

ciation to Dr. J. G. Hamilton, B. Rossi, T. M. Putnam, Jr., and the 60-in. cyclotron crew as well as J. Vale and the other members of the 184-in. cyclotron operating group for making the irradiations.

* This work was performed under the auspices of the AEC.

† Now at the University of Michigan, Ann Arbor, Michigan.

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On the Structural Absorption of Ultrasonic Waves in Ethyl Alcohol

D. SETTE

Istituto Nazionale di Ultracustica, Roma, Italy

March 14, 1950

AN interpretation of the difference between the experimental ultrasonic absorption coefficient in water and the value of the same coefficient to be expected from viscosity and heat conductivity data has been given by Hall.¹ Water can be considered as a mixture of two structures: an open one (ice-like) and a compact one (close-packed); the elastic waves alter the equilibrium between the two structures and the rearrangement of the molecules takes place with a certain time lag. For this reason a relaxation phenomenon occurs and the absorption increases.

Hall has also suggested that a similar structural absorption could explain the excess of the absorption coefficient in other associated or hydrogen-bonded liquids of low viscosity.

It seems worth while giving the conclusions we have reached in considering the absorption of ethyl alcohol, in which the parameter α/f^2 expected on the classical theory is, at 20°C, about 25×10^{-17} sec.² cm⁻¹, whereas the experimental value is about 50×10^{-17} sec.² cm⁻¹ (α =amplitude of the absorption coefficient; f =frequency).

The values of the interaction energy for the case of two alcohol molecules and for that of four molecules, differently arranged,² show that the potential energy of two molecules is a minimum when the two dipole moments lie antiparallel, whereas the stability of four molecules is a maximum when they are arranged in a chain.

We can therefore assume that two states are possible for the alcohol molecules: (1) molecules bonded to one another in chains; (2) molecules arranged in pairs with antiparallel dipole moments. The energy is lower in the first state. A compression during wave propagation will produce an increase in the number of the molecules in state (2).

We have applied Hall's treatment working on the same hypothesis and furthermore assuming that, as a first approximation, the molecules of ethyl alcohol at rest, are mainly bonded in chains of four molecules.

As Hall's treatment requires numerical values of any two of the three quantities: (1) the instantaneous compressibility β_ω , (2) the relative change in volume $\Delta V/V$ involved in the transition 1-2, and, (3) the free energy difference of the two states ΔF , we have calculated ΔF and $\Delta V/V$.

The free energy difference per mole is $\Delta F=0.68$ kcal. and the relaxation time calculated from it is, at 20°C, $\tau \sim 9 \times 10^{-12}$ sec.

We evaluated ΔV approximately from alcohol-carbon tetrachloride mixtures, assuming that in very dilute solutions the alcohol molecules are mostly in pairs, and, moreover, that the volume of the carbon tetrachloride molecules is not altered by the presence of the alcohol molecules. The volume calculated in this way for the alcohol molecules in the state (2) is only a little lower than that for the state (1), so that $\Delta V/V$ is very small.

In consequence of this, the value of α/f^2 computed for the structural absorption in this way is much smaller than the difference between the experimental value and that obtained using classical theory.

The assumptions made in the calculation, especially as regards ΔV , are undoubtedly very rough ones. Nevertheless, it would appear from this treatment that if we wish to maintain the simple notion of a liquid as a mixture of two structures, while the parameter $\Delta V/V$ is applicable to the case of water where the molecules can pass from a very open structure to a closed one, it does not lend itself to the cases of liquids whose molecules have a large volume and which can pass under the action of ultrasounds from one energy state to another without a large volume difference between the corresponding configurations.

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A Thermodynamic Temperature of 1.5 Millidegrees Absolute

D. DE KLERK, M. J. STEENLAND, AND C. J. GORTER

Kamerlingh Onnes Laboratory, Leiden, Netherlands

April 3, 1950

TWO years ago¹ we announced that we had measured very low thermodynamic temperatures obtained by adiabatic demagnetization of a large crystal of chromium potassium alum. These temperatures were determined by straightforward application of the second law of thermodynamics. Coherent results were obtained with three different thermometric parameters and two different ways of heat supply.

At a molar magnetic entropy of $-1.0 R$ (relative to high temperatures) the magnetic susceptibility has a maximum and a small magnetic hysteresis appears.² This was found to occur at a thermodynamic temperature of 4.0 millidegrees absolute, while the lowest temperature measured was about 3 millidegrees at a molar magnetic entropy of $-1.1 R$.

Since then we have been measuring thermodynamic temperatures in several other substances.³ Quite recently we studied powdered mixed crystals of chromium alum and aluminium alum containing 1 part of Cr on about 20 parts of Al, a substance similar to that with which de Haas and Wiersma⁴ obtained very high susceptibilities in 1935. Even with a molar entropy as low as $-1.1 R$, no maximum of the susceptibility was found. Thermodynamic temperatures between 1.5 and 20 millidegrees were measured by using the susceptibility as a thermometric parameter and by heating with an oscillating magnetic field at 225 c.p.s. The accuracy of the temperature measurements is not better than 10 to 20 percent.

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The Nuclear Magnetic Moment of Niobium⁹³

ROBERT E. SHERIFF,* WILLIAM H. CHAMBERS, AND DUDLEY WILLIAMS

Ohio State University, Columbus, Ohio

March 27, 1950

THE nuclear magnetic resonance absorption peak for niobium (columbium)⁹³ has been located in a field of approximately 6300 gauss with a solution of Nb₂O₅ in HF. By super-regenerative oscillator techniques similar to those described in earlier reports,^{1,2} the niobium resonance peak was compared with the B¹¹ peak observed simultaneously in the same magnetic field. The tentative value of the ratio of the Nb⁹³ resonant frequency to the B¹¹ resonance frequency is

$$\nu(\text{Nb}^{93})/\nu(\text{B}^{11}) = 0.76187 \pm 0.00040.$$