[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Heterogeneity of Catalyst Surfaces for Chemisorption. I. Zinc Oxide[1]

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The examination of catalyst surfaces which show chemisorption has been greatly facilitated by the development of the method of surface area determinations due to Brunauer, Emmett and Teller (BET),[2] which permits a definition of the surface, reproducible in different laboratories. Chemisorption is often largely dependent on the nature of the catalyst preparation and the variables which enter into the preparation. A knowledge of the BET values for different preparations facilitates intercomparison of the results of chemisorption obtained. For these reasons it has appeared desirable to re-examine the chemisorption of hydrogen on a number of oxide surfaces where the rate of adsorption proceeds at measurable rates because of the magnitudes of the activation energies involved. With this objective, we have studied once more the case of zinc oxide since earlier work by Taylor and Strother[3] indicated that, in this case, two different types of chemisorption with different activation energies might be operative. This earlier work was performed before the development of the BET method and therefore was made without knowledge of the total surface available. Our studies have led to observations which escaped the original investigators and which have important bearing on the problem of heterogeneity in such catalyst surfaces. This problem is of first importance in the kinetics of catalyzed reactions. In the years 1925–1930 considerable research was focused on the possibility of "active centers" on such surfaces to account for the facts of poisons and promoters in catalyzed reactions. More recently, largely due to the researches of Beeck and co-workers,[4] Emmett, Brunauer and their co-workers[5] as well as the work from the laboratories of E. K. Rideal,[6] emphasis has shifted in catalytic reactions to interpretation in terms of the properties of the normal crystal faces of the catalytic materials. Quantitative data on the extent of heterogeneity of a given preparation are much to be desired.

In previous researches from this Laboratory, chemisorption on catalyst surfaces has been measured at different temperatures by following the rate of adsorption of a gas with time on clean surfaces obtained before each separate experiment by a standardized evacuation technique. In the present researches this procedure was abandoned in favor of a measurement of the extent of adsorption at a regulated pressure and a given temperature, followed by a change in the working temperature without intermediate evacuation of the sample. It was expected that, by this procedure, a more rapid method of obtaining an adsorption isobar could be secured. Instead, the procedure revealed hitherto unsuspected changes in the extent of adsorption as the working temperatures were changed, phenomena which could not possibly have been learned by the techniques previously employed and which are of prime significance in the interpretation of the nature of the catalyst surfaces; they reveal a marked heterogeneity of such surfaces.

Experimental

Apparatus.—The adsorption apparatus used was a modification of that employed by Taylor and Strother.[3] It was found possible to maintain the constant pressure by hand regulation without employing the electrolytic cell device employed in the earlier work.

Materials.—Helium, nitrogen and hydrogen from commercial cylinders were used with suitable purification over hot copper at 450° followed by drying over calcium chloride, ascarite and phosphorus pentoxide tubes. In the case of helium, the gas was freed from nitrogen by passage through a previously evacuated charcoal trap kept at liquid air temperatures.

The zinc oxide was prepared, according to the method employed by Sickman,[7] by ignition of zinc oxalate.

Procedure.—The dead space in the apparatus was measured with helium. The surface areas were measured with nitrogen, at liquid nitrogen or liquid air temperatures, the computations being made following the BET method. The adsorptions of hydrogen by the several preparations were studied at various temperatures and pressures; −195, −78, 0, 56, 111, 154, 184, 218, 256 and 302° with suitable liquid, liquid–solid or vapor baths; beyond 302° an electric furnace with chromel–alumel thermocouples was used; pressures of 1, 0.5 and 0.25 atm. were employed.

All the catalysts were evacuated at 410 ± 10° for ten hours as a standard technique before adsorptions were measured. With ZnO I, adsorptions were measured immediately after preparation and evacuation. With ZnO II, a two-hour treatment with hydrogen at 400° preceded the first evacuation. With ZnO III a two-hour treatment with hydrogen at 400° was carried out between the first and second runs on hydrogen adsorption. ZnO IIIa was a separate sample prepared from the same oxalate batch as ZnO III.

