Thermal Conductivity of an Equimolar H2O—D2O Mixture

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Thermal Conductivity of an Equimolar H_2O–D_2O Mixture

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IN order to assess the importance of resonance transfer of energy of rotational excitation in the conduction of heat by polar gases, Baker and Brokaw[1] studied an equimolecular mixture of H_2O and D_2O.

An appreciable proportion of the collisions between two water molecules is likely to produce hydrogen-bonded pairs[2] with a life time greater than a rotation period. This has two consequences which Baker and Brokaw did not consider fully. Firstly, the opportunities and time available for energy transfer by a non-resonant mechanism are likely to be greater for water[2] than for polar molecules with a weaker tendency to associate.[3–7] Secondly, and most importantly, an H_2O/D_2O double molecule can break up into *either* H_2O+D_2O *or* $DOH+DOH$. At the temperatures used by Baker and Brokaw[1] the equilibrium $H_2O+D_2O \rightleftharpoons 2DOH$ should be established rapidly.

According to naive statistical reasoning, the equilibrium mixture should consist of 50% DOH, 25% H_2O and 25% D_2O. Actually, owing to the operation of secondary isotope and related effects,[8] the proportion of DOH at equilibrium may be appreciably less or greater than 50% (the direction of the effect cannot be predicted *a priori*) and may vary with temperature.

Before the theoretically expected conductivity of a 1:1 H_2O–D_2O mixture can be calculated, experimental determinations are required of (I) the exact composition of the mixture; and, if DOH is present in considerable quantity, of (II) the thermal conductivity of[9] DOH, and (III) the conductivity coefficients for collisions between unlike molecules[9] (λ_{12}, etc., in Baker and Brokaw's[1] notation). Baker and Brokaw did not determine these, but calculated the theoretical conductivity assuming H_2O and D_2O to be the only species present. Their conclusions, therefore, though probably correct, lack a really firm experimental basis.

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[1] C. E. Baker and R. S. Brokaw, J. Chem. Phys. **40**, 1523 (1964).

[2] Estimates of the average size of the hydrogen-bonded cluster in liquid water at 345°K range from 25 to 60 molecules [G. Nemethy and H. A. Sheraga, J. Chem. Phys. **36**, 3382 (1962); K. Buijs and G. R. Choppin, *ibid.* **39**, 2035 (1963)].

[3] For example, the number of collisions required for deactivation of vibrational excitation is 400 for[4] H_2O at 486°K and 200 for[5] SO_2 at 473°K; the corresponding values of exp $(-h\nu_{min}/kt)$ are $1/113$ ($\bar{\nu}_{min}=1595$ cm^{-1})[6] and $1/4.85$ ($\bar{\nu}_{min}=519$ cm^{-1}).[6] Thus, assuming this simple form for the exponential term in the probability of deactivation by collision when "incipient dimers" are formed,[7] one may deduce the average effective lifetime of

"$(H_2O)_2$" to be $113\times200/4.85\times400$, i.e., about 11 times as long as that of "$(SO_2)_2$". The author thanks Brokaw and Baker [J. Chem. Phys. **42**, 812 (1964)] for pointing out the relevance of vibrational relaxation in this connection.

[4] P. W. Huber and A. Kantrowitz, J. Chem. Phys. **15**, 275 (1947).

[5] P. G. Corran, J. D. Lambert, R. Salter, and B. Warburton, Proc. Roy. Soc. (London) **A244**, 212 (1958).

[6] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 281, 285.

[7] See P. G. Dickens and A. Ripamonti, Trans. Faraday Soc. **57**, 735 (1961); J. D. Lambert and R. Salter, Proc. Roy. Soc. (London) **A253**, 277 (1959).

[8] E. A. Halevy, Progr. Phys. Org. Chem. **1**, 109 (1963).

[9] DOH is of lower symmetry than H_2O or D_2O, and conductivity coefficients $\lambda_{DOH,DOH}$, $\lambda_{H_2O,DOH}$, and $\lambda_{D_2O,DOH}$ estimated by interpolation from λ_{H_2O,H_2O} and λ_{D_2O,D_2O} could be appreciably in error. The greater the molecular asymmetry, the easier is the conversion of molecular internal energy into translational energy [J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 511].

Reply to a Comment by E. Spinner: Thermal Conductivity of an Equimolar H_2O–D_2O Mixture

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IT has been suggested by Spinner[1] that the equilibrium

$$H_2O+D_2O \rightleftharpoons 2DOH \qquad (1)$$

is rapidly established so that our mixture thermal-conductivity measurements[2] were, in fact, performed on the ternary equilibrium mixture. This is almost certainly the case since it is known that the analogous equilibria between CH_3OH and D_2O, CH_3OD and H_2O,[3] and C_2H_5OH and D_2O[4] are established almost instantaneously (within a few seconds) both in the liquid and gaseous phases.

The use of statistical mechanics for calculating the thermodynamic properties of small molecules in the gas phase is well established. These methods are especially suited to isotopic exchange reactions[5] (where the heats of reaction arise mainly from zero-point energy differences), and these statistical techniques have been verified experimentally (for example, by Black and Taylor[6]). By using the thermodynamic functions for the isotopic water molecules computed by Friedman and Haar,[7] together with a heat of reaction calculated from zero-point energy differences, the equilibrium constant for Reaction (1) is found to be 3.73 at 478°K and 3.76 at 526°K. After making allowance for vapor-pressure differences between H_2O and D_2O, the mole fractions are calculated to be H_2O—0.266, D_2O—0.242, and HDO—0.492. This is very nearly the composition predicted by simple statistical considerations.

