[Contribution from the Laboratory of Physical Chemistry, University of Cambridge]

THE DECOMPOSITION OF ETHYL ALCOHOL AT THE SURFACE OF THORIA. II. ADSORPTION ON THE THORIA CATALYST

By G. I. Hoover[1] and E. K. Rideal

Received October 20, 1926 Published January 11, 1927

In a previous communication[2] it was shown that ethyl alcohol underwent two types of decomposition at the surface of thoria. Also from the fact that the surface of the catalyst could be selectively poisoned, it was believed that the active patches promoting these reactions differed in their adsorptive powers, at least towards certain substances. Since these active patches represent, in all probability, but a small fraction of the total surface and since, as was shown in Part I, the active areas become bare only at low pressures even at high temperatures—6 mm. at 328°, to detect any difference between the adsorptive powers of the active and inactive areas of the catalytic surface from a study of adsorption, it must be looked for at low pressures. Even in this region, detection of differences in adsorption will depend on the relative magnitudes of the active and inactive adsorptions and upon the nature of the equilibrium between them.

The present investigation of the adsorption of gases and vapor on thoria was carried out with special reference to the low-pressure adsorption.

Apparatus

The apparatus used in the adsorption determinations is shown in Fig. 1.

Essentially it consists of two bulbs, C and D, of about the same size, 25 cc., joined by means of capillary tubing through the tap T_1. The catalytic material is placed in the bulb C. Capillary tubing also leads to the manometer G. The manometer is a constant-level type. The level of the mercury in the left arm of the manometer is adjusted to a glass pointer k by moving the reservoir R and finally by manipulating the screw clips C′ and C″. This setting could be made to 0.1 mm. A Torricellian vacuum is maintained in the right arm by occasionally running the mercury over through the capillary overflow tube L. Pressures were read on a glass scale ruled on both sides to avoid parallax, to 0.1 mm. by means of an eye lens. The system could be evacuated through the tap T_2 by means of a mercury-diffusion pump and a Fleuss pump. A phosphorus pentoxide tube S and a liquid-air trap are inserted in the pump line. A by-pass X is used to facilitate evacuation of the bulb C. Thermostating at 100° was effected by means of a steam jacket, at 0° by a bath of melting ice, and at other temperatures by a water thermostat. Temperatures are read on a mercury thermometer T. Gases for adsorption were admitted from the tube W through the two-way tap T_1, and vapors from the reservoir Z which was sealed to the tube W. Dry air could be admitted to the apparatus through the phosphorus pentoxide tube F. D is also a drying tube through which the tube W could be evacuated.

---

[1] Exhibition of 1851 (Eng.) Scholar at Cambridge, 1924, 1925, 1926.

[2] Hoover and Rideal, This Journal, 49, 104 (1927).

Experimental Part

The adsorption isotherms for hydrogen, nitrogen, ethylene and alcohol vapors were determined at two temperatures. Ethylene of 99.6% purity was prepared by allowing a mixture of phosphorus pentoxide and alcohol to drop on hot pumice. The ethylene was further purified by fractionation by the use of liquid air. Cylinder nitrogen was used, and was purified by passing it through a potassium hydroxide solution and over hot copper. Cylinder hydrogen was purified in the same way. The alcohol used for the adsorption measurements was the same as that used in the catalytic determinations described in Part I of this paper. The adsorption determinations were made as follows.

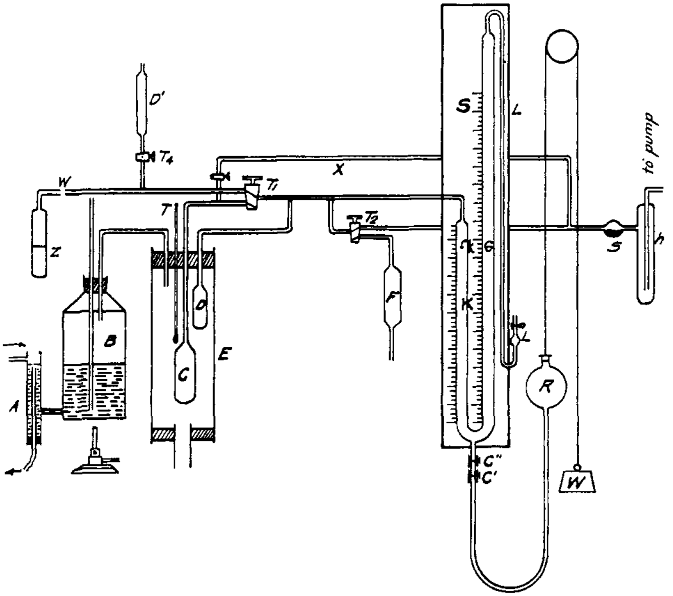

Fig. 1.