The measurement of adsorption of hydrogen was normally begun at 0° on the evacuated surface. At this temperature the extent of van der Waals adsorption of hydrogen should be negligibly small on surfaces such as are here involved.

Experimental Results

Table I gives a comparison of the results on surface areas and the extent of adsorption of hydrogen at 0° and 1 atm. pressure on the three samples studied after saturation at 302° and gradual cooling by stages to 0°. They serve to show the vari-

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[1] A preliminary presentation of this material was communicated to the Division of Physical Chemistry, American Chemical Society, Atlantic City Meeting, April 10, 1946.

[2] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

[3] Taylor and Strother, *ibid.*, **56**, 586 (1934).

[4] Beeck, Smith and Wheeler, *Proc. Roy. Soc.* (London), **177A**, 62 (1940); Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).

[5] Brunauer and Emmett, THIS JOURNAL, **62**, 1732 (1940).

[6] Twigg and Rideal, *Trans. Faraday Soc.*, **36**, 533 (1940); Herington and Rideal, *ibid.*, **40**, 505 (1944).

[7] Taylor and Sickman, THIS JOURNAL, **54**, 602 (1932).

ability of different preparations from the common starting material, zinc oxalate.

TABLE I

SURFACE AREAS AND HYDROGEN ADSORPTION AT 0° AND 1 ATM. ON ZINC OXIDES

Sample	Weight of sample, g.	Surface area Cc.	Surface area sq. m./g.	H_2 adsorbed at S. T. P.,[a] cc.	% Coverage by H_2	H_2 Cc./g.
I	23.2	136	25.7	8.9	6.5	0.39
II	28.4	101	15.6	20.0	19.8	0.70
III	63.1	80	5.56	34.0	45.0	0.54

[a] After previous saturation with hydrogen at 1 atm. pressure and 302°.

The influence of change of temperature on adsorption with time as the temperature is raised by substitution of one vapor-bath for another, maintaining a constant pressure of 1 atm., is shown, typically, in Fig. 1. It is to be noted that, on changing from 111 to 154°, there is a sharp drop in adsorption but, within ten minutes, the amount adsorbed has again reached the previously observed value and rapidly increases. When the temperature was again raised to 184° there is an immediate fall in the amount adsorbed and this time, the recovery to the value at the lower temperature required a period of two hours. A similar sharp decrease in extent of adsorption followed by slow recovery occurs as the temperatures are changed from 184 to 218°, 218 to 256° and 256 to 302°.

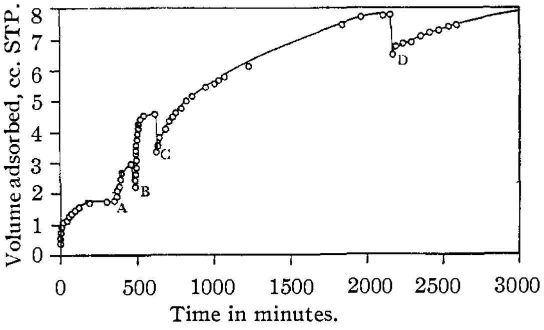

Fig. 1.—Typical adsorption rate curve on raising temperature (hydrogen on zinc oxide I at 1 atm.). Raise temperature (°C.) at A: from 0 to 111°, B: 111 to 154°, C: 154 to 184°, D: 184 to 218°.

The reality of these desorptions which occur on successive rises of temperature is confirmed by the behavior of the sample as the temperatures are lowered successively through the same sequence, always at a working pressure of 1 atm. A sharp increase in adsorption is generally observed at each change to a lower temperature as shown in Fig. 2. The increments on lowering the temperature through a given range roughly parallel the decrements observed as the temperature is raised, though there are occasionally exceptions.

