

changes in the pressure and temperature will make a substance assume a state of new stable equilibrium, i.e., it will cause a transition to a different phase. This process takes place when a substance is melted or its crystal structure changed. The boundary between two thermodynamically stable phases is the equilibrium curve on which these phases have equal thermodynamic potentials. Thus, by plotting on a plane the equilibrium curves between various phases of a substance in the coordinates of pressure  $P$  and temperature  $T$ , we obtain the  $P$ - $T$  phase diagram of this substance.

We cannot find the sequence followed by elements when one crystal structure is transformed into another under pressure without the use of the  $P$ - $T$  diagrams. The  $P$ - $T$  phase diagrams are now known for many elements. In considering the  $P$ - $T$  diagrams one after another in the sequence of elements in Mendeleev's periodic system, we observe a number of interesting features.\*

The first worth noting is the fact that the  $P$ - $T$  phase diagrams of elements of the same group are very similar and as the atomic number increases they gradually change. This change represents a shift of the diagrams toward lower pressures and lower temperatures; in some cases, for example, group IV-B elements, the diagrams are shifted to negative pressures. This feature, which is common to all groups in the periodic table, justifies one's predicting the possible form of the  $P$ - $T$  diagram of any element from a knowledge of the diagrams of its neighbors in the same group.

In considering the  $P$ - $T$  diagrams, we also note that the differences between elements are reflected in the variety of forms of the phase boundaries between various modifications. A consideration of the reasons for this variety—particularly the reasons for the negative slopes of the fusion curves and of the boundaries between solid phases—could be the subject of a special investigation but here we shall only consider one facet of this subject.

The nature of the pressure dependence of the melting point has been discussed very widely. In the opinion of some workers,<sup>[8,9]</sup> the fusion curves should end at the critical points. Moreover, it has been suggested that the fusion curves should rise to a certain temperature maximum and then decrease. In such cases, we may find that, at sufficiently high temperatures, not even the highest pressures will be able to make a substance crystalline.<sup>[10]</sup>

Bridgman concluded from his own experimental data that the normal form of the fusion curve was a monotonic rise with pressure.<sup>[11]</sup> This dependence is described satisfactorily by Simon's equation in the form

$$P + P_0 = bT^c,$$

where  $b$  and  $c$  are constants and  $P_0$  is the internal

\*This review of the  $P$ - $T$  phase diagrams covers work published up to May, 1965.

pressure which must be overcome to melt a solid at absolute zero.<sup>[12,13]</sup>

Bridgman's view was the accepted one for a very long time but, recently, considerable experimental data have been collected over a wider range of pressures. In considering the  $P$ - $T$  diagrams of various elements, we can see that the negative slope of the fusion curve can no longer be regarded as anomalous: it is as normal as the positive slope. Simon's equation is valid only at low pressures and invalid in those cases when the fusion curve has negative slope (as observed in bismuth, antimony, gallium, silicon, germanium, and other elements), or if it passes through a maximum (cesium, barium, or tellurium) or a minimum (cerium).

Evidently, the monotonic nature of the fusion curve is a property of those elements whose atomic packing is not changed by pressure in the solid or liquid phases.

A general tendency in the sequence of polymorphic modifications of elements, observed as the pressure is increased, is the transition to more closely packed and more ordered structures. Such transitions are accompanied by an increase in the coordination number and an increase in the packing factor. Very frequently elements in a given group have the same sequence of polymorphic changes in the crystal structure when the pressure is increased. In some groups—for example, IV-B, V-B—this sequence is identical with the sequence of changes in the crystal structure when one element is transformed into another within the group. These tendencies are closely related to the similarity of the  $P$ - $T$  phase diagrams and, together with the latter, may be used as the basis for predictions of crystal structures not yet investigated or high-pressure modifications which are difficult to produce.

X-ray high-pressure cameras of various constructions are used in high-pressure technique to study the structures of polymorphic modifications.<sup>[14-19]</sup> They are all based on the use of high-pressure chambers made of materials which are relatively transparent to x-rays; in most cases, amorphous boron, beryllium, or diamond is used to make the high-pressure chamber of an x-ray camera. X rays are scattered both in the investigated substance and in the high-pressure chamber, which increases the general background in the x-ray-diffraction patterns and leads to the loss of a number of reflections for a given sample, particularly the low-intensity reflections. X-ray exposure in high-pressure chambers also meets with other problems (which will not be discussed here) all of which make the x-ray-diffraction analysis under pressure one of the most difficult physical experiments. These difficulties explain the absence of structure data for many of the known high-pressure polymorphic modifications of various substances.

In view of this, it becomes obvious how important are well-founded predictions of crystal structures of high-pressure phases. We shall now consider the poly-