THE EFFECT OF PRESSURE ON POLYMORPHIC TRANSITIONS OF SOLIDS

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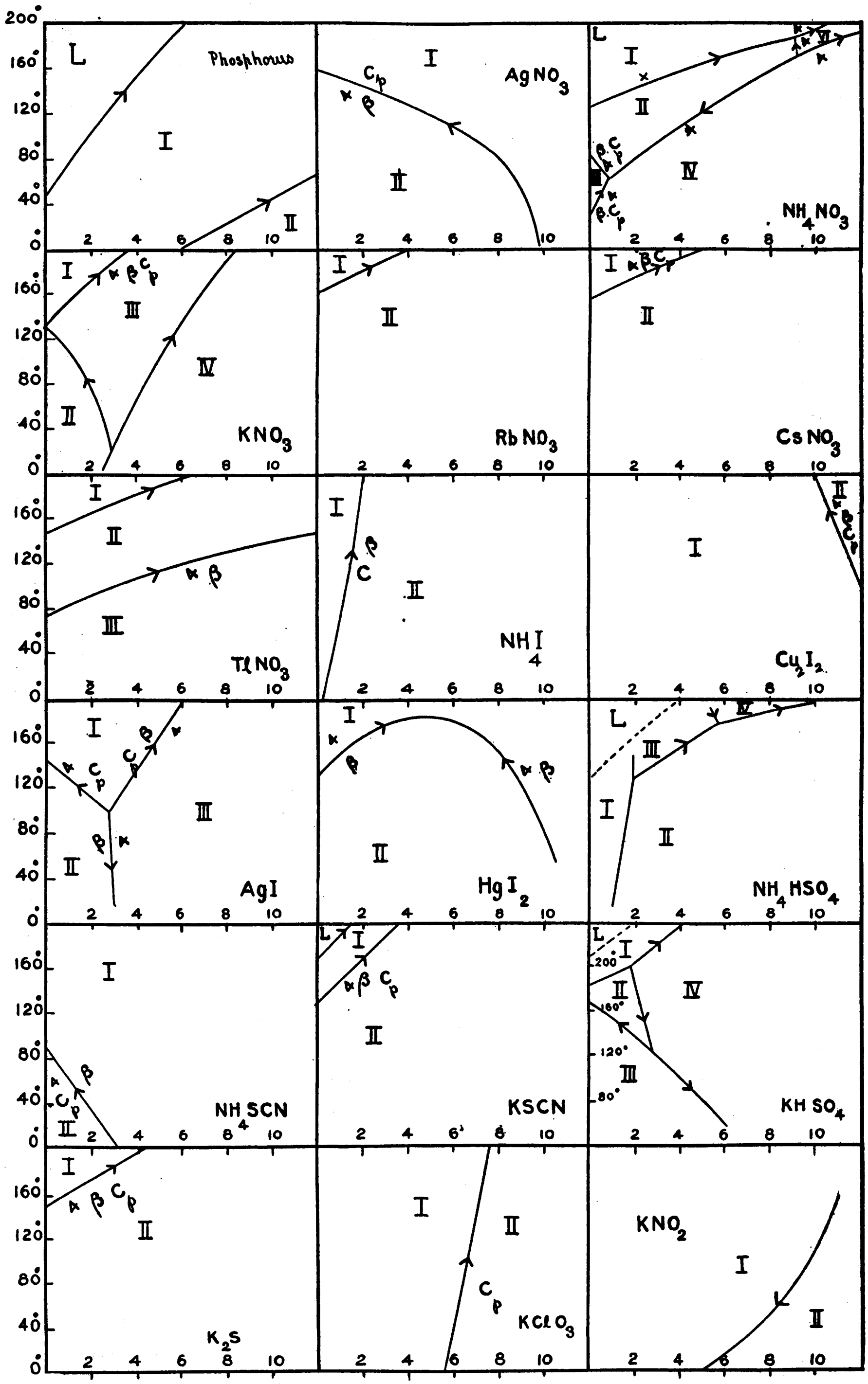
This note presents in a compact form by means of diagrams many of the essential facts concerning the effect of high hydrostatic pressure on the polymorphic transitions of 30 substances. Five of these diagrams have been previously published,[1] eleven are to be published with greater detail in a forthcoming number of the *Proceedings of the American Academy*, and the rest await detailed publication. The experimental methods have been fully described previously. The investigation has been assisted in great measure by generous grants from the Bache Fund of the National Academy of Sciences and from the Rumford Fund of the American Academy of Arts and Sciences.

The diagrams show the transition curves on the pressure-temperature plane of the several solid phases, which are indicated by Roman numerals. The liquid phase, where it occurs, is denoted by an *L*. Notice that the temperature scale is changed in the diagrams for $KHSO_4$ and H_2O. NH_4NO_3 has one transition line not shown, of the ice type, beginning at $-16°$, and $RbNO_3$ has one at 219°, probably of normal type. The arrows on the transition lines indicate the directions in which the difference of volume of the two phases decreases numerically. An α, β or C_p placed on one side of a curve indicates that the phase on that side of the curve has the larger compressibility, thermal expansion, or specific heat. In the detailed presentation of data, the numerical values of all these factors, as well as of the latent heat of transition and change of energy are given.