Data from a later run on ZnO[2] I are shown in Fig. 3. Here again a change in temperature from 111 to 154° shows desorption followed by slow adsorption at the higher temperature. When the rate of adsorption at 154° was small, the bath was changed back to 111°. Immediate readsorption of 1 cc. of gas occurs. After negligible further change of adsorption with time at 111°, a change of temperature to 154° again produces the desorption process. This would seem to indicate the independence of adsorption sites at the two temperatures, the area covered by 1 cc. of hydrogen at 111° being bare at the temperature of 154°.

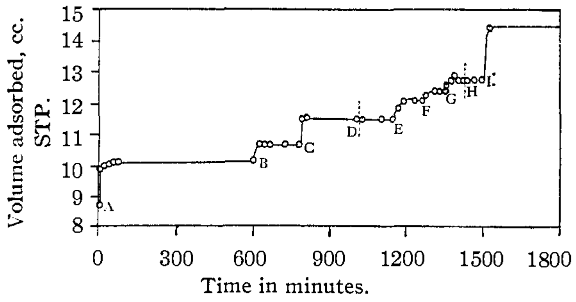

Fig. 2.—Typical adsorption rate curve on lowering temperature (hydrogen on zinc oxide I at 1 atm.). Lower temperature (°C.) at A: 302 to 256°, B: 256 to 218°, C: 218 to 184°, D: 184 to 154°, E: 154 to 111°, F: 111 to 80°, G: 80 to 56°, H: 56 to 0°, I: 0 to −78°.

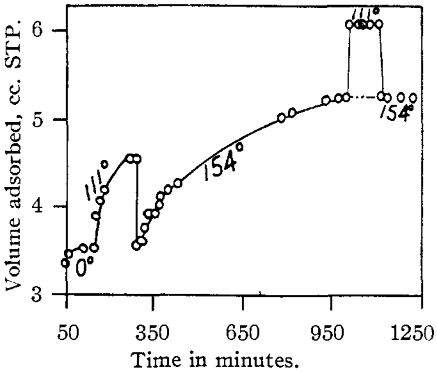

Fig. 3.—Adsorption rate curve on raising and lowering temperature.

Observations similar to those here illustrated were obtained at working pressures of 0.5 and 0.25 atm.

The increments in adsorption as the temperatures are lowered throughout the range from 302 to 0° as shown in Fig. 2 represent, in our view, a measure of the amounts of gas which could be adsorbed at a lower temperature and evolved as the temperature is raised to the higher temperature. On ZnO I this is seen to amount to about 5 cc. in a total of 13 cc. adsorbed on cooling down to 0°.

The data presented in Fig. 4 for ZnO II represent measurements in successive runs in which the surface was first saturated at 302° and 1 atm. pressure and then successively cooled throughout the range of temperatures to Dry Ice temperature. In these cases the increments in

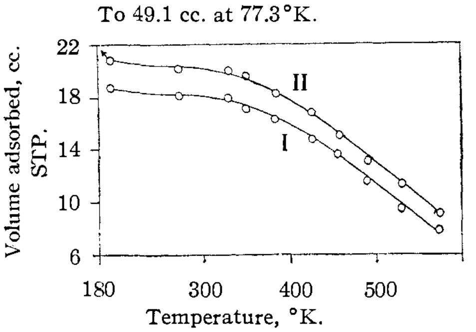

Fig. 4.—Adsorption isobars on lowering temperature (zinc oxide II at 1 atm.): I, first run; II, second run.

adsorption are progressive and amount to 11 cc. in all as the temperature is lowered to 56°, while in the range from 56 to −78° there is no significant change in the amount adsorbed.