The bulb C is nearly filled with a weighed quantity of the material under examination, thoria, which had previously been submitted to evacuation at 300° to remove most of the moisture. The bulbs C and D are then heated to 325° by means of an electric furnace, and the whole apparatus evacuated until the final pressure is less than 0.001 mm. The pumping is continued for at least three hours before a determination is made. The taps T_1 and T_2 are closed. The gas under investigation is admitted to the tube W through drying tubes from an aspirator. In the case of alcohol vapor, the liquid alcohol in Z and the space above were freed from gases by pumping through the side tube D.

A quantity of gas is then admitted through T_1, the level of the mercury adjusted to the pointer, and the pressure read on the manometer. The tap T_1 is then turned so as to join the bulbs C and D. The mercury is now kept nearly at the level of the pointer until equilibrium is reached, then carefully adjusted again and the pressure read. Equilibrium is ordinarily reached in about ten to fifteen minutes. More gas is then admitted, and the process repeated.

The adsorption is calculated by means of the gas laws and a knowledge of the volume of the bulbs D and the connecting tubing, and the volume of the free space in the bulb C. The volume of the capillary connecting tubing and of the space above the pointer in the manometer is kept small compared to the volume of the bulbs. A correction is made for the volume of the gas which is not at the temperature of the thermostat. The volume of the free space in the absorption chamber was determined at the close of the experiment by evacuating, sealing off in the capillary tubing, breaking the tip under benzene, and determining the weight of benzene required to fill the bulb at a definite temperature. An attempt was made to find this volume by the use of nitrogen, but it was found that nitrogen was adsorbed to a considerable degree, so this method was unsatisfactory.

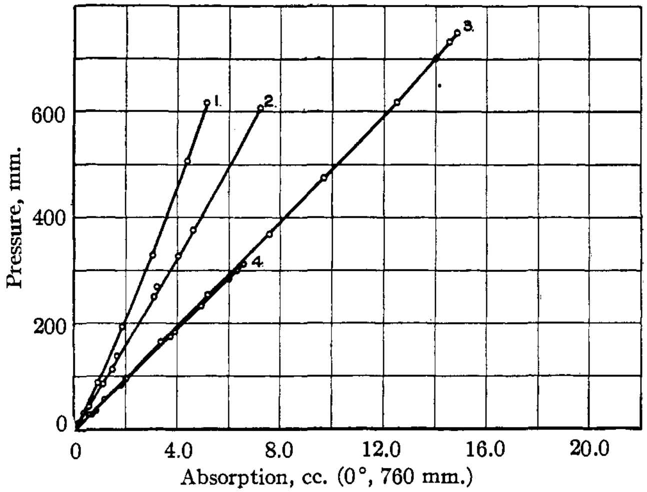

Fig. 2.—Curve 1, adsorption of nitrogen at 0° $\times 10^{-1}$; Curve 2, hydrogen at 100°; Curve 3, hydrogen at 0°; Curve 4, nitrogen at 100°.

Results

The adsorption isotherms were determined for nitrogen, hydrogen and ethylene at 100° and at 0° and for ethyl alcohol vapor at 100° and at 52.3° on the precipitated thoria catalytic material described in Part I of this paper. These are shown graphically in Figs. 2, 3 and 4. Adsorptions are recorded in cubic centimeters of gas adsorbed at N. T. P.

per 100 g. of material except in the case of alcohol vapor where they are given in cubic centimeters of vapor at 100° and 760 mm. per 100 g. of material.

Hydrogen and Nitrogen.—The isotherms for hydrogen and nitrogen are nearly straight lines (Fig. 2). The curve for nitrogen at 0° shows slight curvature towards the pressure axis. These results are in agreement with the work of Lowry and Morgan,[3] on adsorption on graphitic carbon. They obtain straight-line isotherms with nitrogen at 100° and 56.7° and slight curvature at 0°, but with carbon dioxide they obtain the usual type of isotherm, concave towards the pressure axis. Thus it would appear to be the rule that when the amount of adsorption is small, the adsorption is proportional to pressure. In this case it is likely that the surface does not even approach saturation. On the other hand, in the case of a substance which is strongly adsorbed, as carbon dioxide, cited above, the curve flattens out towards the pressure axis, indicating that saturation is being approached. Lowry and Morgan[3] obtain a similar type of curve for hydrogen adsorption at —191°. The adsorption isotherms for ethylene at 100° and 0° obtained in this investigation are of this type (Fig. 3). Thus the shape of the isotherm obtained in any particular case will depend both on the temperature and on the material being adsorbed. Therefore, the information as to the nature of the surface that may be obtained, for example, from a hydrogen-adsorption isotherm, may be quite different from that which may be obtained from an ethylene isotherm. This is an

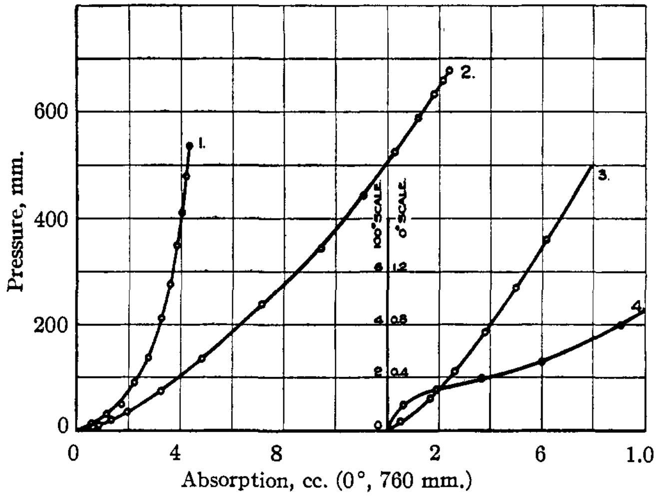

Fig. 3.—Curve 1, ethylene absorption at 0° × 10^{-2}; Curve 2, ethylene at 100° × 10^{-1}; Curve 3, ethylene at 100°; Curve 4, ethylene at 0°.

---

[3] Lowry and Morgan, *J. Phys. Chem.*, **29**, 1111 (1925).

important point, and one not always taken into consideration. Apart from information as to the actual magnitude of the adsorption in any case, the curves that should yield the most information from a catalytic viewpoint are those which indicate saturation of the surface or parts of the surface, or indicate capillary condensation. From this standpoint, the ethylene and alcohol vapor-adsorption isotherms are of interest.

Alcohol Vapor and Ethylene.—The adsorption isotherms for alcohol vapor at 52.3° and 100° are shown in Fig. 4. The upper parts of both curves flatten out parallel to the adsorption axis. This part of the curve may represent condensation of the alcohol vapor in the capillaries of the thoria or isopneumatic liquefaction of a unimolecular layer. The material is probably of the "gel" type.[4] Isotherms of this type were recently found by Munro and Johnson[5] for the adsorption of water vapor on alumina at 40° and 50°. The upper portions of such curves have been studied in detail by Patrick and his co-workers[6] and Pearce and Alvarado.[7] In the present work, however, it was found essential to outgas the material for several hours at 0.001 mm. above 300° to free it completely from adsorbed vapors in order to render the lower portions of the curves reproducible.

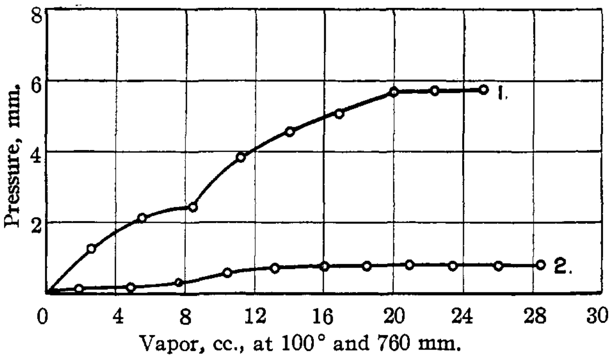

Fig. 4.—Curve 1, alcohol at 100°; Curve 2, at 52.3°.

It will be noted that both in the 100° and in the 52.3° isotherm there exists a reproducible and well-defined break in the adsorption-pressure curve. A similar break occurs in the ethylene isotherm for 0° and to a very slight extent in the 100° isotherm as may be seen from the low-pressure sections of the curve drawn to larger scale (Fig. 3). The break in the 100° ethylene isotherm is very slight but can be detected when a logarithmic plot of the pressure-adsorption measurements is made.

---

[4] Van Bemmelen, "Die Adsorption," Th. Steinkopff, **1910**, p. 214.

[5] Munro and Johnson, *J. Phys. Chem.*, **30**, 172 (1926).

[6] McGavack and Patrick, THIS JOURNAL, **42**, 946 (1920). Davidheiser and Patrick, *ibid.*, **44**, 1 (1922). Patrick and Long, *J. Phys. Chem.*, **29**, 336 (1925). Patrick, Preston and Owens, *ibid.*, **29**, 421 (1925).

[7] Pearce and Alvarado, *ibid.*, **29**, 256 (1925).

On the hypothesis of capillary condensation the mean radius of the capillaries in which condensation is occurring may be calculated from the pressures at which the curves flatten out with the aid of the expression $r = 2\sigma \Delta_0/\delta.P_0 \log (P_0/P)$, where σ is the surface tension, Δ_0 and δ are the vapor and liquid densities, P_0 is the saturation and P the actual pressure of the vapor outside the curved surface. For ethyl alcohol at 100°, $\sigma = 20$ dynes per cm.; $\Delta_0 = 0.000,011,5$; $\delta = 0.80$; $P_0 = 1695$ mm.; and $P = 5.8$ mm. Inserting these values we obtain a value of $r = 14$ Å. giving a mean diameter for the capillaries of 28 Å. or some five alcohol molecular diameters. The capillary radius calculated from the upper break of the 52.3° isotherm with the values $P = 255$ mm., $\Delta_0 = 0.000,001,82$, is likewise 14 Å. Several interpretations may be given of the first break in the alcohol-adsorption curves. With Patrick, it might be assumed that this represents the filling up of smaller capillaries or the first stages in filling up V-shaped capillaries. The mean radius of these capillaries calculated in the same way from the following data on the 100° isotherm, $P = 2.5$ mm. $\Delta_0 = 0.000,004,9$, is 5.2 Å., or the diameter is only the thickness of two alcohol molecules or one alcohol molecule long. It is difficult to visualize either the structure or the mechanism of filling for such minute capillaries and it appears much more reasonable to reject the capillary conception and to assume that this first break, at any rate, represents the attainment of saturation of an active portion of the surface with concomitant isopneumatic liquefaction of the unimolecular layer. A value for the area of this active surface can be obtained from the adsorption at this critical pressure. That this view is more probably correct is supported by the fact that approximately equal amounts of alcohol are adsorbed at both temperatures at the points where the breaks in the curves occur. We may take the average value of the adsorption at this point to be 0.050 cc. of alcohol vapor at 100° and 760 mm. per g. of thoria. Adopting a value of 6.06×10^{23} for the Avogadro constant and a molecular diameter of 5.3 Å. for the ethyl alcohol molecule, on the assumption of a packed unimolecular layer, we obtain an area of 0.280 sq. meters per g. for the area of the active patches. To find the fraction of the total area which this 0.280 sq. meter per g. of active area represents, it is necessary to evaluate the specific surface. The usual method[8] of obtaining the saturation maximum of such dyes as methylene blue proved unsatisfactory but it was found that copper ions were strongly adsorbed from solutions of cupric sulfate.

A weighed amount of material was shaken at intervals for 24 hours with solutions of various concentrations. The copper-ion content before and after adsorption equilibrium had set in was determined by the potassium iodide-thiosulfate method with the following results.

---

[8] Paneth and Radu, *Ber.*, **57**, 1221 (1924). Rideal and Wright, *J. Chem. Soc.*, **127**, 1347 (1925).

Expt.	1	2	3	4
Concn., mg. of Cu^{++} per cc.	9.73	4.92	2.41	0.52
Adsorption, mg. of Cu^{++} per g. of thoria	5.76	6.14	4.61	1.54

The adsorption is seen to rise to a saturation maximum. The slightly lower value observed for Expt. 1 is due to the fact that but a short interval was allowed for equilibrium to be reached. The adsorption value for Expt. 2 is used in calculating the surface area. Taking the area occupied by a hydrated copper ion as approximately 40 sq. Å., we obtain a value of 23 sq. meters per g. of thoria as the specific surface. The active area calculated above was 0.280 sq. meter per g. or 1.3% of the total surface.

