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 finding 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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THE PREPARATION OF 9,10-DIHYDROPHENANTHRENE 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, %		H, %	
			Calcd.	Found	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 $\longrightarrow$ methyl ester $\xrightarrow[\text{20 hrs., 300°}]{\text{Se}}$ 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.

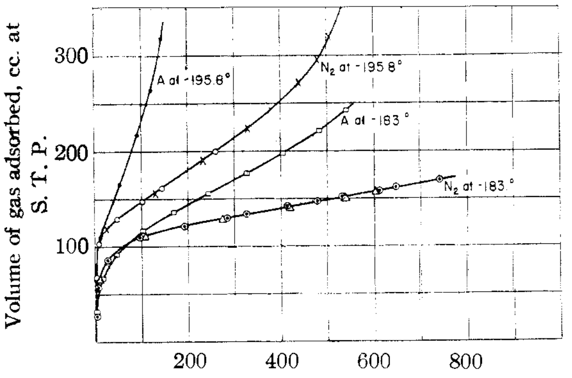

Fig. 1.

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