

tion to the high-pressure phases was extremely slow. This included AgI from two different chemical suppliers, from our own preparation (0.085 molal NaI solution poured into boiling 0.097 molal  $\text{AgNO}_3$  solution), AgI heated overnight at  $140^\circ\text{C}$ , AgI passed through the II-I boundary (to aid in conversion of II' to II), and AgI ground vigorously in a mortar (to convert II to II').\*

Several runs were made at temperatures from  $30$ – $60^\circ\text{C}$  and in all cases the high pressure from created was III alone. This is in agreement with previous results of Davis and Adams[15] but not with those of Bassett and Takahashi[14], where a triple-point of  $65^\circ \pm 2^\circ\text{C}$  was determined for II-III-IV. Transformation kinetics do not explain the discrepancy because if phase IV appears below  $30^\circ\text{C}$  it should certainly appear above this temperature if a true stability field for phase IV existed near the triple point.

Figure 10 presents the results of the AgI experiments. Runs at  $50$  and  $60^\circ\text{C}$  were made with cornstarch pressure medium and all others with kerosene. From the runs completed on fine-grained polycrystalline aggregates it is apparent that the II-IV boundary may exist but cannot be accurately determined with the present apparatus. Most of the data in this figure† can be used only to resitricit the position of the II-III boundary within the dashed lines, inasmuch as the growth of phases were not observed, but only the presence of certain phases after a period of time for growth had elapsed.

These boundaries represent 30 min isocrons† for about 20 per cent conversion; that is, the transformation rate was sufficiently great to accomplish about 20 per cent conversion to the new phase in 30 min, the duration of most experiments. Several long-period experiments, lasting up to 24 hrs, demonstrated that phase III grew along with phase IV at the expense

of phase II+II' at  $25^\circ\text{C}$  and 3350 bars, and that phase II'+II grew at the expense of III and IV at 2800 bars. Again, on the up-pressure leg of the run, phase IV appeared at precisely the same time as phase III and remained with phase III as both inverted to II+II' at 2800 bars.

The long period experiment at 2800 bars (station 1, Fig. 10) shows that the II-III boundary lies closer to the +30 min isocron. Further positioning of this boundary between stations 1 and 2 is arbitrary because these points do not lie on equal but opposite isocrons, nor was the exact amount of conversion determined for the runs. By placing this boundary midway between the stations, and taking the boundary slope to be the average of the isocron slopes, the boundary lies 90 bars above that originally determined by Bridgman[17] for the II-III stability fields, with a slope of  $-0.56$  deg/bar, compared to  $-0.42$  given by Bridgman. Even with the uncertainties occasioned by the sluggishness of inversion, the boundary at  $30^\circ\text{C}$  can be no higher than 3350 bars, no lower than 2800 bars, and is given here as 3100 bars.

### B. Discussion

Many unsuccessful attempts were made to convert AgI II+II' to IV (for times up to 8 hrs) with fine powders of silver iodide in the above manner. Then Van Valkenburg (personal communication) noted that single crystals of hexagonal AgI (II) (some of which were as small as the coarse fraction of the powders used here) transformed under pure hydrostatic pressure to AgI-IV quickly and without polygonization. We therefore attempted another X-ray run with coarse powder (about  $50\mu$ ), also pure phase II. By increasing the pressure at small increments in the 2800–3200 bar region it was possible to convert most of this originally phase II material into phase IV. The optical experiments performed in Van Valkenburg's laboratory, which were observed by one of us (B.L.D.), demonstrated conclusively that

\*For the effects of grinding of the stability of the II and II' phases, see Burley [16].

†Time isolines.

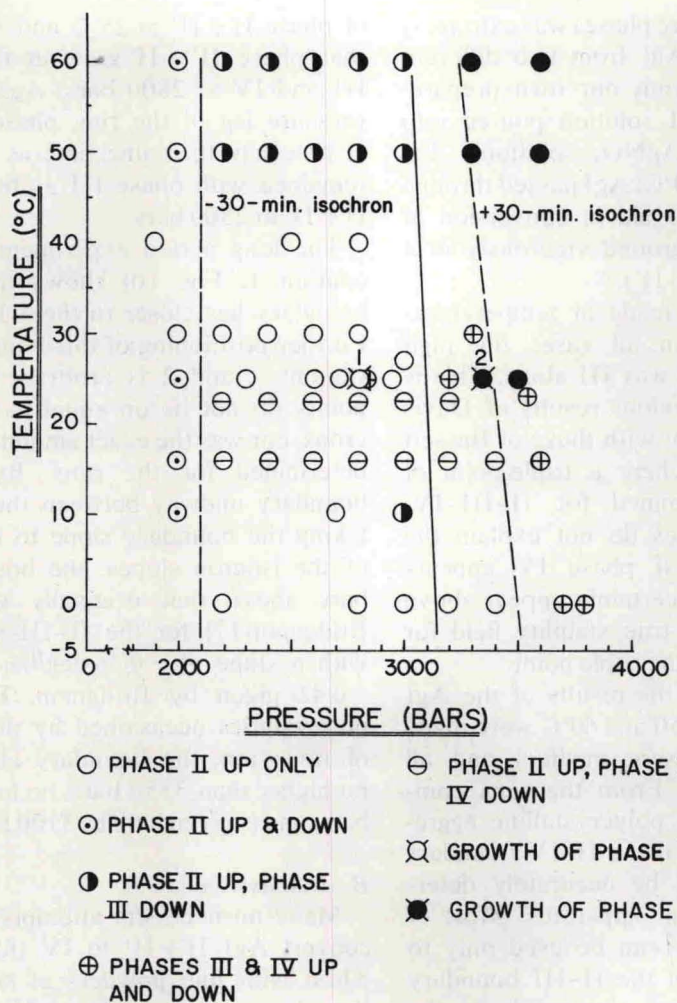


Fig. 10. Observed phase relations for AgI in the II, III, and IV regions. Solid line is estimated II-III boundary. See text for further explanation.

small single grains of hexagonal silver iodide could be converted readily into phase IV. There appear to be no polygonization during this process unless the phase III region was entered and phase III formed.

In view of the X-ray experiments on the coarse powder, and the optical experiments, it appears that the width of the phase IV stability region at room temperature can be no greater than  $50 \pm 25$  bars. It is also becoming more apparent from further X-ray data taken in this laboratory and from the nature

of the II-IV transformation observed optically that there is a close structural relationship between these two phases. Such a relationship was noted to exist in indexing of phases II and IV by Davis and Adams [15].

One of the prime purposes of this investigation was to see if AgI-IV could occur in the atmosphere under quenching conditions from silver iodide generators. It now appears that such a condition would be highly improbable from the following viewpoints: