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ON THE REGION OF INDIFFERENCE FOR HIGH PRESSURE TRANSITIONS IN *d*-CAMPHOR (II–III) AND PHOSPHORUS (I–II)

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Abstract—An investigation has been made of the effect of pressure on the transformation in *d*-camphor and phosphorus. The so-called "region of indifference", reported as approximately 0·6 kilobars (kb) in camphor and approximately 0·38 kb in phosphorus, was found to be less than 0·14 kb and 0·16 kb, respectively. Rates of transformation between phases showed strong dependence on the purity of material, and it is suggested that for sufficiently high purity the region of indifference may become vanishingly small.

INTRODUCTION

MOST of the polymorphic transformations reported in the numerous works of BRIDGMAN are prompt from either direction as the pressure rises or falls toward equilibrium.(1) However, he frequently mentions a sluggishness of transformation and reports in some detail on several materials in terms of a "region or band of indifference" (region within which transformation will not occur).(2,3) This band spans a considerable pressure range on either side of the equilibrium point.

The purpose of the present work was to study the effects of the application of high pressure on selected materials and to determine whether the so-called *region of indifference* exists. The program was designed to be exploratory in nature. In some cases there was little known theoretical basis for expecting that this condition should occur. An interest in specific rates of transformation and crystal growth prompted one of us (A.V.)(4) to suggest that an investigation of the region of indifference would prove useful.

EXPERIMENTAL

1. *Pressure apparatus*

An unsupported tungsten-carbide piston one inch in diameter was moved into a one-inch by two-inch long supported tungsten-carbide pressure chamber. Essential features of the pressure chamber are given in Fig. 1. The mechanical advance of the piston in the pressure chamber was translated into an electrical equivalent by a potentiometer, linearly accurate to about one part in a thousand. The signals from the potentiometer and pressure signals from calibrated Baldwin pressure cell were simultaneously plotted on an x–y recorder. Details of this and similar arrangements of pressure and recording apparatus have been recorded elsewhere.(5,6)

Perhaps worth mentioning is an adaptation used to extend the pressure range of the hydropress used in these experiments. The basic unit consists of dies which can be stacked for one or two stage operation. Pressures up to approximately 50 kb have been obtained in the 0·5 in. dia. cavity single stage operation. With two stages up to 80 kb pressure in the 0·5 in. cavity can be obtained. An engineering feature of possible interest is the adaptation, to the basic unit, of a girdle,(7) or modified belt,(8) apparatus designed for operation at pressures in the cavity in excess of 120 kb (revised pressure scale).(9) This is believed to be near the upper pressure limits for present-day high-pressure, high-temperature apparatus of the

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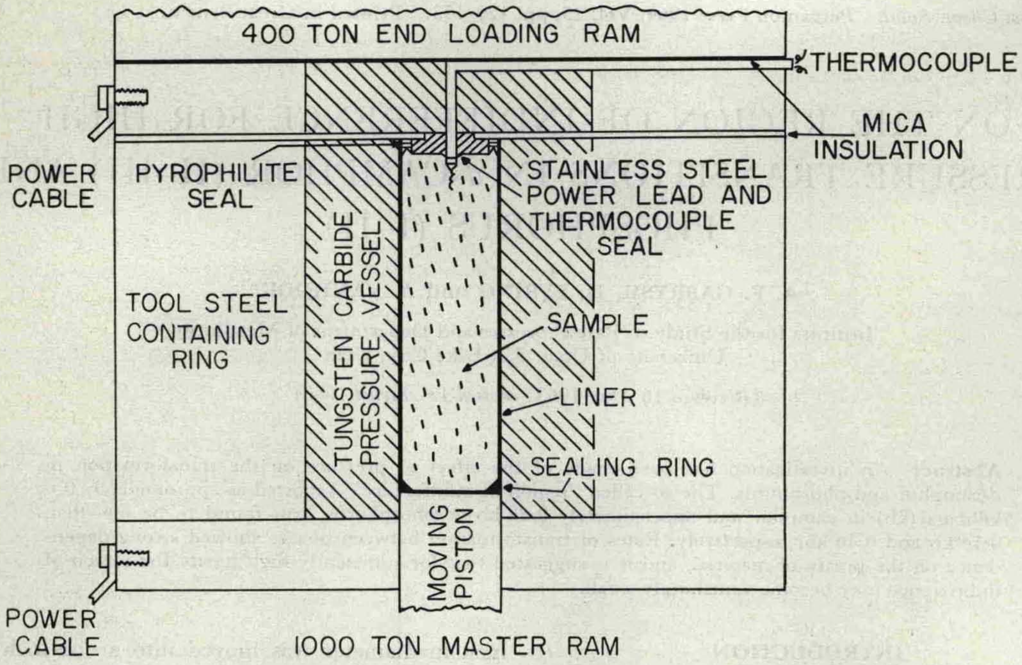

