AN ANOMALY FOUND IN THE THERMAL CONDUCTIVITY OF METHYL NITRITE

By P. G. Wright * and (in part) Peter Gray

School of Chemistry, The University, Leeds 2

Measurements of the thermal conductivity of methyl nitrite over a range of pressures gave experimental values (correct to about $\pm 1\%$) which decreased from $3 \cdot 63 \times 10^{-5}$ to $3 \cdot 27 \times 10^{-5}$ cal cm^{-1} sec^{-1} deg.$^{-1}$ as the pressure was reduced from 98 to 3 mm Hg. This anomaly cannot be explained in terms of gas imperfections, dimerization, isomerization, or an abnormally long temperature jump distance. It is attributed to a relaxation effect involving a slow exchange of vibrational and translational energy. The extent of the fall is discussed in terms of calculated contributions to the specific heat.

In a polyatomic gas, the conduction of heat normally involves both translational and internal (rotational and vibrational) motions. The possibility of the disappearance at low pressures of any transport of heat by the internal modes of molecular motion was considered by Ubbelohde.[1] Although translational and rotational energy are brought to an equilibrium distribution after a few collisions, for vibrational energy thousands of collisions may be needed. Thus, at low pressures there might be too few collisions for excess vibrational energy of polyatomic molecules to be given up.

Ubbelohde [1] calculated a value for the apparent thermal conductivity as measured in an apparatus of the parallel-plate type. On the assumption that a molecule reaching a plate makes only a few collisions with it and that the transfer of vibrational energy is therefore negligibly small, an equation may be deduced of the general form

$$K^* = K \bigg/ \left(1 + \frac{K_s}{K_\sigma} \frac{\tanh \beta}{\beta}\right), \tag{1}$$

where K^* is the apparent thermal conductivity as measured between parallel plates distant l apart; K is the complete high-pressure value of the thermal conductivity, all modes of motion contributing; K_s is the (probably vibrational) part which fails to contribute at low pressures; K_σ is the part which contributes at low pressures;

$$K_\sigma + K_s = K. \tag{2}$$

β is given by

$$\beta^2 = (K/K_\sigma)\,(l^2/4D\tau). \tag{3}$$

D is the self-diffusion coefficient; τ is the relaxation time for exchange of energy between the modes of motion s and the translational modes.

The relaxation time τ is inversely proportional to the collision frequency, and thus τ, as well as D, is inversely proportional to the pressure. Hence

$$\beta \propto p. \tag{4}$$

Since β is proportional to l, the apparent thermal conductivity K^* depends on the dimensions of the apparatus, and a true thermal conductivity no longer exists.

* present address : Chemistry Department, Queen's College, Dundee.

The pressure-dependent apparent conductivity varies between upper and lower limits. For large p, β is large, tanh $\beta \simeq 1$, and K^* tends to the limiting value K. For small p, β is small, tanh $\beta \simeq \beta$, and K^* tends to the limiting value K_σ. In an apparatus of different geometry, the apparent thermal conductivity likewise varies with pressure between the same limiting values K and K_σ.

Schäfer, Rating and Eucken [2] claimed to have detected such a vibrational relaxation effect in the thermal conductivity of carbon dioxide, and Waelbroeck and Zuckerbrot [3] to have detected an effect involving rotational relaxation in the thermal conductivities of hydrogen and of oxygen. In the present paper, results are reported for gaseous methyl nitrite which show a fall in apparent thermal conductivity at low pressures: evidence is given for attributing this anomaly to a relaxation effect, and the extent of the fall is discussed in terms of calculated contributions to the specific heat.