Zinc oxide III was investigated in several ways. Initially a large sample (63 g.) was studied. It was prepared by as mild heating as was necessary to convert the oxalate through the carbonate to oxide. It was therefore more slowly decomposed than the two previous samples and shows some marked divergencies in characteristics from the other two. The original measurement of chemisorption at 0° showed it to possess a greater comparative adsorptive capacity for hydrogen at that temperature. Curves showing the data in two successive runs as the temperature was raised and then lowered in the intervals 0 to 302° and 302 to 0° are shown in Fig. 5. The first run shows a practically continuous decrease in adsorption during the rising temperature runs. Desorption followed by readsorption was consistently observed in the temperature range 0–150°. The curve for the descending range, 150 to 0°, indicates the magnitude of desorption occurring in this range. In the second run (II) much less time was consumed in obtaining the points on the ascending portion of the curve. Ascending and descending points coincide in the range 184 to 302° but below 150° the evidence for the desorption phenomena occurring on heating is apparent from the plotted points. During the prolonged heating periods in run I it is evident that some degree of sintering occurred.

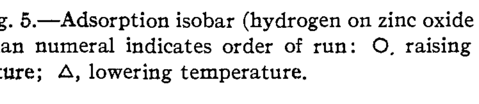

Fig. 5.—Adsorption isobar (hydrogen on zinc oxide III); Roman numeral indicates order of run: ○, raising temperature; △, lowering temperature.

These conclusions reached with the large sample were confirmed by taking a small fraction of ZnO III after Runs I and II and repeating the work with a sample of 21 g. The data on the smaller sample checked those obtained with the large 63-g. sample. This indicated that the results were not to be ascribed to the size of sample employed.

Four experiments were also made on the 63-g. sample of ZnO III using the technique of Taylor and Strother in which measurements of the velocity of adsorption were made at 0, 111, 154 and 184° on the oxide surface cleaned of adsorbed gas by the standard evacuation technique for ten hours at 410 ± 10°, prior to each measurement of velocity of adsorption. The data so obtained may be used to measure "activation energies of adsorption." A summary of these results is presented in the following tables. Table II gives the times required to adsorb different quantities of gas at different temperatures.

TABLE II

TIMES IN MINUTES FOR ADSORPTION OF STATED VOLUMES OF HYDROGEN BY CLEAN ZnO III SURFACE

Adsorbed, cc.	Time in minutes at— 0°	111°	154°	184°
10	29	9	10	9
11	72	36	22	16
12	160	102	52	25

It is obvious that such data will yield fantastically irregular data for "activation energies" of adsorption when inserted in the equation

$$\log \frac{t_1}{t_2} = \frac{E}{4.58}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Data so obtained are shown in Table III.

TABLE III

"ACTIVATION ENERGIES" OF HYDROGEN ADSORPTION ON CLEAN SURFACES OF ZnO III

Vol. adsorbed, cc.	"Activation energy," E, in kcal. from data at 0–111°	111–154°	154–184°
10	2.2	−0.8	1.4
11	1.3	3.7	4.1
12	0.8	5.1	9.5

As will emerge from the discussion this method of determining activation energies has no significance in the light of the desorption-readsorption phenomena previously emphasized in the range 0–154°.

A sample of ZnO IIIa, 16.45 g. in weight, was used to follow change in surface area with use during three measurements of the 1 atm. isobar from −78 to 302° and then on lowering the temperature to liquid nitrogen temperatures. The data obtained in the three runs are shown in Table IV. At the beginning of the first run the value of v_m, the monolayer, was 33 cc. After the third run this had decreased to v_m = 22.6 cc.

After the data on isobars had been secured a set of adsorption isotherms of nitrogen at −196,

TABLE IV

ADSORPTION ISOBARS AT P = 1 ATM. ON ZnO III

	Temp., °C.	v adsorbed (cc., S. T. P.) 1st run[a]	2nd run	3rd run[b]
Raising temp.	− 78	6.02[c]	6.06[c]	5.22[c]
	0	3.86	4.42	3.71
	111	4.17		....
	302	1.73	2.46	1.68
	256	2.28	2.98	....
	218	3.10	4.39	3.44
	184	....	5.40	....
Lowering temp.	154	4.08	5.66	4.44
	111	4.85	6.09	4.87
	80	....	6.39	....
	56	5.49	7.07	5.35
	0	5.94	7.52	5.75
	− 78	8.04	8.32	6.32
	−126	15.08	14.83	....
	−196	42.4	37.00	29.3

[a] v_m = 33 cc. [b] v_m = 22.6 cc. [c] These values were recorded after 3, 2 and 26 hours, respectively, at 1 atm. pressure and −78°. This accounts for the discrepancy between these data and the value recorded in the isotherm in Fig. 6, where the 760 mm. point was recorded seventy-five minutes after the start of the determination. The difference in values at −78 and 0° in the 3rd run on raising and lowering the temperature shows a discordance also because of the twenty-six hours consumed in reaching the initial value of 5.22 cc.

