Dec., 1935

Sir:

obtained, to the liquefaction pressure  $P_s$  of the gas at temperature T. Nitrogen isotherms for the above two temperatures have also been obtained for a pure iron and a doubly promoted iron catalyst. In all of these cases the adsorption of a given gas on a particular catalyst at two or more temperatures could be represented by a single potential curve of the type shown in Fig. 2.

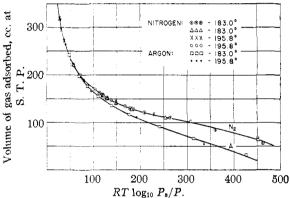


Fig. 2.—Potential-volume curves for the adsorption of nitrogen and argon on a single promoted iron synthetic ammonia catalyst.

The potential plots seem to represent the isotherms very closely throughout the entire pressure range covered, including: (a) the region concave to the pressure axis where probably less than a molecular layer of gas exists, (b) the linear portion which we have postulated represents the building up of a second layer of gas on the catalyst surface [THIS JOURNAL, 57, 1754 (1935)], and (c) the higher pressure portion which is convex to the pressure axis and which, it is generally believed, represents the condensation of the gas to liquid in the capillaries of the adsorbent. The inclusion of this last region in the portions represented by the potential theory is rather unexpected since the theory was not intended to include such capillary condensations.

One other characteristic of the potential curves is worth noting. Polanyi and Goldman found that for their data the adsorbed mass-potential plots did not coincide at different temperatures, the higher temperature curves being slightly below the lower temperature curves in every case. They explained this displacement by postulating constancy of adsorption volume and thermal expansion of the adsorbed gas, so that less gas was required to fill the adsorption volume at higher temperatures than at lower. As shown in Fig. 2 our potential curves exhibit no such variation with temperature, the -183 and  $-195.8^{\circ}$  points falling on the same curve. The significance of this result is not certain as yet.

BUREAU OF CHEMISTRY AND SOILS P. H. EMMETT U. S. DEPARTMENT OF AGRICULTURE STEPHEN BRUNAUER WASHINGTON, D. C.

**RECEIVED NOVEMBER 1, 1935** 

## THE AUTO-OXIDATION OF KETONES

Several ketones of the type R'COCH<sub>2</sub>R

(R = phenyl) on standing in the presence of light and air for varying periods of time were observed to acquire an aldehyde-like odor. On further investigation it was found that an acid R'COOH and an aldehyde RCHO could be isolated.

Benzyl-2-chlorophenyl ketone, which is a liquid [Jenkins and Richardson, THIS JOURNAL, 55, 1618 (1933)] on standing slowly solidifies and acquires a strong odor of benzaldehyde. The solid is shaken up with dilute sodium carbonate solution and extracted with ether. The aqueous layer is acidified with hydrochloric acid and 2chlorobenzoic acid is obtained. The ether is distilled and the oil which remains is steam distilled. The distillate is treated with phenylhydrazine acetate and benzalphenylhydrazone is obtained. The solid gives a strong peroxide reaction using the test of Kharasch [Kharasch, McNab and Mayo, *ibid.*, 55, 2523 (1933)].

The course of the reaction may be illustrated as

$$\begin{array}{ccc} R'COCH_2R \longrightarrow R'C(OH) = CHR \xrightarrow{O_2} \\ & & & \\ & \\ & &$$

These reactions are being fully investigated and the results will be reported later.

THE CHEMISTRY DEPARTMENT OF SANFORD S. JENKINS THE JOHNS HOPKINS UNIVERSITY BALTIMORE, MARYLAND

RECEIVED OCTOBER 24, 1935

CHEMICAL STUDIES ON TOAD POISONS. VIII. THE DEHYDROGENATION OF CINOBUFAGIN

Sir:

In our investigation of the chemical relationship of the bufagins (cardiac principles present in toad secretions) to the cardiac plant aglucones, possessing similar pharmacological and chemical properties, and to the sterols, it seemed of in-