EXPERIMENTAL AND RESULTS

The thermal conductivity of methyl nitrite was measured at 25°C over a range of pressures using an apparatus [4] of the Callear-Robb two-wire type.[5] The apparatus consisted of a glass tube (diam. 20 mm) in which there were two nearly parallel longitudinal wires (about 2 mm apart) supported between 1 mm tungsten leads. Heat was supplied by passing a known current through one wire, a nichrome spiral of resistance 50 ohm. The other wire, a thin tungsten spiral of resistance 40 ohm at 25°C, served as a resistance thermometer indicating the rise in temperature at a point between the heating wire and the wall. This form of cell is particularly suited to measurements at low pressures.[5]
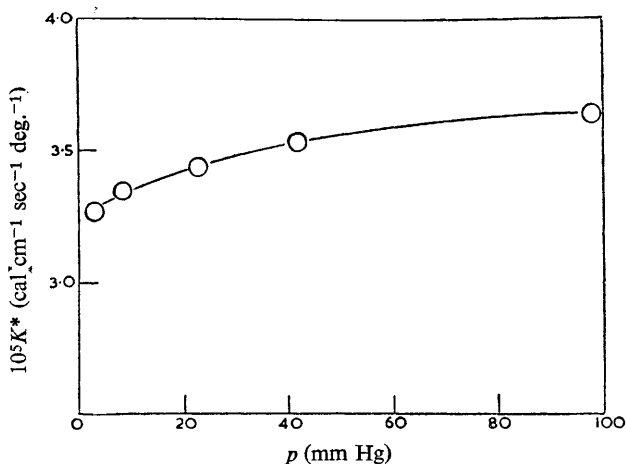

FIG. 1.—Pressure dependence of apparent thermal conductivity K^*.

The results obtained are shown in fig. 1. The measured thermal conductivity decreased as the pressure was reduced, from a value $3 \cdot 63 \times 10^{-5}$ cal cm^{-1} sec^{-1} deg.$^{-1}$ at 98 mm Hg to a value $3 \cdot 27 \times 10^{-5}$ cal cm^{-1} sec^{-1} deg.$^{-1}$ at 3 mm Hg. (These measured values of the thermal conductivity are accurate to about ± 1 %.)

Such a decrease of measured thermal conductivity (increase of instrument deflection) was (fig. 2) not observed with other gases (N_2, NH_3, H_2, CO_2) nor with mixtures of gases (air, $N_2 + NH_3$, $N_2 + H_2$, $NH_3 + H_2$, $N_2 + NH_3 + H_2$), and it is therefore not a spurious effect.

DISCUSSION

The transport properties of alkyl nitrites have apparently not been investigated previously. Vines and Bennett [6-8] have measured the thermal conductivities of nitromethane and of ethyl nitrate, and have reported values of the pressure

coefficients. The measured thermal conductivity of nitromethane increased by 4 % atm⁻¹ at 126°C, and for ethyl nitrate at 101°C the corresponding figure was 2 % atm⁻¹. These coefficients were discussed in terms of the effect on the specific heat of dimerization or gas imperfection, and it was concluded [8] that the pressure coefficient for nitromethane could be explained very satisfactorily in terms of dimerization. However, their measurements [6,7] were all made at pressures above about 100 mm Hg. In the present work on methyl nitrite, the pressure dependence of the measured thermal conductivity was (fig. 1) particularly noticeable at pressures below 10 mm Hg (which can be investigated directly only by means of the two-wire cell) where gas imperfection (and dimerization) are necessarily absent.
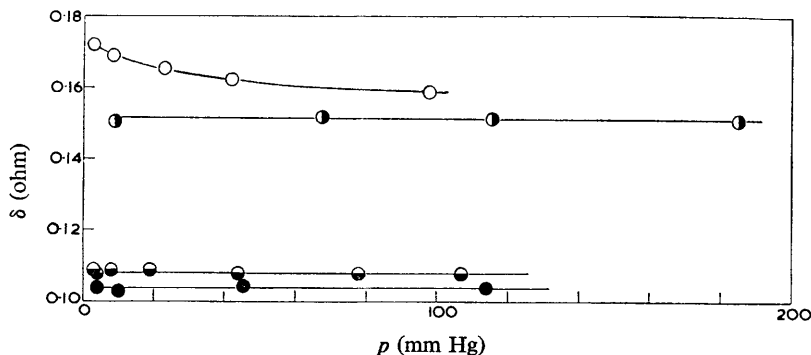

FIG. 2.—Instrument deflection δ for various gases. ○, CH₃ONO; ◑, CO₂; ●, N₂; ◔ NH₃.

