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.
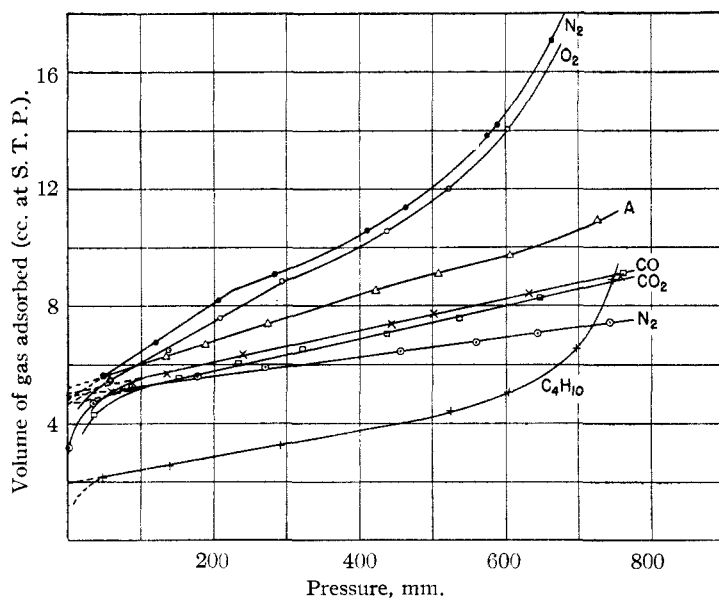

Fig. 1.

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^*
N₂	-183	-195.8	4.9	18.3	22.5
N₂	-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
O₂	-183	-183.0	4.7	15.4	17.9
CO₂	-78.5	-78.5	4.7	17.9	23.4
n-C₄H₁₀	0.0	-0.3	2.0	17.3	17.3

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

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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

$$P_0^{\infty} = 75.5 \text{ cc.} \qquad \mu = 1.91\,D$$

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
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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 epicholestanol 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
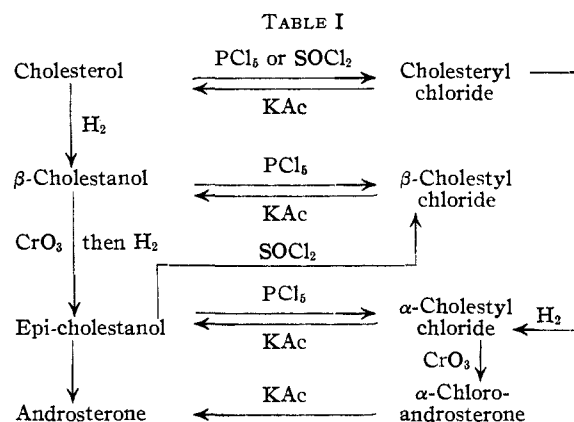
When cholesterol is treated with either phosphorus pentachloride or thionyl chloride, cholesteryl chloride is produced. This on reduction with platinum catalyst gives α-cholestyl chloride. This reduction can be carried out in quantity, fifty grams being reduced completely by 2 g. of catalyst in 500 cc. 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 epicholestanol. 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

cholesteryl chloride is reduced to α-cholestyl chloride and this is hydrolyzed it gives epicholestanol. In the preparation of cholesteryl chloride and its hydrolysis there is no Walden inversion in the final product, but when this is reduced and then hydrolyzed a Walden inversion occurs in one of the steps.

When α-cholestyl chloride is oxidized, α-chloroandrosterone is formed which is identical with the product produced by Butenandt and Dannenbaum [Z. physiol. Chem., 229, 192 (1934)] by the reduction of an unsaturated chloroketone isolated from urine. This α-chloroandrosterone when hydrolyzed with potassium acetate gives androsterone. This work was completed several months ago, but since Ruzicka and co-workers [Helv. Chim. Acta, 18, 998 (1935)] have recently prepared α-chloroandrosterone from epi-cholestanol, it was thought advisable to publish our results in brief form since the new method possesses distinct practical advantages for producing androsterone. The experimental work and androsterone derivatives and their physiological properties will be reported in THIS JOURNAL at a later date.

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            RECEIVED JULY 30, 1935

THE SEPARATION OF EUROPIUM FROM OTHER RARE EARTHS

Sir:

The writer has lately isolated considerable quantities of quite pure europium by a process which seems to be simpler than any heretofore described. He has found that if 2 or 3 ml. of a rather concentrated solution of rare earth chlorides is stirred with a pinch of zinc dust it will bleach a piece of blue litmus paper; instantly if much europium is present and definitely if even a small fraction of one per cent. of the rare earths is europium. The bleaching is caused by the europous chloride, $EuCl_2$, formed by the action of zinc on the trichloride.

This reaction serves not only for the detection of europium but leads to a simple and rapid means of separating europium from the accompanying rare earths. If a rather concentrated solution of the chlorides of the rare earths, acidulated with a little acetic acid, is run through a column of amalgamated zinc, substantially in the form of a Jones reductor such as is used in the analysis of iron, practically complete reduction of the europium present takes place.

The writer has used a 30-cm. column of twenty to thirty mesh zinc in a tube 1.7 cm. in diameter. The reduced solution was run into a bottle containing a solution of magnesium sulfate with an atmosphere of carbon dioxide present to prevent oxidation by air. The europous sulfate thus obtained is a white microcrystalline precipitate of a high degree of purity. One or two repetitions of the reduction and precipitation by the same process frees the europium from all traces of the other rare earths.

A quantitative determination of europium is easily made by running a reduced solution into a small excess of standard iodine solution and titrating the excess iodine with thiosulfate.

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            RECEIVED AUGUST 15, 1935