−78, 0 and 56° were carried out as well as the adsorption isotherm of hydrogen at −196 and −78°. The data thus obtained are recorded in Fig. 6. Their significance is discussed in the succeeding section.

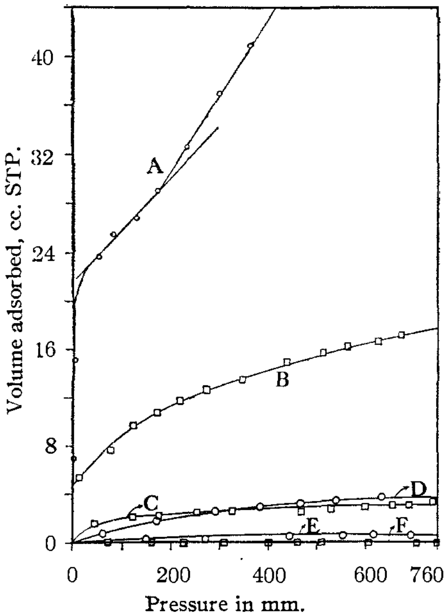

Fig. 6.—Adsorption isotherms for zinc oxide IIIa (v_m = 22.6 cc.): A, nitrogen at 77.3°K.; B, hydrogen at 77.3°K.; C, hydrogen at 195°K.; D, nitrogen at 195°K.; E, nitrogen at 273°K.; F, nitrogen at 329°K.

Discussion

In the original formulation of the concept of activation energy in adsorption processes, it was pointed out[8] that, on a non-uniform surface, it was possible that, due to the combined operation of the heat of adsorption, λ, and activation energy, E, of adsorption, there might result a set of conditions such that, at a given temperature, only a fraction of the available surface might be involved in the activated adsorption. It was emphasized that such a condition would be of first importance in those chemical reactions where activation was a condition precedent to reaction.

This aspect of a non-uniform surface deserves, in the light of the preceding experimental results, a more detailed analysis. Let us consider a given adsorbent having, hypothetically, two distinct adsorbent areas A and B, characterized by two distinct activation energies of chemisorption E_A and E_B and two characteristic heats of adsorption, λ_A and λ_B. It is possible to conceive two temperatures T_1 and T_2 such that, at the lower temperature T_1, only the area A is sensibly covered while B remains practically bare, whereas at the higher temperature T_2 the area A will be bare and area B sensibly covered. These two possibilities are illustrated in Fig. 7. The conditions which must be fulfilled for such a state of affairs may be summarized. If, at T_1, the magnitude of the activation energy E_A is sufficiently low and λ_A sufficiently high, the area A will be progressively covered. The condition for B to remain sensibly bare is that the activation energy E_B be sufficiently large so that negligible chemisorption will occur due to the Boltzmann factor e^{-E_B/RT_1} in the equation for the velocity of adsorption. For the reversal of this condition at temperature T_2, the necessary conditions are (1) that the magnitude of $(E_A + \lambda_A)$, the energy of desorption from area A, shall be low enough to permit rapid evaporation from this area, governed by the Boltzmann factor $e^{-(E_A+\lambda_A)/RT_2}$ in the equation for the velocity of desorption, and (2) E_B shall be of such magnitude that adsorption shall occur with measurable velocity and $(E_B + \lambda_B)$ sufficiently large that the surface will be progressively covered.

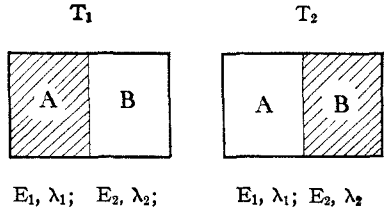

Fig. 7.—Hypothetical adsorbent with two areas of different characteristics.

Given such conditions it would obviously be possible to select a pressure P such that at T_1 the

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[8] Taylor, THIS JOURNAL, 53, 584 (1931).

fraction φ of a given area covered would approach $\varphi_A = 1$ and $\varphi_B \sim 0$ while, at T_2, $\varphi_A \sim 0$ and φ_B would approach unity. Further, at such a pressure, the composite absorbent AB saturated on the area A at T_1 would, on changing the temperature to T_2 keeping the pressure constant, suffer desorption of gas from area A and adsorption eventually reaching saturation on area B. If the desorption process from A were more rapid than the adsorption process on B the observer would record, on changing the temperature, first an evolution of gas followed by a readsorption. It is this observation which is a characteristic feature of the preceding experimental results.

On actual adsorbent surfaces the conditions would never be as simple as those just discussed. As has previously been emphasized,[9,10] both the activation energy and the heat of adsorption on a surface may vary markedly with the fraction of the surface covered. The algebraic sum of these magnitudes at a given coverage determines the activation energy of the desorption process at that coverage. Desorption occurs most readily from that area of a heterogeneous surface where the sum $E + \lambda$ is a minimum. With a partially covered surface, the condition for desorption followed by readsorption on transfer from a lower temperature T_1 to a higher temperature T_2 is again that the velocity of desorption from the area of minimum $E + \lambda$ is greater than the velocity of adsorption with an activation energy characteristic of the surfaces left bare at the lower temperatures. The experimental data present, in our judgment, a demonstration of the reality of such a possibility in the case of zinc oxide.

The existence of such behavior with actual surfaces has an important consequence in respect to the evaluation of experimental measurements of activation energies from measurements of velocity of adsorption. This may be conveniently illustrated by further consideration of the composite AB discussed in preceding paragraphs and illustrated in Fig. 7. Measurements of the velocity of adsorption of a given gas on a clean surface AB at temperature T_1 would record the number of cc. of gas adsorbed with time *on area* A. At temperature T_2 the measurement would record the gas adsorbed with time *on area* B. The two velocities thus found have, in reality, *no relation one to another*. They should not be used to determine activation energies in the manner first employed by us, using the equation

$$\ln \frac{v_2}{v_1} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where v_2/v_1 is the ratio of the velocities at the two temperatures or alternatively is the inverse ratio of the times required for the adsorption of a given volume. Because the processes at each temperature are occurring on different areas, they have no connection one with another. They cannot be employed to determine an activation energy characteristic of a process. In so far as activation energy is concerned they are two entirely different processes as different as they would be if A and B had entirely different chemical composition. The activation energy can only be properly derived in those cases where the given volume of gas is adsorbed *on the same area* at the two temperatures. The experimental work indicates definitely that this is not the case on the zinc oxide samples examined. The very varied values for the activation energy found with hydrogen on ZnO III as recorded in Table III at several temperatures are in agreement with this conclusion concerning activation energy of chemisorption on surfaces so heterogeneous as are here under consideration.

Consideration must now be given to the possibility that the hydrogen which is released from the surfaces on raising the temperature is not chemisorbed but is residual gas adsorbed by van der Waals forces. The data obtained with ZnO IIIa are decisive in this respect. The nitrogen adsorptions at −78 and 0° and 1 atmosphere pressure, respectively, were found to be 3.9 and 0.5 cc., respectively, and at 56° the nitrogen adsorption was immeasurably small. We are forced to conclude that the van der Waals adsorption of hydrogen is less than that of nitrogen at the same temperatures and pressures. Nevertheless, the quantities of hydrogen desorbed by elevation of the temperature between 56 and 302° in the case of this ZnO IIIa amount to at least 3.1 cc. This gas must be held at the zinc oxide surface by forces which are much stronger than the van der Waals forces; they must involve the forces of chemisorption.

From comparison of the adsorptions of nitrogen and hydrogen on ZnO IIIa one may conclude that considerable chemisorption of hydrogen occurs on this surface even at liquid air temperatures. In Fig. 8 we have plotted the hydrogen adsorption at −195.8° and the nitrogen adsorption at −78° on the same pressure abscissas but with the ordinates so adjusted that the adsorptions at 760 mm. pressure practically coincide. The comparison should be favorable to the van der Waals adsorption of nitrogen since −78° is only 1.55 times the critical point of nitrogen whereas −195.8° is some 2.34 times the critical point of hydrogen. Nevertheless the isotherm for hydrogen lies markedly to the left of the nitrogen isotherm and the marked adsorption of more than 5 cc. of hydrogen at 10 mm. pressure is strong indication of a binding of hydrogen involving forces markedly stronger than the van der Waals forces. The adsorption of hydrogen amounts to 18 cc. at a pressure of 1 atmosphere or some 80% of a monolayer (22.6 cc.). This is further indication that other than van der Waals forces must be involved.

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(9) Taylor, *Chem. Rev.*, **9**, 1 (1931).

(10) Brunauer, Love and Keenan, THIS JOURNAL, **64**, 751 (1942).

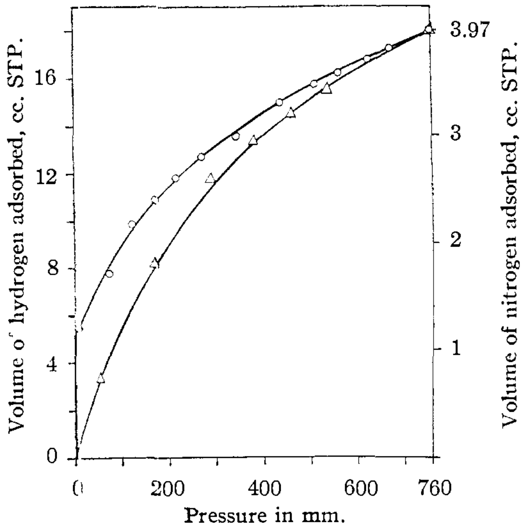

Fig. 8.—Comparison of hydrogen and nitrogen isotherms on zinc oxide IIIa (V_m = 22.6 cc.): O, hydrogen at 77.3°K.; △, nitrogen at 195°K.

We wish now to suggest the manner in which desorption of chemisorbed gas may be quantitatively evaluated in those cases in which for both van der Waals adsorption and chemisorption true isobars can be established. Referring to Fig. 9, if the continuous lines AB, CD represent true equilibrium isobars it is obvious that, on raising or lowering the temperatures in the chemisorption region CD, the same experimental values will be obtained. If the dotted line BC represents values obtained while the temperature is being increased it is obvious that they are below the true equilibrium values because these latter cannot be reached in practicable times of observation since the velocity is too slow. If the surface were uniform and no intermediate desorption occurred in the ascending portion BC the adsorption data which would be obtained on cooling below the point C would be *horizontal* until the van der Waals adsorption again began to occur. This is indicated by the horizontal section CE and the ascending portion EF. If, however, desorption does occur, as indicated in Figs. 1 and 3 during measurements at increasing temperatures in the region BC, then, on cooling down, we should no longer have a horizontal section CE but continuously increasing values of the adsorption CG, measuring, in excess of the values in the horizontal section, the quantity of gas which was desorbed during the measurements of the points obtained in going from B to C. Figures 2, 4 and especially 5 supply experimental evidence of this behavior in the case of zinc oxide. In a later communication we shall offer other studies in which there is a complete absence of desorption in the ascending section BC and, on cooling, the curve follows the horizontal path CE. It is evident that this will always occur when the binding energy of hydrogen to the adsorbing surface is sufficiently great as to make desorption in the prescribed temperature interval negligible.

