COMMUNICATIONS TO THE EDITOR

THE RELATIVE ATOMIC WEIGHT OF OXYGEN IN WATER AND IN AIR

Sir:

Washburn, Smith and Smith [*Bur. Standards J. Res.*, **13**, 599 (1934)] burned oxygen and hydrogen from an electrolytic cell separately with "normal" hydrogen and oxygen, respectively, obtaining in the first fraction a difference of density in p. p. m., γ, between these waters and normal water -13.2 for the cell oxygen plus "normal" hydrogen and -7.8 for the cell hydrogen plus atmospheric oxygen. The cell hydrogen and oxygen burned together gave water of γ value, -20.5, approximately the sum of the first two data. A little reflection will show that if this work is correct, there is no difference between the atomic weight of oxygen in air and in water. Unfortunately it now appears that due to an unlucky compensation of effects this agreement is merely a coincidence and that there is a significant difference in the atomic weight of oxygen from the two sources.

I have electrolyzed water made from tank hydrogen and Linde oxygen (whose atomic weight in reference to atmospheric oxygen was corrected for) and burned the oxygen with tank hydrogen. Two electrolyses gave γ equal to -6.9 for this water. Two electrolyses of normal water, followed by combustion of the oxygen with the same tank hydrogen gave water having a γ value of -11.5; the difference between the results is 4.6, from which the atomic weight of oxygen in the air can be calculated to be 16.00008 if the atomic weight of oxygen in Lake Michigan water is 16.00000.

Understanding this fact makes easy the explanation of several anomalous and unexplained results of other workers. In the work of Washburn mentioned above neither his tank hydrogen nor his oxygen was "normal," *i. e.*, had the same atomic weight as the two elements in water, the hydrogen being too light and the oxygen too heavy. It is also clear why Washburn, Smith and Smith's conclusion that the oxygen isotopes fractionate more rapidly than those of hydrogen on electrolysis is erroneous. Greene and Voskuyl's [THIS JOURNAL **56**, 1649 (1934)] anomalous find-

ing that tank hydrogen burned with air resulted in water denser than normal is explained, and the results of W. Heinlen Hall and Johnston [THIS JOURNAL, **57**, 1515 (1935)] indicating that the isotopes of hydrogen fractionate on combustion will now have to be largely modified. The increase in density of water obtained by myself and many others in the combustion of organic substances will have to be reinterpreted.

Incidentally the data reported here confirm the prediction of Urey and Greiff [THIS JOURNAL, **57**, 321 (1935)] that when water and oxygen are brought into equilibrium, the O^{18} concentrates in the oxygen, and the conclusion that it is meaningless to express the atomic weight of oxygen to more than four decimal places.

It is hoped to repeat more accurately the experimental work described in this paper.

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          RECEIVED NOVEMBER 18, 1935

THE PREPARATION OF 9,10-DIHYDROPHENAN- THRENE AND ITS DERIVATIVES

Sir:

The selective activity of copper–chromium–barium oxide catalyst permits the expectation that in phenanthrene only, or chiefly the 9,10-double bond, which in some respects exhibits a decidedly olefinic character, would be saturated by hydrogenation in the presence of this catalyst.

Phenanthrene, purified according to Cohen and Cormier [THIS JOURNAL, **52**, 4363 (1930)] and treated with, and distilled over sodium, was dissolved in 2 to 3 parts of absolute alcohol and mixed with about 10% (by weight) of catalyst 37 KAF [Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932)]. The hydrogenation was carried out at pressures from 2000 to 4000 lb./sq. in., maintaining a temperature of 220° for twenty-four to thirty-six hours. After separating from the reaction mixture 10 to 20% of unchanged phenanthrene (as the picrate), 60 to 80% of crude 9,10-dihydrophenanthrene was obtained (after distillation *in vacuo*). No tetrahydro- or octahydrophenanthrene could be detected. The

Substance	M. p., °C.	Formula	C, % Calcd.	Found	H, % Calcd.	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 ⟶ methyl ester $\xrightarrow[20\ hrs.,\ 300°]{Se}$ 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.

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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.
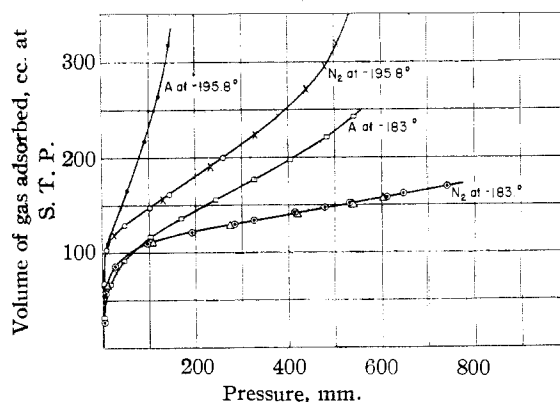

Fig. 1.

