

the boiling point and then shaken with hydrogen in the usual way in the presence of a platinum oxide catalyst. Hydrogen was absorbed and 50% of the theoretical yield of *p*-isopropylaminophenol was recovered from the reaction mixture.

On the other hand, it was found that a mixture of 0.05 mole of *p*-aminophenol, 3.5 moles of acetone and 0.1 g. of Adams' platinum oxide catalyst did not absorb any more hydrogen than was necessary to reduce the platinum oxide when the temperature of the reaction mixture was kept at 4–5° or at 26–32.5°. The mixture was shaken at 4–5° for one hour and at 26–32.5° for two and three-quarter hours.

It was also found that in one and one-half hours very little *p*-isopropylaminophenol was formed during the reduction of a solution of 0.05 mole of *p*-nitrosophenol in 3.5 moles of acetone in the presence of the platinum oxide catalyst at 4–5°. On the other hand, in one hour at 16–32.5° the catalytic reduction of 0.05 mole of *p*-nitrosophenol in 3.5 moles of acetone gave a 60% yield of *p*-isopropylaminophenol.

It seems fairly evident, then, that while catalytic reduction of a mixture of *p*-aminophenol and acetone at elevated temperatures will produce *p*-isopropylaminophenol, this reduction does not occur to any appreciable extent during a few hours at room temperature. However, catalytic reduction of a mixture of *p*-nitrosophenol and acetone at room temperature does give *p*-isopropylaminophenol. Accordingly, it seems most likely that *p*-hydroxyphenylhydroxylamine is formed as an intermediate during the reduction and that due to its somewhat greater activity than *p*-aminophenol it condenses with the ketone and the condensation product is in turn reduced to *p*-*sec.*-alkylaminophenol.

LABORATORY FOR PURE RESEARCH
MERCER AND CO., INC.
RAHWAY, N. J.

RANDOLPH T. MAJOR

RECEIVED JUNE 11, 1931
PUBLISHED JULY 8, 1931

AN ADSORPTION METHOD FOR THE DETERMINATION OF THE AREA OF A POWDER

Sir:

The writers have devised a simple procedure which seems to give information that is more definite with respect to the area of a fine powder than that given by any earlier method.

The powder, titanitic oxide or silicon dioxide, for example, is dried in a high vacuum at as high a temperature as can be used without affecting the area of the crystals. The cool, dry powder is immersed in a solution of oleic acid, butyric acid or some other suitable acid, in very dry benzene, and the suspension is shaken until equilibrium is attained. After the

powder has settled, a sample of the supernatant liquid is drawn off. The benzene of this sample and of a sample of the initial solution is evaporated off, if oleic acid is the solute chosen, and the oleic acid left from each solution is dissolved in 95% ethyl alcohol. The alcohol solutions are then titrated with carbonate-free sodium hydroxide dissolved in water. The difference in concentration is considered to give the amount of acid adsorbed by the surface of the powder. Only air that is thoroughly dried by phosphorus pentoxide is allowed to enter the vessel in which the solution is prepared and the flasks in which the adsorption experiments are carried out.

Figure 1 shows how the amount of oleic acid adsorbed by the surface of one gram of powder varies with the concentration of the final or equilibrium solution of oleic acid in benzene. At concentrations above 0.01 to 0.02 mole per kilogram of benzene, the adsorption becomes practically constant, and the oleic acid on the surface of the grains of powder may be said to form a condensed film. There is some evidence which seems to indicate that this film is monomolecular.

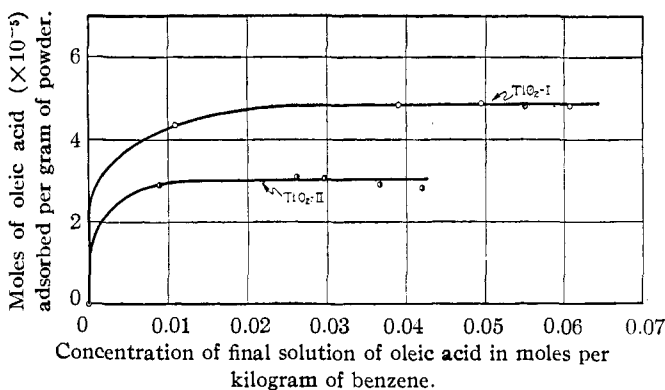


Fig. 1.

It may be assumed that the area occupied per molecule of oleic acid at the interface is 20.0 sq. Å., which is about the mean value for condensed films of the acid on water at a zero film pressure. On this basis, the area for TiO₂-I was calculated as 22.9 sq. m. per cc. of titanic oxide (3.89 grams), and for TiO₂-II as 14.4 sq. m. per cc. The ratio of these values is 1.59, while the ratio for the energy of immersion [Harkins and Dahlstrom, to be published] in ethyl acetate for the same two powders is 1.53, and the ratio of the weights of propyl alcohol adsorbed [Gans and Brooks, to be published] from the vapor per unit weight of these powders at a constant vapor pressure equal to one-half the saturation pressure at room temperature is 1.53.

The area of the powder TiO₂-II as determined for us by a microscopic

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

RECEIVED JUNE 12, 1931
PUBLISHED JULY 8, 1931

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° , it loses its water of crystallization and partially dissolves in this water. At 80° 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° 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