Letters to the Editor

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Behaviour of Condensed Helium near Absolute Zero

THE recently published measurements[1] on some properties of condensed helium, in conjunction with the facts known from the work of Keesom and his co-workers[2], allow us to draw some conclusions on the behaviour of helium at very low temperatures.

It has already been shown by Keesom, who found the melting pressure to become nearly independent of temperature, that the entropy difference between the two phases tends towards zero with falling temperature (Nernst's theorem)[3]. This means that the liquid phase has to go into an ordered state[4]. This change takes place at the λ-point and is associated with a large loss of energy which, though continuous, occurs in a relatively small temperature range. (One cannot say yet in which way this ordered state—called once by the author "liquid degeneration"—is realised. Keesom[5], who recently published very similar considerations, calls it a "quasi-crystalline" state ; Clusius[6] also speaks of a "crystalline" state and adds the more specialised assumption of an association starting in the λ-region.)

Since the entropy difference vanishes, the heat of fusion $(\rho - T\Delta S = \Delta U + p\Delta V)$ must tend towards zero *a fortiori*[7]. This can be realised in two possible ways : (1) both ΔU and $p\Delta V$ may become zero, and this could scarcely be interpreted in any other way than that both phases become identical. (The same would happen if the temperature coefficient of the melting pressure were not to disappear completely.) (2) ΔU and $p\Delta V$ become equal but of opposite sign, that is, (a) ΔU or (b) ΔV changes its sign. Our measurements now enable us to find both components of ρ and to extrapolate their values to absolute zero. Although such an extrapolation entails some uncertainty, we think it accurate enough to draw the following conclusions.

One finds that along the melting curve the volume of the liquid remains always higher than that of the solid ; the volume difference even increases appreciably with falling temperature. The energy of the liquid at 4° is greater than that of the solid, just as with the normal liquid. At about 2·5°, however, the energy difference begins to fall rapidly, passes zero a little below 2° and approaches finally a value of about − 2 cal./gm.-atom. This would mean that the possibility 2 (a) is realised.

Thus the energy of the liquid at very low temperatures is smaller than that of the solid, contrary to the normal. Compressing the liquid to the solid, one has to do work against the repulsive forces, this work being greater than that done by the attractive forces. Now arises the question of the origin of these strong repulsive forces ; for at the interatomic distances realised in liquid helium there can be no appreciable repulsion originating in the atomic fields, every atom in the liquid having at its disposal a cube of 3·6 A. length, compared with the gas kinetic diameter of about 1·9 A.

In order to understand this we have to consider the part played by the zero point energy. Extrapolation of the measured latent heats of evaporation[8] to absolute zero gives an energy difference between the liquid without external pressure and the gas of about 14 cal. From our data it then follows that the corresponding values for the liquid and the solid under the equilibrium pressure are 13 cal. and 11 cal. respectively. Now the zero point energy of the solid under equilibrium pressure has a value of about 60 cal., so that the 'lattice energy' originating in the interatomic forces would amount to about 70 cal. Thus we see that the zero point energy compensates by far the greater part of the 'lattice energy' and therefore it must be the chief factor in the behaviour of the substance. Having made a first estimate of the magnitude of the zero point energy from the deviations from Trouton's rule, we have previously emphasised[9] that its large value probably is the explanation for helium remaining liquid. The attractive forces cannot diminish the volume until they are compensated by the atomic repulsive forces ; the helium cannot crystallise with the normal volume, but has to take up a bigger volume with corresponding smaller zero point energy[10]. Only high external pressure can compress it into the close-packed crystalline state.

With diminishing volume, the zero point energy must increase. So on compressing, one has to do work in order to increase the zero point energy, and this is equivalent in many respects to the existence of a repulsive force. At the interatomic distances realised in the liquid, this greatly exceeds the repulsive forces resulting from the atomic fields, and the most important factor in the compressibility is due to this.

Before going into further details, especially for explaining the negative coefficient of expansion below the λ-point, it seems necessary to have more specialised ideas on the structure of the liquid and to make assumptions for the way in which it passes into the ordered state. It may be possible that the expansion coefficient will become normal again at lower temperatures and that the negative value in the λ-region is of merely local character. For this reason we will await the result of investigations at very low temperatures, which are now in progress, before going into further discussion.

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March 1.

[1] R. Kaischew and F. Simon, NATURE, **133**, 460, March 24, 1934.
[2] *Leid. Comm.*, No. 184b, 190b, 216b, 219e, 221e, *Physica*, **1**, 128, 161 ; 1934.
[3] *Leid. Comm.*, Suppl. 61b.
[4] F. Simon, *Z. Phys.*, **41**, 808 ; 1927. *Erg. ex. Naturw.*, **9**, 235, 247ff ; 1930. *Z. anorg. Chem.*, 203, 222 ; 1931.
[5] *Leid. Comm.*, Suppl., 71e.
[6] Paper read in Breslau, 1933, unpublished.
[7] See also the measurements at higher temperatures made with Steckel, *Z. phys. Chem.*, Bodensteinband, 737 ; 1931.
[8] L. I. Dana and H. Kamerlingh Onnes, *Leid. Comm.*, 179c.
[9] K. Bennewitz and F. Simon, *Z. Phys.*, **16**, 183 ; 1923.
[10] Compare also K. Wohl, *Z. phys. Chem.*, B, **2**, 104 ; 1929.

Wave Mechanics and Structural Chemistry

THE modern applications of wave mechanics to molecular structure, and in particular the method of molecular orbitals developed by Mulliken and Lennard-Jones, have shown that it is not expedient to treat the individual links between atoms separately, and that the electrons in the molecule must be treated as a whole. The organic chemist, on the other hand, regards the molecule as held together by links from