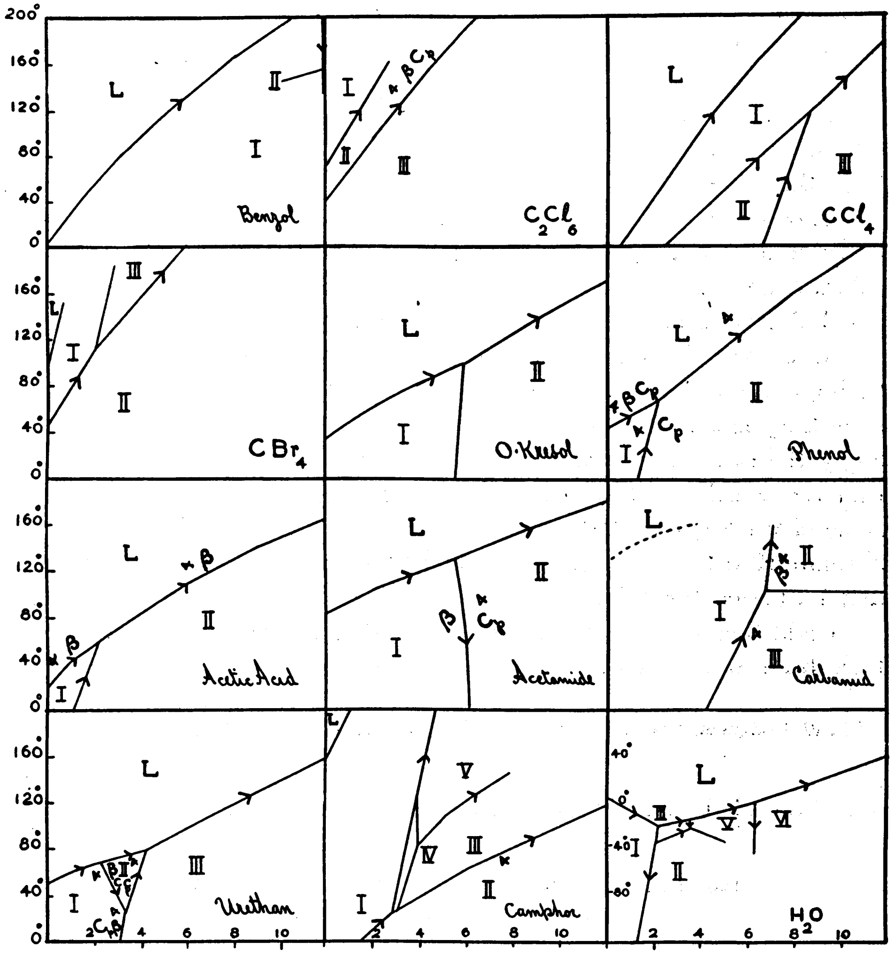
The number of substances is perhaps sufficient to justify an enumeration of the relative frequency of different types of behavior. The first impression is one of bewildering complexity, it is obvious that the phenomena of polymorphism, even under high pressures, do not tend to any simple type. The apparent complexity is rather increased when one considers the diagrams of chemically related substances, such as the six nitrates, the four iodides, the two sulfocyanides, and acid sulfates. It is possible, however, to detect traces of regularity among the nitrates and sulfocyanides by putting into correspondence the phases which belong to the same crystalline system.

The variety of shapes possible for the individual curves is in striking contrast with the case for melting curves. Every rising melting curve



Pressure in Thousands of Kilograms per Square Centimeter.

is concave toward the pressure axis, and rises continuously, and the two known falling melting curves are also concave downward. We have here examples of rising and falling curves with curvature in either direction, curves with a maximum temperature (HgI_2), and curves with a maximum or minimum pressure (H_2O and Benzol). No cases have



Pressure in Thousands of Kilograms per Square Centimeter

been found of a critical point, however. In the diagrams several curves are indicated as coming to an end; this simply means that for one reason or another further measurements were impossible. The relatively high frequency of falling transition curves is in contrast to the case for melting. A falling curve means that the phase stable at the higher temperature has the smaller volume. There are only two known cases for melting, whereas more than one quarter of the cases above are of this type. $KHSO_4$ affords a notable example where three curves of this type meet in a triple point. For a liquid, Δv always decreases with increasing temperature on either a rising or a falling curve. On the rising transition curves there are 37 cases of normal variation of Δv and 5 of abnormal variation; on the falling curves 8 normal and 8 abnormal cases.

The relative compressibility, thermal expansion, and specific heat of neighboring phases is significant. It is natural to expect that the phase of smaller volume will have the smaller compressibility and thermal expansion, and that the phase stable at the higher temperature will have the higher specific heat. If we call this behavior 'normal,' then on rising curves we find 9 cases of normal and 11 of abnormal compressibility, and on falling curves 1 normal and 7 abnormal. The expansion shows 5 normal and 7 abnormal cases on rising curves and 2 normal and 4 abnormal on falling curves. C_p is normal in 5 cases and abnormal in 7 cases on rising curves, and normal in 6 cases and abnormal in 1 on falling curves. The fact of abnormal C_p is of considerable significance from the point of view of the quantum hypothesis. It means (if we may apply the same considerations to C_p as to C_v, which is usually done) that the specific heat curves of the two modifications cannot be of the same character, but that somewhere between the transition point and absolute zero the one which is lower at the transition point must cross and lie above the other.

In addition to the substances enumerated above, about 100 others have been examined without finding other forms.

[1] P. W. Bridgman, *Proc. Amer. Acad.*, **47**, 439-558 (1912); *Physic. Rev.*, 3, 126-203 (1914).

ON ISOTHERMALLY CONJUGATE NETS OF SPACE CURVES

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Bianchi[1] has called a parametric net of curves on a surface isothermally conjugate if, when the surface is referred to these curves, the second fundamental form, $D\,du^2 + 2D'\,du\,dv + D''\,dv^2$, may by a transformation $\bar{u} = U\,(u), \bar{v} = V\,(v)$ be made to take on the same shape as does the first fundamental form when the parametric net is isothermal; i.e., the parametric net is isothermally conjugate if $D' = 0$, $D = D''$. These nets have lately attained increased importance, so that Wilczynski's recent geometric interpretation[2] of Bianchi's condi-