COMMUNICATIONS TO THE EDITOR

THE USE OF VAN DER WAALS ADSORPTION ISOTHERMS IN DETERMINING THE SURFACE AREA OF IRON SYNTHETIC AMMONIA CATALYSTS

Sir:

In an endeavor to obtain an estimate of the extent of the surface of an iron synthetic ammonia catalyst, we have determined the low temperature van der Waals adsorption isotherms for nitrogen at −195.8 and −183°; oxygen, carbon monoxide, and argon at −183°; carbon dioxide at −78.5° and normal butane at 0°. The pure iron catalyst (46.2 g.) had been sintered at 500° to a constant and reproducible adsorptive capacity. The results are so striking that we are submitting a portion of them in the present communication.

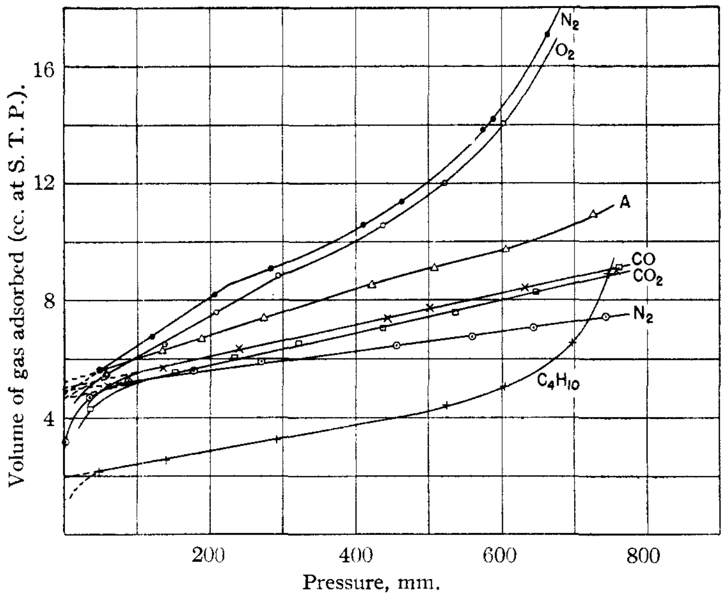


Fig. 1.

The isotherms (Fig. 1) of each gas except butane when extrapolated back to zero pressure from the linear portion of the curves lying between about 60 mm. and 250 to 760 mm. intercept the ordinate at about the same value of gas adsorbed, 4.9 ± 0.2 cc.; the butane isotherm has the intercept at 2.0 cc. In the case of both oxygen and carbon monoxide the van der Waals isotherms were obtained after first saturating the catalyst with the activated adsorption at −78° for carbon monoxide and at −183° for oxygen and then evacuating with a diffusion pump for about one-half hour at these respective temperatures.

For a number of reasons it seems likely that the linear portion of each isotherm extending from about 60 mm. to 250 mm. or higher pressures corresponds to the building up of a second layer of adsorbed molecules on the surface of the catalyst. If this be the case, the extrapolation to zero pressure should indicate the volume of gas needed to form a monomolecular layer upon the catalyst. Proceeding on this assumption we have calculated the area of the catalyst surface as judged by each of the isotherms of Fig. 1. The results are summarized in Table I. Assuming close packing of the adsorbed molecules one calculates the unweighted mean value of the catalyst surface to be 17.6 square meters if the molecular diameters are those gotten from the densities of solidified gases (S^*) and 20.6 square meters if the diameters are those obtained from the densities of the liquefied gases (L^*).

The agreement among the values for the surface area is surprisingly good. Furthermore, the areas here calculated are consistent with those deduced from as yet unpublished data on the activated adsorption of carbon monoxide and hydrogen on this same sample of catalyst. It therefore seems that the determination of van der Waals adsorption isotherms of gases close to their boiling points affords a convenient method for measuring the extent of surface of iron synthetic ammonia catalysts. Further work is in progress to determine how

Table I

Gas adsorbed	Temp. of isotherm. °C.	B. p. of gas, °C.	Extrap. zero press. intercept, v_0, cc.	Calcd. area of catalyst S^*	L^*
N_2	−183	−195.8	4.9	18.3	22.5
N_2	−195.9	−195.8	4.8	17.9	21.0
CO	−183	−192.0	5.0	18.5	21.5
A	−183	−185.7	5.2	18.0	20.3
O_2	−183	−183.0	4.7	15.4	17.9
CO_2	− 78.5	− 78.5	4.7	17.9	23.4
n-C_4H_{10}	0.0	− 0.3	2.0	17.3	17.3

generally the method may be used for measuring the surfaces of other catalytic materials.