FIG. 1. Schematic of the high-pressure plate and details of sample assembly.

compressible-gasket variety. The general principles of the compressible-gaskets have been thoroughly discussed by HALL.(10)

To decrease the intensity of antagonistic pressure ripples(11) caused by the action of the pumping system, use is made of a Vanguard Y26–A hydraulic pumping unit obtained from the Owatonna Tool Company, Owatonna, Minnesota. The unit is a five-cylinder, axial-piston pump which is supercharged by a gear pump for the high pressure stage. It is equipped with a 4-way lever-operated, "shear-seal, open center" type control valve. A pressure regulating valve which bypasses oil when a predetermined pressure has been reached can be adjusted from 1000 to a safe 10,000 lb/in.^{2} but with an upper limit of 15,000 lb/in.^{2} Pumping speeds can be finely controlled by a needle valve used to bypass proportional amounts of oil back to the oil-reservoir.

Specifically for this type of pressure apparatus, this system affords a means to produce extremely slow or rapid, but smooth, pressure changes so that transition reversibility can be followed from either side of a high-pressure transition state. The value of this was observed during calibration runs where the Bismuth II–III transition did not come sluggishly(9) but appeared as equally strong and smooth in either direction as did the I–II transition. Further, very rapid step-wise mechanical displacements of the piston can be produced when needed to study shear-motion effects within the sample. For example, Figs 2 and 3 show that the finality of the running transition is the same as the non-interrupted transitions.

2. *Calibration*

The pressures in the stainless steel lines feeding the end-loading and the master rams were checked with calibrated gages. The equipment gages which monitor the end-load and master ram pressures were thus standardized.

Micrometer-controlled displacements of the linear potentiometer, before and after an experimental run, showed that while the potentiometer remained in one position reproducibility was within 0·1 per cent. When the potentiometer itself was moved, between micrometer-calibration displacements, reproducibility was no better than 0·6 per cent.

The free-piston technique(9,12) was then used for advancing the piston into the high pressure chamber. The Heise-Bourdon gage showed a maximum hysteresis of 15 lb/in.^{2} in a range maximum of 40 kb. Using a similar apparatus, KENNEDY and LAMORI(9) showed that a Heise gage, calibrated against a free piston gage, had an accuracy of better than one part in a thousand for maximum range of the apparatus, which was approximately 80 kb. Corrections to sample volume, piston displacement and pressure were made for master-ram weight and slight ram-cylinder distortions.

3. *Sample purity*

The *d*-Camphor used in the first experiments was a shelf product with a melting point of 169–171°C. Some of this product was later purified by crystallization from alcohol-water (middle fraction) and resublimation. The melting point of the purified material, 176–7°C, agreed with the handbook value of 176°C.

The phosphorus (J. T. Baker, N.F. VII) product was purified by washing in the dark with dilute H_2SO_4–$K_2Cr_2O_7$.(13) The melting point of the purified material was 44·2°C. This compares well with the handbook value of 44·1°C.

