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.

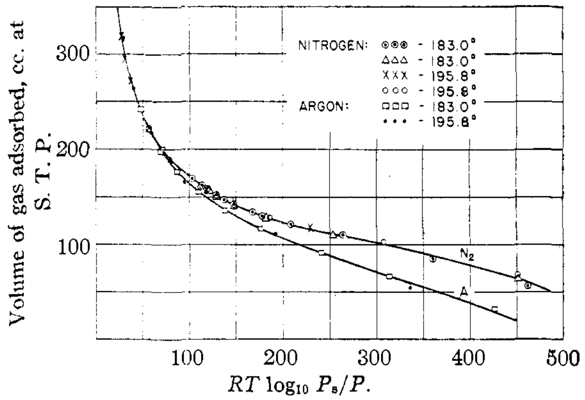

Fig. 2.—Potential–volume curves for the adsorption of nitrogen and argon on a single promoted iron synthetic ammonia catalyst.

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° points falling on the same curve. The significance of this result is not certain as yet.

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RECEIVED NOVEMBER 1, 1935

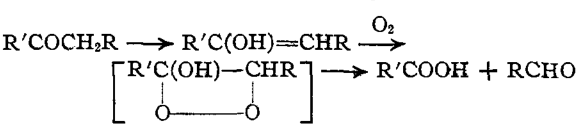
THE AUTO-OXIDATION OF KETONES

Sir:

Several ketones of the type $R'COCH_2R$ (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 2-chlorobenzoic 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



$$R'COCH_2R \longrightarrow R'C(OH){=}CHR \xrightarrow{O_2} \left[\begin{array}{c} R'C(OH)\text{—}CHR \\ |\qquad\quad | \\ O\text{———}O \end{array}\right] \longrightarrow R'COOH + RCHO$$

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

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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 interest to ascertain whether the bufagins, on dehydrogenation with selenium, would yield methylcyclopentenophenanthrene. The formation of this hydrocarbon, $C_{18}H_{16}$, is generally considered a characteristic of the sterol ring system. Cinobufagin, $C_{25}H_{32}O_6$ [Jensen and Evans, *J. Biol. Chem.*, **104**, 307 (1934)] (the analytical data obtained for cinobufagin and certain of its derivatives would also agree with $C_{26}H_{34}O_6$ [Crowfoot, *Chem. and Ind.*, **54**, 568 (1935)]), was therefore subjected to dehydrogenation by the procedure of Diels [Diels, Gaedke and Koerding, *Ann.*, **459**, 1 (1927)]. As only a limited amount of material was available for this study, and losses were involved in the separation of compounds closely related chemically, the quantity of the hydrocarbon finally obtained was so small that a complete characterization was impossible. From the mixture of the reaction products about 10 mg. of a hydrocarbon fraction was secured which melted at 120–121°. This hydrocarbon is believed to be identical with methylcyclopentenophenanthrene. Its analytical data agree with the formula $C_{18}H_{16}$, and on mixing it with methylcyclopentenophenanthrene obtained by Elderfield and Jacobs [*J. Biol. Chem.*, **107**, 143 (1934)] by dehydrogenation of strophanthidin, no melting point depression was observed. It appears, therefore, that cinobufagin and probably also the various other bufagins contain the same ring system as the cardiac plant aglucones and the sterols. After completing this work, a paper by Ikawa [*J. Pharm. Soc. Japan*, **55**, 144 (German abstract), 748 (original Japanese) (1935)] appeared, in which he reports the isolation of the Diels hydrocarbon $C_{18}H_{16}$ from the dehydrogenation mixture of ψ-bufotaline. In this connection it might be mentioned that Wieland and Hesse [*Ann.*, **517** 22 (1935)] recently have obtained a hydrocarbon from the dehydrogenation mixture of bufotaline which they believe to be identical with chrysene. Investigations are now in progress to determine, in the bufagins, the exact nature of the side chain which contains the lactone ring.

Five grams of cinobufagin, dried at 110° *in vacuo*, was mixed with 6 g. of selenium and heated in a flask with a glass joint ascending tube for thirty-five hours at 310–320° and then for ten hours at 320–340°. The reaction mass was extracted with ether and the residue from evaporation of the solvent was subjected to fractional distillation at 12 mm. The fraction distilling at 200–230° was semi-crystalline and was fractionally recrystallized from alcohol according to the triangle scheme. After numerous crystallizations a hydrocarbon fraction was secured which melted at 120–121° and showed a m. p. of 121–122° when mixed with methylcyclopentenophenanthrene (m. p. 123–124°) prepared from strophanthidin (Elderfield and Jacobs). *Anal.* (by Dr. Ing. A. Schoeller, Berlin-Schmargendorf, Germany). Calcd. for $C_{18}H_{16}$: C, 93.05; H, 6.95. Found: C, 92.81; H, 6.82.

The author is greatly indebted to Dr. W. A. Jacobs, of the Rockefeller Institute for Medical Research, New York, for a sample of methylcyclopentenophenanthrene, and would like also to express his thanks to Dr. K. K. Chen, Lilly Research Laboratories, Indianapolis, for a supply of an extract of Ch'an Su.

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RECEIVED NOVEMBER 22, 1935

THE COLLAPSE OF MONOMOLECULAR FILMS OF PALMITIC ACID UPON ACID SOLUTIONS

Sir:

When monomolecular films of palmitic acid were compressed on very pure hydrochloric acid or phosphate buffer solutions contained in a Langmuir film-pressure trough, in the range 15–20°, it was noticed that after each increment of weight had been placed in the balance pan, and the barrier advanced to establish equilibrium, a slow shrinkage followed, the area, however, finally attaining a value which was reproducible to a high degree. When the compression was carried out in this manner, with an attempt to obtain "equilibrium areas" at every point of the force–area curve, the films collapsed at a pressure apparently connected with the hydrogen-ion concentration (*i. e.*, the films could be compressed without limit when a definite pressure was reached, the value of which has been called the "collapse pressure" in the literature). When the collapse pressure values were plotted against *p*H values of the substrate (which varied from *p*H 1 to *p*H 6) an S-shaped curve resulted, similar to the percentage neutralization curve in the case of a weak organic acid in water solution. However, the mid-point of this curve was about *p*H 3, as compared to *p*H 5, the