

displacements, reproducibility was no better than 0.6 per cent.

The free-piston technique<sup>(9,12)</sup> was then used for advancing the piston into the high pressure chamber. The Heise-Bourdon gage showed a maximum hysteresis of 15 lb/in.<sup>2</sup> in a range maximum of 40 kb. Using a similar apparatus, KENNEDY and LAMORI<sup>(9)</sup> 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<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.<sup>(13)</sup> 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.<sup>(2)</sup>

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.

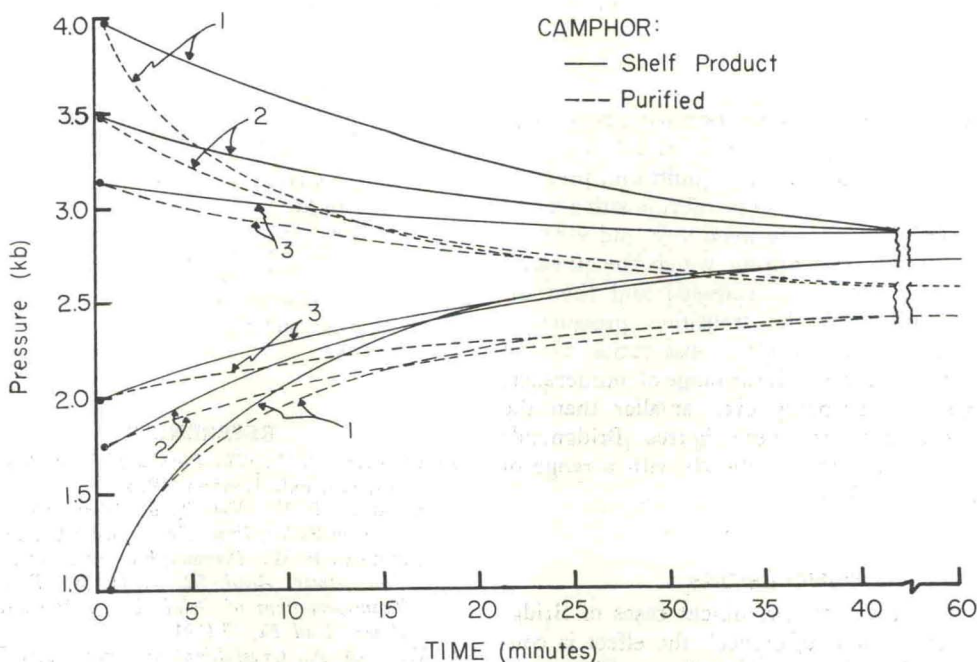


FIG. 2. Camphor: Representative traces of three successive runs, indicated by 1, 2 and 3, for the observed reversible II  $\rightleftharpoons$  III transition in impure and pure samples:  $T = 19.1^\circ\text{C}$ .



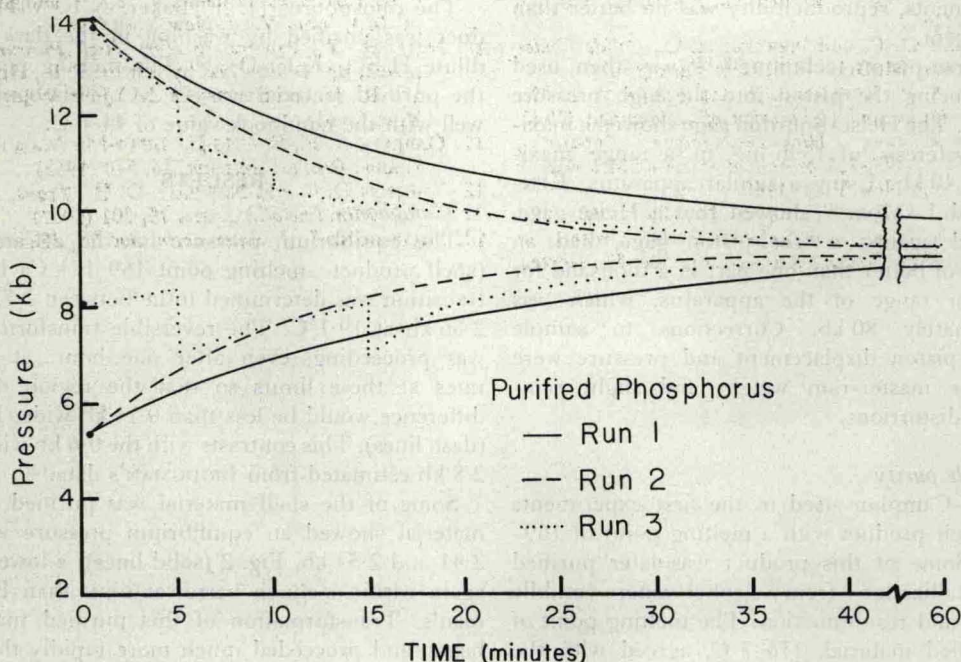


FIG. 3. Representative trace for the pressure effect on purified (m.p.  $44.2^{\circ}\text{C}$ ) yellow-phosphorus transition:  $T = 21^{\circ}\text{C}$ .

## 2. Phosphorus

Representative results for purified phosphorus (see Sample Purity) are given in Fig. 3. The first run at  $T = 21^{\circ}\text{C}$  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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