Another factor which cannot account for the anomaly here discussed is the rapid cis-trans isomerization [9-15] which occurs in gaseous methyl nitrite (and even in the liquid at −40°C). In general, chemical equilibrium has a pronounced effect on the thermal properties of a mixture, as for example in the system, $N_2O_4 \rightleftharpoons 2 NO_2$. An equilibrium mixture has an anomalously high specific heat, and consequently an anomalously high thermal conductivity. However, the contribution of isomerization to the specific heat (and therefore to the thermal conductivity) of methyl nitrite is very small. In terms of the heat ΔH of isomerization and the mole fractions x_1, x_2, of the two isomers, the contribution to the specific heat is $x_1 x_2 (\Delta H/RT)^2 R$. For methyl nitrite,[16] ΔH is about 350 cal mole⁻¹ whence at 25°C $(\Delta H/RT)^2 = 0.34$, and the maximum contribution to the specific heat is thus $0.08\,R$. Moreover, although such an anomaly is pressure-dependent in a dimerization, because the degree of dissociation varies with pressure, for an isomerization it is not, because the equilibrium composition depends on temperature alone.

The most satisfactory explanation of the results obtained ascribes the variation in apparent thermal conductivity to a relaxation effect of the type postulated by Ubbelohde.[1,2] It is often difficult to distinguish clearly between such a decrease of apparent thermal conductivity at low pressures and a decrease due to the temperature jump at the wire of a thermal conductivity cell. For this reason the present two-wire apparatus, in which the temperature jump is eliminated,[5] is particularly well adapted to the investigation of relaxation effects.* It must be noted that Ubbelohde's [1] original treatment, by assuming negligible transfer of

* Although Schäfer, Rating and Eucken [2] found a relaxation effect in the thermal conductivity of carbon dioxide, none was found either by Callear and Robb [5] or in the present work. However, the conclusion of Schäfer, Rating and Eucken [2] was drawn rather indirectly, the experimental results having first to be corrected for accommodation effects; the interpretation of results obtained with the two-wire thermal conductivity cell is quite direct.

vibrational energy to the wall, sets the vibrational accommodation coefficient equal to zero, but without a non-vanishing relaxation time this would merely reduce the value of the overall effective accommodation coefficient without leading to an anomalous pressure-dependence of the thermal conductivity. For if τ is zero, β is infinite, and thus $K^* = K$. The more general case of a non-zero vibrational accommodation coefficient together with a non-zero relaxation time has been discussed by Schäfer, Rating and Eucken,[2] by Prigogine and Buess,[17] by Meixner [18] and by Hirschfelder.[19]

The present results for methyl nitrite cannot be accounted for by an accommodation effect in the absence of a relaxation effect, for this would require an abnormally long temperature jump extending out as far as the measuring wire of the cell. Now, according to a well-known formula [20] for the temperature jump distance g,

$$g = \frac{2-\alpha}{\alpha} \frac{2(1-\varepsilon)}{\gamma+1} \frac{K}{\eta c_v} \lambda, \tag{5}$$

where α is the accommodation coefficient,

  γ is the ratio of the specific heats,

  ε is a small number whose value, lying between 0·002 (for hard spheres) and 0·018 (for an inverse fifth power repulsion), depends on the law of intermolecular force,

  η is the viscosity,

  λ is the mean free path,

  c_v is the specific heat at constant volume, referred to unit mass.