RESULTS

1. *Camphor*

The equilibrium pressure for the *d*-Camphor (shelf product—melting point 169–171°C) II–III transition was determined to lie between 2·72 and 2·86 kb at 19·1°C. The reversible transformation was proceeding, even after one hour, at finite rates at these limits so that the region of indifference would be less than 0·14 kb wide, Fig. 2 (dash lines). This contrasts with the 0·6 kb width at 2·8 kb estimated from BRIDGMAN's data.(2)

Some of the shelf material was purified. This material showed an equilibrium pressure within 2·41 and 2·54 kb, Fig. 2 (solid lines); a lower and again within a much narrower limit than Bridgman's. Transformation of this purified material began and proceeded much more rapidly than in the case of the unpurified specimens.

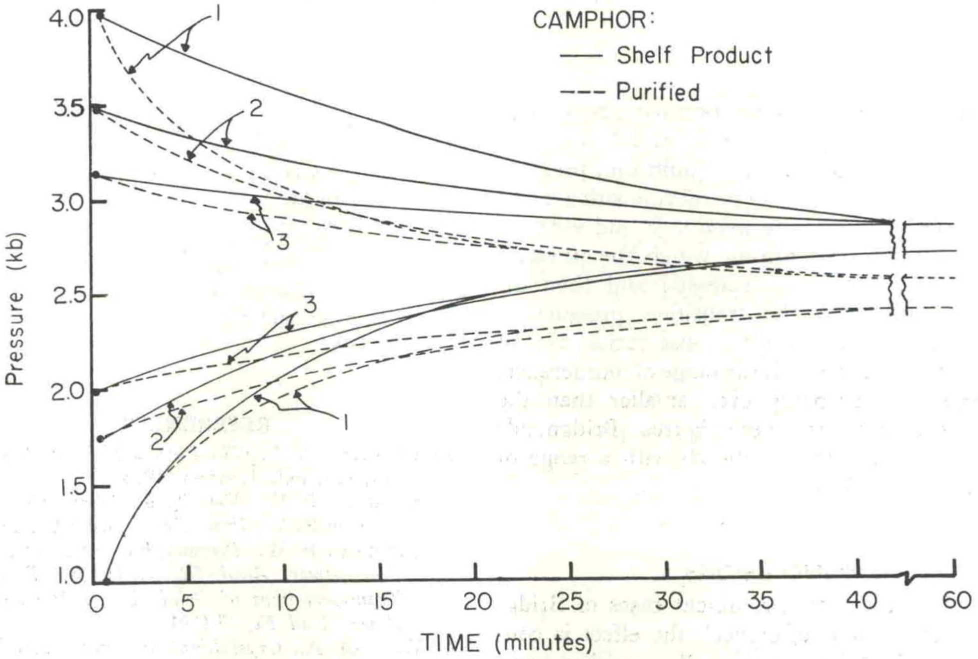

FIG. 2. Camphor: Representative traces of three successive runs, indicated by 1, 2 and 3, for the observed reversible II $\rightleftarrows$ III transition in impure and pure samples: $T = 19{\cdot}1$°C.

