both on the structure of the molecule and on the temperature.

Internal degrees of freedom are involved in differing ways in the transfer of momentum and energy by the molecules – they play virtually no part in viscosity but have a very strong influence on the thermal conductivity. As a result, relation (1) is not satisfied, as is well-known, for polyatomic gases.

Eucken [4] was the first to modify formula (1) making it more accurate for the case of polyatomic molecules by proposing that the fluxes of energy transferred by the translational and internal (both rotational and vibrational) degrees of freedom be treated separately. This assumption is equivalent to the expression

$$\lambda=\lambda_{\text{trans}}+\lambda_{\text{int}}, \tag{2}$$

which is used with elementary molecular-kinetic theory as a basis for deriving

$$\frac{\lambda M}{\eta}=\frac{5}{2}\,c_{\text{trans}}+c_{\text{int}}. \tag{3}$$

Bearing in mind that

$$c_{\text{trans}}=\frac{3}{2}\,R\ \text{and}\ c_v=c_p-R, \tag{4}$$

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where R is the universal gas constant, Eucken derives the relation known now as the "Eucken factor":

$$f=\frac{\lambda M}{\eta c_v}=\frac{1}{4}\left(9\frac{c_p}{c_v}-5\right). \tag{5}$$

Chapman and Cowling [5] point out two inaccuracies assumed in the derivation of formula (5).

1. The reasoning used in deriving it is true only when the transfer of energy from the internal degrees of freedom to the translational (i.e., to other molecules) takes place so rarely that the process should be ignored. This assumption is not true when applied to rotational and certain types of vibrational degrees of freedom.

2. It is quite clear that the transfer of energy by the internal degrees of freedom of molecules is due to the transfer of the molecules themselves, i.e., to a self-diffusion process. Hence it is postulated in [5] that these processes are not identical and the coefficient of transfer of the internal degrees of freedom D_{int}, which is not necessarily equal to the coefficient of self-diffusion D_{11},† is inserted.

After this modification for greater accuracy, expression (3) takes the form

$$\frac{\lambda M}{\eta}=\frac{5}{2}c_{\text{trans}}+\frac{\rho D_{\text{int}}}{\eta}c_{\text{int}}. \tag{6}$$

After several transformations taking account of (4), we obtain

$$\frac{\lambda M}{\eta c_v}=\frac{1}{4}\left[\left(15-6\frac{\rho D_{\text{int}}}{\eta}\right)\frac{c_p}{c_v}-15+10\frac{\rho D_{\text{int}}}{\eta}\right]. \tag{7}$$

The Eucken formula (5) can be obtained from expression (7) if it is assumed that $\rho D_{\text{int}}/\eta = 1$.

In [7] for nonpolar molecules it is assumed that $D_{\text{int}} = D_{11}$. For this case a specific result is obtained on the basis of molecular-kinetic theory;

$$\frac{\rho D_{11}}{\eta}=\frac{6}{5}\frac{\Omega^{(2,2)}}{\Omega^{(1,1)}}=\frac{6}{5}A^{*}. \tag{8}$$

The experimental data and calculations made for various types of molecular interaction [3] show that $6/5A^{*} \simeq 1.3$, with this magnitude being virtually independent of temperature.

The systematic analysis of the influence of inelastic collisions of polyatomic molecules made by Mason and Monchik [7, 8] gives a more complete expression for the Eucken factor:

$$\frac{\lambda M}{\eta}=\frac{5}{2}c_{\text{trans}}+\frac{\rho D_{\text{int}}}{\eta}c_{\text{int}}-\frac{\left[\frac{2c_{\text{int}}}{\pi z}\left(\frac{5}{2}-\frac{\rho D_{\text{int}}}{\eta}\right)^{2}\right]}{1+\frac{2}{\pi z}\left(\frac{5}{3}\cdot\frac{c_{\text{int}}}{R}+\frac{\rho D_{\text{int}}}{\eta}\right)}. \tag{9}$$

It is easy to see that the first two terms of this expression coincide with formula (6). The third term, which includes the number of collisions z required to establish the equilibrium between the translational and various different forms of internal movement in the molecule, is a correction for inelastic collisions. As $z \to \infty$, i.e., when exchange is inhibited, expression (9) becomes identical to formula (6). This formula is compared in [7, 8] with experimental data for a series of low-atomic gases with a low number of internal degrees of freedom for which the exchange of energy with the translational movement is inhibited (nitrogen, methane, CO_2).

Recent systematic investigations into the transfer properties of the normal homologs of alkanes and alkenes [1, 2] have made it possible to extend the comparison of theory and experiment to complex polyatomic molecules for which the number of internal degrees of freedom is more than one order of magnitude greater than the overall number of degrees of freedom of any previously examined gas. Reliable data on the thermal capacity of gaseous hydrocarbons are published in [6, 12, 13].

In the opinion of the present authors it is better to compare the Eucken factor, as calculated from experimental data, with the analytical expressions in (5), (6), and (9) for a wide range of substances at all the temperatures under investigation as a function of the molar thermal capacity c_v rather than of the temperature as has been the practice always in the past [7, 8, 11]. The thermal capacity of the substance is related directly to the structure of the molecule, to the number of internal degrees of freedom, and to the distribution of energy

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†It is interesting to note that in the case of the rough sphere model Mason, Monchik, and Pereira [7, 8] reveal a connection between the number of collisions z and D_{int}/D_{11}. As $z \to \infty$ this ratio is found to be equal, in fact, to 1, and in the other extreme case when the energy exchange proceeds easily ($z \sim 1$), $D_{\text{int}}/D_{11} = 1.52$.

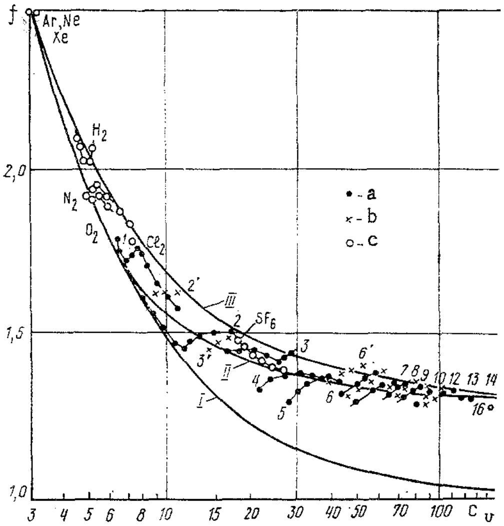

Fig. 1. Eucken factor $f = \lambda M/\eta c_v$. Comparison of experimental and calculated values: a) 1, 2, 3,... are experimental values for methane, ethane, propane, and other paraffin hydrocarbons [1, 2, 6]; b) 2', 3'... are the same for olefin hydrocarbons; c) experimental values for inorganic gases from [6, 7, 9]; I is calculated by the Eucken formula (5); II and III are calculated by the Mason and Monchik formula (9) for cases of $z = 1$ and $z \to \infty$, respectively. c_v, cal/mole·deg.

through these degrees of freedom [12, 13]. The temperature dependence of f is also then traced clearly, since the rise in temperature causes the generation of new internal degrees of freedom and the thermal capacity of the polyatomic molecules then rises steadily.

Figure 1 illustrates the results of the comparison. All the substances are grouped clearly according to the degree of complexity of the molecules so that it is easy to identify general patterns related to their structure. The Mason and Monchik formula (9) is represented by two limiting cases: curve II ($z = 1$, exchange of energy between degrees of freedom occurs immediately) and curve III ($z \to \infty$, elastic impact), coinciding with the Chapman and Cowling formula (6). The original Eucken formula (5) is represented by curve I.

The validity of formula (9) and the role of the exchange of energy between the degrees of freedom can be checked in the case of hydrocarbons. All the substances currently under investigation, from monatomic and diatomic gases to extremely complex polyatomic molecules (for example, hexadecane $C_{16}H_{34}$), are packed closely along curves II and III. Obviously, the original premises on which formulas (8) and (9) are based are fairly realistic.

On the basis of investigations into the dispersion of ultrasound it is established by Lambert and his colleagues in [10] that the exchange of energy between the translational and vibrational degrees of freedom in hydrocarbon molecules proceeds easily. The mean number of collisions required for the energy exchange is found to be not greater than five. They associate so rapid an exchange between the degrees of freedom of normal hydrocarbons with their flexibility and the low frequencies of the torsional vibrations through which all the other types of vibrations of the hydrocarbon core of the molecule can be generated. In addition, they observe the special role of the hydrogen atoms which surround the hydrocarbon core and readily absorb kinetic energy from another molecule, distributing the energy between the internal degrees of freedom [14, 15].* It can be concluded from an analysis of formula (9) that the Eucken factor of complex molecules is affected only slightly by taking account of inelastic collisions. In fact, the difference between cases of totally elastic and inelastic impact (curves II and III in Fig. 1), which are modified by the number of degrees of freedom of the molecule, is slight. For the simplest particles ($c_v = 3$ cal/mole·deg), and for very complex particles ($c_v \to \infty$) curves II and III coincide. The maximum discrepancy between the curves is 7% when $c_v = 6$–30 cal/mole·deg.

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*A low number of collisions ($z \sim 1$–4) is also characteristic of the small, but polar, molecules of the hydrogen compounds H_2O, NH_3, etc.

The influence of temperature on the Eucken factor, examined in [7, 8, 11] for biatomic-pentatomic molecules, also applies to more complex molecules. The nature of the variations can be explained within the framework of the assumptions made in those papers. In particular, the nonmonotonic variation with temperature of the f of methane, ethane, and propane (dashed curves 1, 2, and 3 in Fig. 1) is due to the influence of two opposing tendencies – the increase in f with a growth in z and the reduction in f with a growth in c_V as the temperature rises and as "deeper" and "deeper" degrees of freedom are generated.

For polyatomic molecules, for example, hexane (6), octane (8), and decane (10), only a slight rise in f is observed over the whole range of temperatures under investigation from the normal boiling point to the beginning of the thermal decomposition of the molecules. For sulfur hexafluoride the Eucken factor is reduced steadily with a rise in temperature, remaining at all investigation temperatures (270-800°K) between curves II and III [9]. The Eucken formula (5), which is known to be inaccurate, coincides with experiment, as noted by Chapman and Cowling [5, 7], only in the case of low-atomic molecules (c_V from 3 to 6 cal/mole·deg. For polyatomic molecules it is perfectly clear that formula (5) is incorrect (the curve corresponding to it on the figure is 25% too low).

From the results of a comparison of experimental and theoretical values for the Eucken factor for various substances, relations can be recommended for calculating f and the Prandtl number ($\mathrm{Pr} = \eta c_p/\lambda M$) of any nonpolar substance with an error not greater than ±5%:

$$f = \frac{\lambda M}{\eta c_v} = 1.3 + \frac{3{,}6}{c_v} - \frac{0.92 c_v - 2{,}75}{(z + 0.53 c_v - 0.76)\, c_v}, \tag{10}$$

$$\mathrm{Pr} = \frac{1}{f} \cdot \frac{c_p}{c_v}. \tag{11}$$

In the case of substances with $c_V \gtrsim 50$ the third term in expression (10) can be omitted for all values of z without damaging the accuracy of the calculations.

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