A somewhat greater specific surface is obtainable from the ethylene-adsorption isotherm. Saturation is apparently attained at 0° when some 425 cc. of ethylene is adsorbed per 100 g. of thoria, or 4.25 at N. T. P. per g. Taking the area of an ethylene molecule, when adsorbed on the surface, as 25 sq. Å., we obtain as the area per g. $2.70 \times 10^{19} \times 4.25 \times 25 \times 10^{-20}$ sq. meters, or 28.7 sq. meters.

The second break in the alcohol adsorption isotherms commences after adsorption of some 20 cc. of vapor; that is, capillary condensation commences long before the whole surface of the thoria is covered with a unimolecular layer, for this would require an adsorption of some 400 cc.

The heat of capillary adsorption of alcohol vapor in the capillaries may also be determined on the assumption that at the pressures $P_1 = 5.8$ mm. at 373° K. and $P_2 = 0.80$ mm. at 325.3° K., corresponding to the flat portions of the curves, the surface is completely saturated and the capillary liquid in true equilibrium with the vapor. Inserting these values in the Clapeyron equation $L = [4.57\ T_1T_2/(T_2-T_1)]/\log P_2/P_1$, we obtain a value of the latent heat of adsorption of 9900 calories per g. mole. For the heat of adsorption on the active portions as shown by the lower breaks we obtain for P_2, 2.5 mm., and as a very approximate value for P_1, 0.15 mm., whence $L_2 = 14{,}000$ cal. per g. mole.

Summary

1. The adsorption isotherms for nitrogen, hydrogen and ethylene at 100° and 0° and for alcohol vapor at 100° and 52.3° on thoria have been determined.

2. It is shown that precipitated catalytic thoria is of the "gel" type in adsorption.

3. The gases, nitrogen and hydrogen are adsorbed in proportion to their pressure, and surface saturation is not obtained at one atmosphere's pressure.

4. A saturation maximum for ethylene at 0° can be obtained at about 600 mm. and an irregularity is noted in the low-pressure portion of the 0° and 100° isotherms attributed to a specially active area.

5. Adsorption and capillary condensation or surface liquefaction occurs with ethyl alcohol both at 52.3° and at 100°. A break at low pressures is obtained which is attributed to a specially active adsorbing area.

6. The specific surface is evaluated by adsorption of copper ions to be about 23 sq. meters per g. and the fraction of this surface strongly adsorbing and probably catalytically active is 1.3%.

7. The latent heat of capillary condensation is evaluated at some 9900 cal. per g. mole and that of surface adsorption at 14,000 cal. per g. mole.

CAMBRIDGE, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 525]

AMMONIUM MONOMETAPHOSPHATE. PHOSPHATE III

BY SAMUEL J. KIEHL AND THOMAS M. HILL

RECEIVED OCTOBER 21, 1926 PUBLISHED JANUARY 11, 1927

The metaphosphates studied by Graham[1] were, in all probability, mixtures of various so-called polymers. Since his work, which outlined the possibilities in connection with the metaphosphates, the research in this field has been prolific but along rather restricted lines. In reviewing the literature we find that the investigations may be classed in one of the following groups. 1. Attempts to classify the metaphosphates in general. 2. Methods of determining the rate and products of hydration. 3. Methods of preparing various mixed salts or polymers, and the evidence pointing to their classification. 4. A disagreement of authors on methods of preparation and products formed.

Tammann,[2] in a general review of previous work along with his own, attempts a classification depending on conductivity measurements and freezing-point determinations. In his classification both isomerism and polymerism are assigned as properties of metaphosphoric acid. His salts were mostly prepared from the interaction of salts or bases with glacial metaphosphoric acid. Pascal[3] pointed out that the compounds and classifications considered by Tammann are open to doubt, due to methods of preparation and inaccuracies in analytical work as great as 8%.

Metaphosphoric acid, according to Holt and Myers[4] and Tilden and Barnett,[5] when prepared from phosphorus pentoxide and water, or by dehydration of orthophosphoric acid, is in an associated condition according to evidence obtained from freezing-point determinations.

[1] Graham, *Phil. Trans.*, **123**, 253 (1833).

[2] Tammann, *Z. physik. Chem.*, **6**, 122 (1890).

[3] Pascal, *Bull. soc. chim.*, **33**, 1611 (1923).

[4] Holt and Myers, (a) *J. Chem. Soc.*, **103**, 532 (1913); (b) **99**, 384 (1911).

[5] Tilden and Barnett, *ibid.*, **69**, 158 (1896).