

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

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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).

and that physically adsorbed molecules possess mobility in the plane of the surface.

Details will follow shortly.

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### HAZARDS IN CATALYTIC HYDROGENATION AT ELEVATED TEMPERATURES AND PRESSURES

*Sir:*

T. S. Carswell [THIS JOURNAL, 53, 2417 (1931)] has reported an explosion which occurred while he was attempting to hydrogenate *o*-nitroanisole in the liquid phase with a nickel catalyst. He states that the purpose of his communication "is to call the attention of other investigators to the dangers of this type of reduction when carried out on other than a very small scale." There is no doubt that a warning is needed but in my opinion it should be against the procedure used by him and not against catalytic hydrogenation at elevated temperatures and pressures. This general method has been in successful use in this Laboratory for the past three years [THIS JOURNAL, 52, 4349, 5192 (1930); 53, 1091, 1095, 1402, 1425, 1868, 2012 (1931); *J. Phys. Chem.*, 35, 1684 (1931)] using a wide variety of compounds and dealing with quantities similar to those used by Dr. Carswell. The procedure used by him is, in my opinion, ill-advised in several respects. The bomb was inadequate and sufficient information was not available to him before the attempt was made to hydrogenate 400 g. of nitroanisole. A bomb for experimental purposes 15 cm. in diameter should have a wall thickness several times as great as that (5 mm.) used by Carswell. Our own bombs have a wall thickness of 2 to 2.5 cm. and are only 6 cm. in internal diameter. They were bored out of properly annealed rolls of nickel-chromium steel [*cf.* Ernst, *Ind. Eng. Chem.*, 18, 664 (1926)]. In order to control the rate of hydrogenation it is important that the bomb be provided with a thermometer or thermocouple well, so designed that there is little lag between the actual temperature of the liquid contents of the bomb and the reading of the temperature measuring device.

The temperature and amount of catalyst used by Carswell were excessively high for the compound to be hydrogenated, and apparently he made no attempt to control the rate of hydrogenation by control of the rate of shaking of the bomb. The reactions are quite exothermic and would result in local superheating if heat was being liberated more rapidly than it could be dissipated. In the hydrogenation of 100 g. of toluene with less than 0.5 g. of nickel, for example, we have observed a temperature rise of as much