Now $(\gamma+1)$ and $(K/\eta c_v)$ do not vary very much for different gases; both are larger for simple than for complex molecules. The variation of their quotient from one gas to another will be even less. Hence the value of g depends mainly on the quantity

$$\lambda(2-\alpha)/\alpha.$$

At a given pressure the mean free path λ is inversely proportional to the molecular collision cross-section, and thus is larger for smaller molecules. The accommodation coefficient α is always smallest, and thus $(2-\alpha)/\alpha$ is largest, for the lightest species, i.e., for H_2 and He. Thus, g will be largest for H_2 and He, and will be smaller for more complex molecules such as CH_3ONO. Since there was no sign of a temperature jump effect in the present apparatus even for hydrogen at pressures of 3 mm Hg, there can be no such effect for methyl nitrite.

It is also easy to show that the Knudsen regime was never approached. At 25°C and 1 atm the mean free paths of H_2 and He are respectively $1·2 \times 10^{-4}$ mm and $1·9 \times 10^{-4}$ mm (Kennard,[20] p. 149), so that at 25°C and 2·5 mm Hg the mean free paths are 0·037 mm and 0·058 mm. The most important dimensions of the apparatus, the radius of the outer wall (ca. 10 mm) and the distance between the two wires (ca. 2 mm), were both much larger. Since heat transfer was being investigated, the value of the temperature jump distance g is probably more important than that of the mean free path λ. From (5), assuming the accommodation coefficient to have the value 0·5 in both cases, the values of g at 25°C and 2·5 mm Hg were 0·19 mm for H_2 and 0·32 mm for He, both of which are still small compared with the dimensions of the apparatus. For methyl nitrite, g would be even smaller.

From the present results at the highest and the lowest pressures at which observations were made, it is evident that

$$K \geq 3·63 \times 10^{-5} \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg.}^{-1},$$

$$K_\sigma \leq 3·27 \times 10^{-5} \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg.}^{-1},$$

whence

$$K_s \geq 0·10K. \tag{6}$$

It is customary [21] to express the thermal conductivity of a polyatomic gas as a sum

$$K = (f_{trans}c_{v\ trans} + f_{rot}c_{v\ rot} + f_{vib}c_{v\ vib})\eta$$

in terms of a set of numerical factors f. f_{trans} has the value 2·5 (as for a monatomic gas). Eucken [21] supposed f to be unity for all internal modes. Simple theory [19, 22, 23] shows that for certain cases the value 1·3 is more reasonable, but there are cases [19, 24] where the exchange of quanta of rotational energy is very easy, and the theory then does not apply. For polar gases up to quite high temperatures [7, 25] and for normal polyatomic gases [26] below, and possibly at, room temperature, experiment shows that Eucken's original assumption [21]

$$f_{rot} = f_{vib} = 1 \tag{7}$$

is more correct. Since methyl nitrite is a polar gas (effective dipole moment 2·2D), this value of f will be employed, giving

$$K = (1·5c_{v\ trans} + c_v)\eta. \tag{8}$$

It follows from (6) that C_s, that part of the total molar specific heat which fails to contribute at low pressures, satisfies the inequality

$$C_s \geq 0·225R + 0·10C_v. \tag{9}$$

There appear to be no experimental results on the specific heat of gaseous methyl nitrite. A simple calculation (see appendix) using the vibrational frequencies and the barrier restricting internal rotation, shows that at 25°C the molar specific heat at constant volume C_v is 6·77 R. Thus

$$C_s \geq 0·90R = 1·78 \text{ cal deg.}^{-1} \text{ mole}^{-1}. \tag{10}$$

Such a contribution could be due to the vibrational modes (calc., 2·16 R) or possibly (though less probably, exchange of energy with the translational modes almost certainly being easier in this case) to the two internal rotations (one unrestricted, 0·50 R; one restricted, 1·02 R).

Ubbelohde's calculations, expressing the measured thermal conductivity as a function of the relaxation time and the dimensions of the apparatus, refer [1] to a system of particularly simple geometry (infinite parallel plates). To interpret the present results in terms of explicit numerical values of the relaxation time, it would be necessary to set up and solve equations appropriate to the particular geometry of the two-wire cylindrical thermal conductivity apparatus.

