[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Examination of Certain Solid–Solid Transformations in Crystals in an Attempt to Detect the Formation of Microcrystals[1]

BY T. E. HOPKINS AND W. F. GIAUQUE

RECEIVED NOVEMBER 21, 1959

Measurements of surface by nitrogen adsorption at the boiling point of nitrogen have been used in an attempt to detect the formation of microcrystals during crystal transformation in NH_4Cl, $(NH_4)_2SO_4$ and Na_2SO_4. The results were negative.

Previous work[2] in this Laboratory has disclosed evidence that crystalline transformations which occur in $ZnSO_4 \cdot 6H_2O$ and $MgSO_4 \cdot 6H_2O$ at low temperatures result in the formation of microcrystals. These cases were interpreted as being due to the difficulties of distributing water molecules in the solid when the respective hexahydrates were transformed to higher and lower hydrates. The opacity which develops in pseudomorphic crystals is evidence of the formation of extensive new phase boundaries but this in itself does not, of course, imply that the resulting agglomerated crystals do not consist of macroscopic units.

It seemed of interest to examine several cases where the composition of the phases would remain unaltered, to see if any substantial number of small crystals were produced. The case is of considerable interest in calorimetry since the heat content of microcrystals would be greater than that of the substance in macro form. Transformation temperatures could also be influenced by such effects.

Although most of the interface area between agglomerated microcrystals probably would be unavailable for gas adsorption, it seems reasonable that such a method would give a considerable increase in surface if substantial formation of microcrystals occurred.

The apparatus was similar to that described elsewhere.[3]

After the transformations had been caused to occur by cooling through the transition regions, the adsorption of nitrogen was observed as a function of pressure over the applicable range to the upper limit of the B.E.T. isotherm equation.[4]

The substances investigated were NH_4Cl, $(NH_4)_2SO_4$ and Na_2SO_4(III). The ammonium salts which have gradual transitions near 242 and 233° K., respectively, were selected because of the considerable volume changes. The Na_2SO_4, solid III was investigated because it is of interest in calorimetric investigations in progress in this Laboratory. It was prepared by heating Na_2SO_4 to fusion and cooling to form solid I, which undergoes a transition to solid III at about 500° K. We were interested in finding out whether this transition produced any appreciable fraction of microcrystals in the solid III.

As a check on the apparatus some MgO known to be in a microscopic state was utilized and found to give 161 $m.^2\ g.^{-1}$ in terms of a B.E.T. plot.[4] To insure that no accidental dust was included, particles of the samples to be investigated which would pass a mm./4 mesh screen were discarded.

Surfaces in the range 0.2–0.3 $m.^2\ g.^{-1}$ were found in each case. Since the limit of accuracy was about this quantity, the method gave no reliable indication of microscopic phase formation. If the value 0.25 $m.^2\ g.^{-1}$ is taken literally, it would indicate a particle size of about 0.02 mm. and such particles would be well within the macroscopic range of properties. A major source of error is the inaccessibility of interface areas with respect to adsorption of gases.

It would be possible to increase the accuracy of the experiment about ten fold with respect to accessible areas but it is evident that this could not change the inference.

(1) This work was supported in part by the National Science Foundation.

(2) W. P. Cox, E. W. Hornung and W. F. Giauque, THIS JOURNAL, **77**, 3935 (1955).

(3) W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glass Blowing and Laboratory Techniques," Instruments Publishing Co., 1949, p. 257.

(4) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).