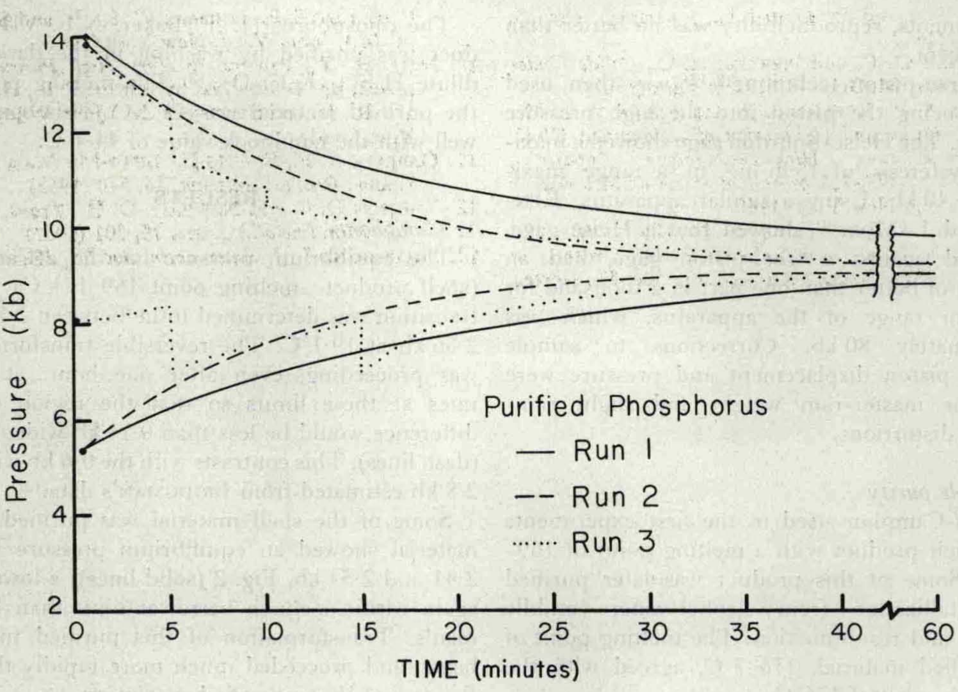

FIG. 3. Representative trace for the pressure effect on purified (m.p. 44·2°C) yellow-phosphorus transition: $T = 21°C$.

2. *Phosphorus*

Representative results for purified phosphorus (see Sample Purity) are given in Fig. 3. The first run at $T = 21°C$ placed the equilibrium pressure between 8·8 and 9·9 kb. A second run with a larger sample fixed the value between 9·08 and 9·24 kb. Two successive runs during which the pressure schedule was regularly decreased and then increased again fixed the transition pressure at around 9·2 kb. The periods of observation were at most only one hour so that the range of indifference, if it exists, is probably even smaller than the 0·16 kb suggested by these figures. Bridgman's equilibrium pressure was 9·0 kb with a range of indifference of 0·38 kb.

CONCLUSIONS

In two of the most prominent cases of Bridgman's "region of indifference" the effect is considerably reduced and practically vanishes upon purification of sample.

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REFERENCES

1. BRIDGMAN P. W., *The Physics of High Pressure* pp. 225, 253. Bell, London (1958).
2. BRIDGMAN P. W., *Velocity of Polymorphic Changes Between Solids, Proc. Amer. Acad.* **52**, 57 (1916).
3. BRIDGMAN P. W., *Polymorphism at High Pressures, Proc. Amer. Acad.* **52,** 91 (1916); *Polymorphic Transformations of Solids Under Pressure, Proc. Amer. Acad.* **51,** 55 (1915).
4. VANHOOK A., *Crystallization Theory and Practice, A.C.S. Monograph* No. 152. Reinhold, New York (1961).

5. BOYD F. R. and ENGLAND J. L., *J. Geophys. Res.* **65,** 741 (1960).
6. KENNEDY G. C. and NEWTON R. C., *Solids Under Pressure*, McGraw-Hill, New York (1962).
7. YOUNG A. P., ROBBINS P. B. and SCHWARTZ C. M., *Description and Calibration of a Modified Girdle High-Pressure, High-Temperature Apparatus*, Paper 62-WA-257 presented at the ASME Winter Meeting, New York (1962).
8. HALL H. T., *Rev. sci. Instrum.* **31,** 125 (1960).
9. KENNEDY G. C. and LAMORI P. N., *Progress in Very High Pressure Research*, pp. 304–313 (edited by BUNDY F. P., HIBBARD W. R., Jr. and STRONG H. M.), John Wiley, New York (1961).
10. HALL H. T., *Progress in Very High Pressure Research*, pp. 1–9 (edited by BUNDY F. P., HIBBARD W. R., Jr. and STRONG H. M.) John Wiley, New York (1961).
11. GABRYSH A. F., EYRING H., SHAO-MU MA and KAI LIANG, *Rev. sci. Instrum.* **33,** 670 (1962).
12. JOHNSON D. P. and NEWHALL D. H., *Trans. Amer. Soc. Min. (metall.) Engrs.* **75,** 301 (1953).
13. HILDEBRAND J., *J. Amer. chem. Soc.* **73,** 2525 (1951).