Substance	M. p., °C.	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found
2-Acetyl-9,10-dihydrophenanthrene	51–52	$C_{16}H_{14}O$	86.44	86.77	6.35	6.64
-Oxime	146–147.5	$C_{16}H_{15}NO$	80.97	80.61	6.38	6.43
-Semicarbazone	236–237	$C_{17}H_{17}N_3O$	73.07	73.05	6.14	6.14
9,10-Dihydro-2-bromoacetylphenanthrene	93.5–95	$C_{16}H_{13}BrO$	63.78	63.71	4.35	4.49
9,10-Dihydrophenanthrene-2-carboxylic acid	211.5–212.5	$C_{15}H_{12}O_2$	80.32	80.34	5.39	5.42
-Methyl ester	Oil	$C_{16}H_{14}O_2$	80.63	80.50	5.93	5.66
2-Acetyl-9,10-phenanthrenequinone	223–224	$C_{16}H_{10}O_3$	76.78	76.67	4.03	4.36

compound thus obtained is sufficiently pure for the reactions described below. After further purification, the 9,10-dihydrophenanthrene melted at 31–32° and showed n^{25}_D 1.6464 [*cf.* Schroeter, *Ber.*, **62**, 645 (1929)].

In the Friedel–Crafts reaction, which proceeds equally well in carbon disulfide or nitrobenzene, only one acetyl compound is formed (purified through the semicarbazone, yield, about 90%). The acetyl group enters the 2-position of the dihydrophenanthrene, which resembles in respect to this reaction diphenyl rather than phenanthrene. Structural proof: (A) acetyldihydrophenanthrene $\xrightarrow{CrO_3}$ 2-acetyl-9,10-phenanthrene quinone; (B) acetyldihydrophenanthrene $\xrightarrow{NaOCl}$ dihydrophenanthrene carboxylic acid $\longrightarrow$ methyl ester $\xrightarrow[20\text{ hrs., }300°]{Se}$ phenanthrene-2-carboxylic acid.

We intend to study substitution products of 9,10-dihydrophenanthrene prepared either by introducing substituents into dihydrophenanthrene or by partial hydrogenation of substituted phenanthrenes. We are interested in particular in the synthesis of compounds with nitrogen-containing side chains and rings similar to the phenanthrene and dibenzofuran derivatives previously described from this Laboratory. The preference shown by the acetyl group for position 2 (and this will undoubtedly hold true for similar substituents) makes starting materials for the synthesis of substances related to sterols and sex hormones easily accessible.

Anthracene, submitted to high pressure hydrogenation with copper chromite, is reduced nearly quantitatively to 9,10-dihydroanthracene. In this case the reduction is completed at a considerably lower temperature (160°) within a few hours. This demonstrates again the marked difference between the reactivities of the meso-positions in anthracene and phenanthrene, respectively.

COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
UNIVERSITY, VA.

ALFRED BURGER
ERICH MOSETTIG

RECEIVED NOVEMBER 23, 1935

THE APPLICATION OF POLANYI'S POTENTIAL THEORY TO THE VAN DER WAALS ADSORPTION OF GASES ON IRON SYNTHETIC AMMONIA CATALYSTS

Sir:

Polanyi's "potential theory" of gas adsorption by solids [*Verhandl. deut. phys. Ges.*, **18**, 55 (1916)] in its original form was interpreted in terms of a postulated thick film of compressed or liquefied gas on the surface of the solid. In 1928 Polanyi and Goldman [*Z. physik. Chem.*, **132**, 321 (1928)] pointed out that the theory can be applied to adsorption in monomolecular layers. Thus far the theory has been applied exclusively to the adsorption of organic vapors, carbon dioxide and sulfur dioxide on amorphous adsorbents like charcoal and silica gel. The present communication shows the applicability of the theory to some low temperature isotherms that we have been obtaining on iron catalysts.

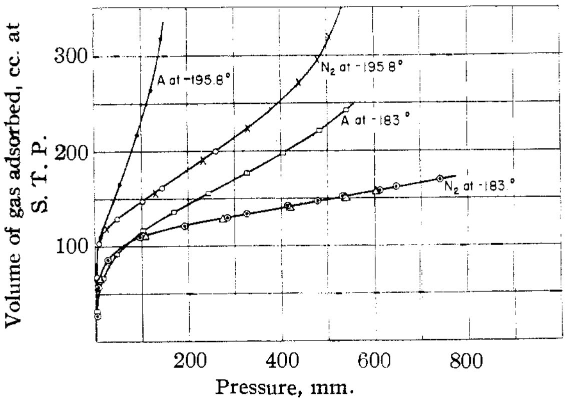


Fig. 1.

Figure 1 shows isotherms obtained for argon and nitrogen on a 25-cc. sample (43.6 g. of iron) of a singly promoted (10.2% Al_2O_3) iron synthetic ammonia catalyst at −183° and −195.8°. These adsorption data plotted according to Polanyi's theory are shown in Fig. 2. As abscissas are plotted $RT \log_{10}P_s/P$; these abscissa values when multiplied by 2.303 give the free energy of compression of the gas from the pressure P, at which a particular adsorption point is 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.

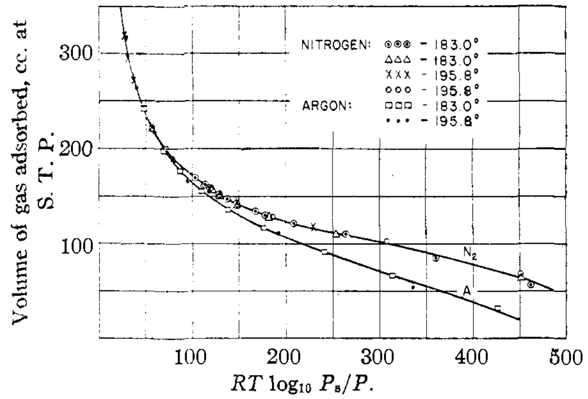


Fig. 2.—Potential–volume curves for the adsorption of nitrogen and argon on a single promoted iron synthetic ammonia catalyst.

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.

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

RECEIVED NOVEMBER 1, 1935

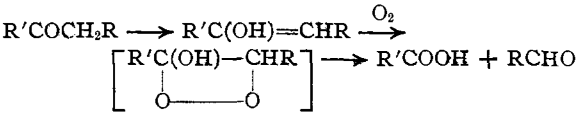
THE AUTO-OXIDATION OF KETONES

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



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

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-