

method [Dunn, *Ind. Eng. Chem., Anal. Ed.*, **2**, 59 (1930)], applicable to crystalline powders, is 13.8 sq. m. per cc. of powder, on the assumption of a spherical shape for each particle. This is in good agreement with the value 14.4 obtained by the adsorption method. However, the closeness of the agreement is to some extent accidental, since the adsorption method includes the area of the colloidal part of the powder, which is not included by the microscopic method. Further comparisons with various other methods will be made later.

GEORGE HERBERT JONES LABORATORY  
UNIVERSITY OF CHICAGO  
CHICAGO, ILLINOIS

WILLIAM D. HARKINS  
DAVID M. GANS

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#### CRYSTALLIZATION OF ANHYDROUS SODIUM ACETATE FROM AQUEOUS SOLUTION AT ROOM TEMPERATURE

*Sir:*

If the trihydrate of sodium acetate,  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ , is placed in a sealed tube and heated to  $58^\circ$ , it loses its water of crystallization and partially dissolves in this water. At  $80^\circ$  all the salt is dissolved. On cooling in the sealed tube, the writer, experimenting under the supervision of Professor Stuart Woodford Young, made the interesting and unexpected observation that the form crystallizing from this aqueous solution is anhydrous. This anhydrous form appears whether the solution be cooled rapidly or slowly, the only difference being in the appearance of the crystal. The slowly cooled solution will start crystallizing at only a few nuclei, from which there is a radial growth of thin needles. The rapidly cooled solution is immediately filled with small nuclei. Both of these are flattened and elongated orthorhombic crystals with the three indices of refraction lower than 1.45. This anhydrous form is shown by crystallographic observation, for which we are indebted to Professor A. F. Rogers, to be the same as the anhydride formed by direct dehydration, and the normal solubility curve is exhibited.

The crystals remain unaltered as long as the tube is kept sealed. Here, then, is a solution that is 2400% supersaturated and yet can be kept indefinitely in contact with the anhydrous form. Cooling below  $0^\circ$  has no effect, but cooling in liquid ammonia or liquid air brings about conversion to the stable trihydrate.

In 1904 and 1905 Dr. Young and W. E. Burke were able to form and identify ten new hydrates of sodium thiosulfate. At the beginning of the work on sodium acetate it was thought that some new hydrates might be produced, but so far none has been found.

This recent work of Dr. Young, who had been on the faculty of Stanford

University since 1892, was halted by his unexpected death on April 9, 1931, and is discontinued for the present,

DEPARTMENT OF CHEMISTRY  
STANFORD UNIVERSITY  
STANFORD UNIVERSITY, CAL.

WILLIAM W. CONNER

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### DISCONTINUITIES IN ADSORPTION ISOTHERMS

*Sir:*

In previous communications<sup>1</sup> we have shown that the adsorption of hydrogen by nickel and copper at low temperatures increases with pressure in a markedly discontinuous manner. Recently Allmand and Burrage<sup>2</sup> have reported a large number of isotherms for charcoal and silica gel which show discontinuities, and have suggested that the failure on the part of other investigators to detect this phenomenon is to be ascribed to an insufficient number of experimental points. In the course of an extended study, during the past four years, of the adsorption isotherms of hydrogen, nitrogen and carbon monoxide by nickel, copper and iron, at pressures up to one atmosphere and at temperatures which cover the range,  $-200$  to  $+200^{\circ}$ , we have found a considerable number of discontinuous isotherms, and have studied them in some detail, particularly from the standpoint of the effects produced by temperature and the presence of poisons.

The evidence now available points clearly to the conclusion that a step-wise increase of adsorption with pressure is a general characteristic of the physical, or "secondary," type of adsorption. There is no evidence that discontinuities ever occur in "chemical" adsorption. The steps have been found under conditions which preclude the existence of liquid films or of multimolecular layers of gas; further, the phenomenon appears to have no direct relation to the "active spots" of catalytic theory.

We have been led to advance a new hypothesis of physical adsorption, according to which the observed steps represent the formation of concentric rows of adsorbed molecules, first at the edges of each crystal face, and building up successively toward the center. The evidence in support of this hypothesis rests primarily on the uniformity in the volumes corresponding to successive steps, and on the actual magnitude of the individual step. The mechanism by which adsorption can occur in successive rows may readily be derived on the assumptions that neighboring adsorbed molecules evaporate from the surface less readily than isolated molecules,

<sup>1</sup> Benton and White, *THIS JOURNAL*, **52**, 2325 (1930); also paper read at the Atlanta meeting of the American Chemical Society, April, 1930.

<sup>2</sup> Allmand and Burrage, *Proc. Roy. Soc. (London)*, **A130**, 610 (1931); *J. Phys. Chem.*, **35**, 1692 (1931).