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

RECEIVED APRIL 3, 1935

THE DIPOLE MOMENT OF ETHYL BENZOATE

Sir:

Recently Svirbely, Ablard and Warner [THIS JOURNAL, **57**, 652 (1935)] have determined the dipole moments of methyl and ethyl benzoates. They found for solutions of the normal concentrations (0.013 to 0.017) the values 2.01 and 2.14, respectively, using lower concentrations too (down to 0.000669) still higher figures (2.52 and 2.43). Even the former values are decidedly higher than the figures reported before in the literature [Estermann, *Z. physik. Chem.*, **B1**, 134, 424 (1928)] and higher than the values we have obtained in the case of ethyl cinnamate (1.84) and similar compounds, the dipole moments of which will be published shortly elsewhere [*J. Chem. Soc.*, in press (1935)]. We have therefore redetermined the dipole moment of ethyl benzoate in benzene solution (24.6°) and again found the moment to be 1.91. Some of our figures may be quoted (c molar fraction, $\overline{M}$ average molecular weight, ρ density, ϵ dielectric constant, η refractive index, determined on the solution, $P_{1/2}$ and $P_{E1/2}$ total and electronic polarization for the solution, P and P_E the same for the solute, P_0 orientation polarization).

c	0	0.02178	0.03648
$\overline{M}$	78	78.568	80.627
ρ	0.8732	0.8780	0.8813
ϵ	2.2747	2.3866	2.4601
n^2	2.2410	2.2410	2.2410
$P_{1/2}$	26.637	28.646	29.951
$P_{E1/2}$	26.118	26.497	26.750
P	...	118.88	117.48
P_E	...	43.52	43.46
P_0	$->$	75.36	74.02

$P_0^\infty = 75.5$ cc. $\mu = 1.91\ D$

The dipole moment of methyl benzoate should hardly show any deviation from that value. We may suggest that the method adopted by the above authors is inadequate since they report at the same time for the hydrocarbons limonene and *d*-pinene dipole moments as high as 0.70 and 1.10 (ordinary concentration), 1.50 and 2.67 (using low concentrations too), against the value of about zero to be expected theoretically.

THE DANIEL SIEFF RESEARCH ERNST BERGMANN
INSTITUTE, REHOVOTH, PALESTINE ANNA WEIZMANN

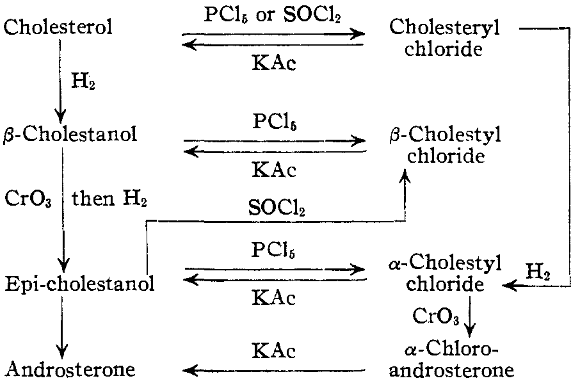
RECEIVED JULY 18, 1935

ANDROSTERONE

Sir:

In the preparation of androsterone in quantity from cholesterol by Ruzicka's method [*Helv. Chim. Acta*, **17**, 1389 (1934)] difficulty is experienced in the conversion of cholesterol into epi-cholestanol in large amounts. This reaction requires two catalytic reductions and an oxidation, which due to the small solubility of the compounds and the large amount of platinum oxide catalyst necessary is very expensive and time consuming. To overcome this, advantage is taken of the following reactions to produce the epi-form of androsterone and other sterols.

TABLE I



When cholesterol is treated with either phosphorus pentachloride or thionyl chloride, cholesteryl chloride is produced. This on reduction with platinum catalyst gives α-cholestyl chloride. This reduction can be carried out in quantity, fifty grams being reduced completely by 2 g. of catalyst in 500 cc. of ether in fifteen minutes. When beta-cholestanol is treated with phosphorus pentachloride, beta-cholestyl chloride is produced, whereas if treated with thionyl chloride α-cholestyl chloride is the product, one case giving a Walden inversion. The same is true for epi-cholestanol. This with phosphorus pentachloride gives α-cholestyl chloride and with thionyl chloride gives beta-cholestyl chloride.

If cholesteryl chloride is hydrolyzed with potassium acetate it gives cholesterol, whereas if