The soundings on which Figs. 1 and 2 are based and several of the contours have been reproduced from British Admiralty Charts Nos. 115, 2182c, 2339, 3057, 1119 and 1118b with the permission of the Controller of H.M. Stationery Office and of the Hydrographer of the Navy, for the usual fee.

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CHEMISTRY

Bond-Lengths in Solid Helium

RECENTLY, Vignos and Fairbank[1] reported the existence of a new solid phase of helium-4 which exists in a narrow range of pressure between $1.45°$ K. and $1.78°$ K. They have designated the new solid as the γ-phase. Its density is less than that of the α-phase (hexagonal closest packing) of helium with which it is contiguous. It is known[2,3] that in helium-3 at a temperature almost as low, there is a phase transition in the solid from hexagonal closest packing to a less-dense phase which is body-centred cubic. Reasoning by analogy, the authors believe the new phase will be found to have the body-centred cubic, $A2$, structure.

In 1947 Pauling[4] developed an equation which has been successful for treating covalent and metallic bonds and for estimating their change in length on a change in co-ordinating number. Thus, for a proposed change in structure, one could in many cases compute the molar volume of the new structure from the cell constants of the old one. The equation is given in the form :

$$R(1) - R_n = 0.300 \log n$$

Here $R(1)$ is the single bond-radius of the element, R_n the radius along a bond direction in a structure, and n is the bond number. Furthermore, n equals v/N, where v is the valence and N is the number of bonds. In the hexagonal closest-packed structure, each atom has twelve nearest neighbours and in the $A2$ structure eight. Because of the fewer neighbours in the cubic structure, the bond-radii will be shorter even though the molar volume may be greater. If bonds were formed with only the nearest neighbours, the decrease in bond-radius would be :

$$\Delta R = R_n(12) - R_n(8) = 0.300 \log 12/8 = 0.053 \text{ Å}.$$

However, in the $A2$ structure, there are six more neighbours at a distance only slightly longer than that of the nearest eight, and therefore some of the bond-forming power of the atom is used to make bonds with them. This results in the bond-number of the shorter bonds being less than $v/8$ and the correction in bond radius becoming less than 0.053 Å. Thus in the case cited by Pauling[4], of zirconium, which undergoes a phase transition of the kind discussed here, the bond-number of the stronger bonds is near $v/9.24$ and ΔR is observed to be 0.037 Å.

Although the bonds in solid helium are mainly van der Waals, it is nevertheless instructive to apply Pauling's equation to the known phase change in helium-3. The molar volumes of helium-3 at $2.805°$ K. at the hexagonal-cubic transition line as deduced

from the results of Grilly and Mills[2] are 19.088 c.c. and 19.206 c.c. respectively. From this one obtains $R_n(12) = 1.776$ Å., $R_n(8) = 1.730$ Å., and $\Delta R = 0.046$ Å. The observed ΔR of 0.046 Å. corresponds to a bond-number of $v/8.43$. This value of the bond-number is larger than that observed for zirconium partly because the unit cell of helium is larger and partly because the van der Waals forces have a short range. One would not expect these forces to form proportionally as strong a bond with the six farther neighbours as would be the case with structures having covalent or metallic bonding.

Returning to helium-4, if the new phase has the cubic body-centred structure as is supposed, one can compute the change in molar volume during the solid–solid transition. Referring again to the results of Grilly and Mills[2], the molar volume of solid helium-4 under a pressure of 29.88 kgm./cm.[2] (near $1.723°$ K.) is 20.742 c.c. The method used in the experimental determination indicates that this is probably the volume of the hexagonal phase (Mills, R. L., and Grilly, E. R., personal communication). In accordance with this, the bond-radius, $R_n(12)$, of 1.826 Å. is obtained. If one uses as a first approximation the correction in bond-radius of 0.046 Å. that occurs in helium-3, then $R_n(8)$ will be 1.780 Å. The latter distance gives a molar volume for the cubic phase of 20.929 c.c. and a ΔV of transition to this form of 0.187 c.c./mol.

Swenson[5] reports the molar volume of solid helium-4 at 28.06 kgm./cm.[2] pressure ($1.6°$ K.) to be 20.95 c.c. If this solid is also in the hexagonal form, then one obtains 0.189 c.c./mole as the ΔV of transition. If, however, the solid has the $A2$ structure, then the ΔV of transition would be higher by only 0.014 c.c./mole.

Preparations are now under way at this Laboratory to determine the crystal structure of the new solid form.

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Thermo-electric Phenomena in Electrodialysis Systems

ALTHOUGH several authors, notably Staverman[1] and Spiegler[2], have applied the methods of the thermodynamics of the steady-state to the treatment of electrodialysis processes, little or no attention has been given to the possible existence of heat fluxes in electrodialysis experiments. Of course, very useful relationships can be obtained between the flow of charge and the flow of matter through an appropriate treatment of an isothermal experiment, but we cannot say that we have described the system unless we consider the possibility of heat flows induced by these transport processes.

The argument in favour of this point of view may be roughly summarized as follows. We should like to find an expression for the rate of entropy genera-