The value of the thermal conductivity of methyl nitrite (3·6 × 10⁻⁵ cal cm⁻¹ sec⁻¹ deg.⁻¹) derived from the present observations at 25°C may be contrasted with that at the same temperature for the isomeric nitromethane (1·95 × 10⁻⁵ cal cm⁻¹ sec⁻¹ deg.⁻¹) derived by a rather long extrapolation, assuming a linear relation between log K and log T, from observations above 100°C made by Vines and Bennett.[6, 7] Since the value of the thermal conductivity of methanol vapour determined in the present apparatus agreed with the value extrapolated from the results of Vines and Bennett, this is a genuine difference. It is too great to arise from differences in molecular dimensions or in specific heats (nitromethane,[27] experiment and calculation agreeing closely, $C_v = 5·895\ R$; methyl nitrite, calc. $C_v = 6·77\ R$). It is an instance of the generalization [7, 23, 25] that the more strongly polar a gas, the smaller is its thermal conductivity as compared with gases whose molecules are of a similar size. In the gaseous phase, the dipole moment of nitromethane [28] is 3·6 D, that of methyl nitrite * is 2·2 D.

* This value [29] is for the gas as a whole. The estimated dipole moment [15, 16] of the trans form of methyl nitrite is 3D and that of the cis form 1·3D. The cis form, being both less polar and more abundant, makes the greater contribution to the measured thermal conductivity.

APPENDIX

The vibrational assignment,[12] rotational barrier and specific heat of gaseous methyl nitrite at 25°C.

1. VIBRATIONAL CONTRIBUTION

wave number (cm^{-1})	characteristic temp. (°K)	contribution * to specific heat C/R
364	524	0·778
617	888	0·501
844	1214	0·2925
993	1428	0·194
1132	1628	0·128
1176	1692	0·111
1434	2063	0·047
1445	2079	0·046
1468	2112	0·042
1630	2345	0·024
2944	4235	0·000
3048	4384	0·000 × 2
(doubly degenerate)		
		2·164

* from tables of Einstein functions given by Stull and Mayfield [30] taking $hc/k = 1·4385$ cm deg. and assuming : (i) all modes strictly separable, (ii) anharmonicity negligible.

The vibrational assignment is taken from ref. (10) and (12).

2. ROTATIONAL CONTRIBUTION

	(C/R)
rotation of molecule as a whole	1·500
free internal rotation of CH_3 group	0·500
hindered rotation of NO group †	1·024
	3·024

† Calculated by interpolation from the tables given by Pitzer and Gwinn.[31] It is assumed (cf. Aston [32]) that the maxima separating the two isomers are spaced half a revolution apart. The mean barrier height [12] is 7800 cal mole^{-1}; accepting Chiba's [16] value for ΔH for the isomerization, the barrier for the cis form is 350 cal mole^{-1} greater than that for the trans form. The reduced moment of inertia [12] is $21·4 \times 10^{-40}$ g cm^2. These values give (in the notation of Pitzer and Gwinn,[31] V is barrier height, I is reduced moment of inertia, n is number of maxima per revolution, $Q^{-1} = hn[8\pi^3 IkT]^{-\frac{1}{2}}$) :

$$Q^{-1} = 0·090, \ V/RT = 12·7 \ \text{(trans form)},$$

$$= 13·4 \ \text{(cis form)},$$

whence, from the tables,[31] the contribution to the specific heat is

$$1·027R \ \text{(trans)}, \ 1·021R \ \text{(cis)}.$$

(Since these values are nearly equal, the slight asymmetry of the barrier has little effect on the specific heat.)   The contribution to the specific heat of the mixture is thus $1·02_4 \ R$.

3. TOTAL SPECIFIC HEAT

	(C/R)
translation	1·500
vibration	2·164
rotations	3·02$_4$
isomerization (reaction)	0·08
	6·77

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