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.
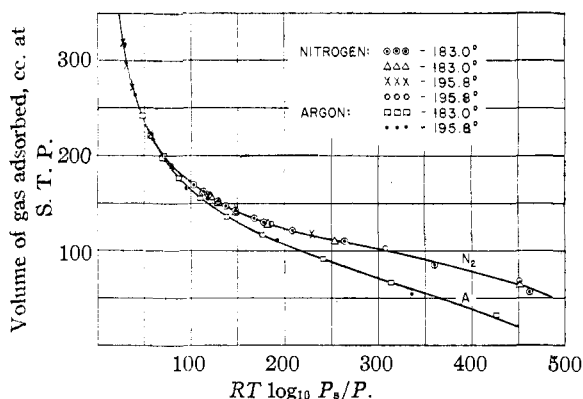

Fig. 2.—Potential-volume curves for the adsorption of nitrogen and argon on a single promoted iron synthetic ammonia catalyst.

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
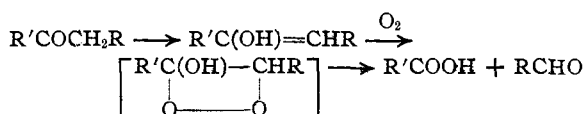U. S. DEPARTMENT OF AGRICULTURE   STEPHEN BRUNAUER
WASHINGTON, D. C.

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

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

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

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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-

terest 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, $C_{26}H_{32}O_6$ [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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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 pH values of the substrate (which varied from pH 1 to pH 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 pH 3, as compared to pH 5, the

mid-point of neutralization curves of fatty acids. Since the variation of collapse pressure with pH may be considered as related to neutralization, this appears to be evidence of increased activity of palmitic acid when oriented on a water surface.

The collapse pressure was specific for hydrogen ions alone, although increased spread at low pressures was noticed when calcium or magnesium ions were present in the hydrochloric acid solution. A specific effect, in causing what may be either collapse or solution of the film at room temperatures, has been noticed in the case of neutral potassium permanganate solutions. This was not noticed with hydrogen peroxide, potassium ferricyanide or potassium dichromate solutions.

In view of the work of Cary and Rideal [Proc. Roy. Soc. (London), A109, 301 (1925)] on the spreading of fatty acid crystals on acid solutions, which indicates that many of the films should be thermodynamically unstable above 8 dynes, in the neighborhood of 20°, work is now in progress on a repetition of the above studies, using mixtures of higher hydrocarbons, such as tetradecane, with palmitic and other acids, to determine whether this relation between collapse pressure and hydrogen-ion concentration holds for an interface where the acid film may collapse in a reversible manner. It is planned further to apply thermodynamic interpretation, such as Harkins' spreading coefficient to the collapse phenomena. The results with the monomolecular films alone will be reported more fully in the near future, together with those obtained with mixed films.

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          RECEIVED OCTOBER 17, 1935

THE ACTIVATION OF SPECIFIC BONDS IN COMPLEX MOLECULES AT CATALYTIC SURFACES

Sir:

It has now become possible to examine the activation of specific bonds in complex molecules at catalytic surfaces, a fundamental problem in surface catalysis, that of specificity. We shall illustrate a method capable of quite general applicability by a specific example, that of the molecule ethane. In this we are concerned with two types of bond, the C–C and the C–H bond. We have followed the activation of these bonds on an active nickel surface by the study of the two reactions (a) the exchange reaction $C_2H_6 + mD_2 \longrightarrow$

$C_2H_xD_y$ where $x + y = 6$ and m may be varied arbitrarily; (b) $C_2H_6 + H_2 = 2CH_4$. The former involves only the C–H, the latter the C–C bond, the other reactant in each case being hydrogen (or deuterium) adsorbed on the surface in the activated form. We find that, on this catalyst, the exchange reaction proceeds quantitatively at 138° under conditions in which reaction (b) is quite negligible. The production of methane sets in, under our conditions about 150° and is sensibly complete around 200°. We thus define the temperature, catalyst and reactant concentration conditions necessary to activated adsorption of ethane molecules producing either the C–H or the C–C bond split or both. By extension of these studies to other catalyst surfaces, to molecules which contain a wide variety of other bonds, e. g., O–H, N–H, C–O, C–N, etc., and to varied operating conditions we plan to determine in detail the factors which produce specific activity of catalysts in general.

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PRINCETON, N. J.   W. S. BENEDICT
          RECEIVED NOVEMBER 8, 1935

SYNTHESIS OF DEUTERO-ACETALDEHYDE

Sir:

By absorbing deutero-acetylene in an acid solution of mercury salts in deuterium oxide we have succeeded in synthesizing deutero-acetaldehyde. About 25 cc. have been prepared so far. The aldehyde freed from deuterium oxide by repeated distillations at low temperatures is a colorless mobile liquid. Preliminary determinations indicate a vapor pressure of 327 mm. at 0°. It shows the usual aldehyde reactions: reducing ammoniacal silver solutions, forming a white crystalline compound with ammonia and a phenylhydrazone with phenylhydrazine.

The D_2O used in generating the acetylene and in the absorbing solution was 99.6% pure. The burning of about 2 cc. of the aldehyde over copper oxide in a current of oxygen gave D_2O of 99.2% purity, both values determined by the interferometer method.

The determination of the physical constants of this compound as well as its chemical properties is proceeding in this Laboratory.

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          RECEIVED OCTOBER 23, 1935