Assuming this composition, it is again possible to compute a mixture thermal conductivity assuming resonant exchange on self-collisions only; this computed conductivity is found to be some 11% larger than experiment. (The previous calculation[2] was only 8% high—simply a consequence of the fact that there are more self collisions in the binary mixture.) Spinner[1] points out that in a ternary mixture it is necessary to infer a larger number of coefficients characterizing the interactions among the various species. Unfortunately, there is a paucity of information on the interactions between isotopically substituted polar molecules; however, the scanty data on diffusion do not suggest any unusual phenomena.[8] In other words, the diffusion cross sections are in substantial agreement with the viscosity cross sections of the pure gases.

Spinner's[1] statement that "An appreciable proportion of the collisions between two water molecules is likely to produce hydrogen-bonded pairs," is a statement of opinion rather than established fact. (It seems to us that a triple collision would be required for the formation of such a dimer.) However, if such collisions *are* frequent, they should be very effective in bringing about vibrational relaxation. The data of Huber and Kantrowitz[9] indicate that vibrational relaxation of water requires 200–300 collisions around 500°K. Thus it seems unlikely that dimers are formed more frequently than this, and it is permissible[10] to compute the effect on the heat conductivity using the theory of Butler and Brokaw.[11] The influence must be very small because of the small dimer concentration as well as the small heat of reaction.

Consequently, we see no reason to alter the conclusions of our paper,[2] to wit:

(1) The data on the mixtures suggest that a resonant exchange of rotational quanta is not an important factor in determining the thermal conductivity of water vapor.

(2) We suggest, tentatively, that exchange of rotational energy on grazing collisions is important but is of a classical nature.

We are indebted to Spinner for pointing out that these mixtures were equilibrated.

[1] E. Spinner, J. Chem. Phys. **41**, 812 (1964) (preceding comment).
[2] C. E. Baker and R. S. Brokaw, J. Chem. Phys. **40**, 1523 (1964).
[3] H. Kwart, L. P. Kuhn, and E. L. Bannister, J. Am. Chem. Soc. **76**, 5998 (1954).
[4] J. Hine and C. H. Thomas, J. Am. Chem. Soc. **75**, 739 (1953).
[5] H. C. Urey, J. Chem. Soc. **1947**, 569.
[6] J. F. Black and H. S. Taylor, J. Chem. Phys. **11**, 395 (1943).
[7] A. S. Friedman and L. Haar, J. Chem. Phys. **22**, 2051 (1954).
[8] L. Monchick and E. A. Mason, J. Chem. Phys. **35**, 1676 (1961).
[9] P. W. Huber and A. Kantrowitz, J. Chem. Phys. **15**, 275 (1947).
[10] R. S. Brokaw, J. Chem. Phys. **36**, 2517 (1962).
[11] J. N. Butler and R. S. Brokaw, J. Chem. Phys. **26**, 1636 (1957).

Nuclear Magnetic Resonance in KCoF₃

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RECENTLY Tsang[1] has reported nuclear magnetic resonance measurements on ^{19}F in powdered samples of $KCoF_3$. He analyzed the observed isotropic shifts and anisotropic broadenings in terms of the isotropic and anisotropic hf interactions, A_s and A_p, respectively. It is the purpose of this note to confirm Tsang's results from measurements made on single crystals of $KCoF_3$.
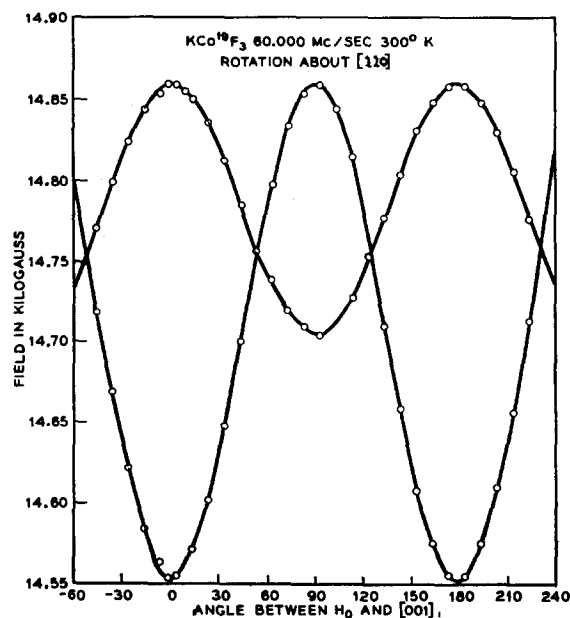

FIG. 1. Resonance field for ^{19}F as function of angle between H_0 and [001] in the (110) plane.

The fields required to observe the ^{19}F resonance at a frequency of 60.000 Mc/sec are shown in Fig. 1 for the external magnetic field in the (110) plane. At this frequency in a diamagnetic compound the ^{19}F resonance should occur at 14 979 G. From these measurements and by use of the same analysis we have obtained values of $A_s = (26.0 \pm 1.0) \times 10^{-4}$ cm^{-1} and $A_p = (8.0 \pm 0.5) \times 10^{-4}$ cm^{-1} in good agreement with Tsang's powder values of 25.0×10^{-4} cm^{-1} and 9×10^{-4} cm^{-1}. Furthermore, this value of A_p is in slightly better agreement with the value obtained from ESR measurements[2] of Co^{++} in $KMgF_3$ of $A_p = 6 \times 10^{-4}$ cm^{-1}.

[1] T. Tsang, J. Chem. Phys. **40**, 729 (1964).
[2] T. P. Hall, W. Hayes, R. W. H. Stevenson, and J. Wilkens, J. Chem. Phys. **39**, 35 (1963).