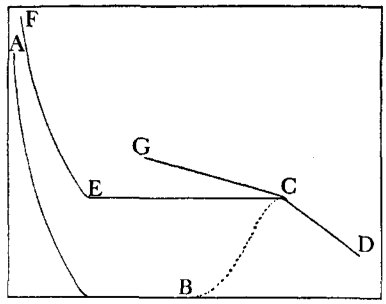

Fig. 9.—Schematic representation of chemisorption on lowering temperature with uniform and heterogeneous surface.

We wish now to discuss other data already in the literature which are in harmony with the results here recorded. As early as 1930 Garner and Kingman[11] reported that hydrogen or carbon monoxide adsorbed at low pressures and room temperatures on ZnO-Cr_2O_3 catalysts was given off at 100–120° but after twenty to thirty minutes was readsorbed. At that time this was cited by the senior author as evidence for adsorption with an activation energy but it could not then be stated whether the evolved gas was adsorbed by chemisorption or by van der Waals forces. In a later communication we shall give evidence that the former is the case.

Beebe and Dowden[12] measured the heat of adsorption of hydrogen on chromium oxide gel at liquid air temperatures and found a heat of adsorption of 5 kcal. which can hardly be the heat of van der Waals adsorption of this gas. Yet such chemisorbed gas, with the low energy of activation allowable at the temperature of liquid air, cannot be held to the surface in the temperature interval of 100–300° where chemisorption is conveniently measurable with time and shows an activation energy of 21.7 kcal. "on an area relatively uniform and large in extent" as Burwell and Taylor found.[13] These authors found definite evidence in their own data (see p. 701) for the phenomenon which we have exhibited definitely here in the case of zinc oxide and which we shall demonstrate using our technique in the case of chromium oxide gel.

Eucken and Hunsmann[14] have indicated a heterogeneity of nickel catalyst surfaces in the chemisorption of hydrogen by measurement of the calorimetric heats of adsorption and determination of the desorption of the gas from loaded surfaces. Already at 90°K. the heats of adsorption indicate chemisorption with heats ranging from 20–12 kcal. per mole of hydrogen adsorbed. Nevertheless, by measuring the temperatures at

[11] Garner and Kingman, *Nature*, **126**, 352 (1930).

[12] Beebe and Dowden, THIS JOURNAL, **60**, 2912 (1938).

[13] Burwell and Taylor, *ibid.*, **58**, 697 (1936).

[14] Eucken and Hunsmann, *Z. physik. Chem.*, **B64**, 163 (1939).

which gas chemisorbed at −78° could be released from the surface into a vacuum they found desorption occurring in two steps sharply separated from one another. Some 14% of the gas readily was liberated below 0° while the remainder required temperatures above 50° for release into a vacuum. The authors deduce from their data a marked distribution of centers of activity over their total surface. Evidence already available to us indicates that such data with metallic nickel catalysts are to be obtained in even more definite degree with copper catalysts. Dr. P. H. Emmett has called our attention to the fact that the earlier work of Emmett and Brunauer[15] on the chemisorption of hydrogen on iron synthetic ammonia catalysts also reveals the same phenomenon of increased adsorption on decreasing the temperature which we have noted above as characterizing the chemisorption of zinc oxide and revealing the heterogeneity of the catalyst surface.

The data obtained in the present research are in best agreement with the earlier data by E. A. Smith and Taylor[16] on the interaction of deuterium and hydrogen on zinc oxide catalysts. In that research it was shown that the catalyst operated in the range 143–491°K. with activation energies which increased from 0.6 kcal. in the temperature range 143–178°K. through a region 195–373°K. with an activation energy of 7 kcal. to a high temperature region with an activation energy of 12 kcal. In this latter there was a temperature range 405–430°K. where the apparent activation energy was zero. This abnormality was explained on the basis of a decrease in the active surface covered with increase of temperature. The exchange reaction was shown to occur from 50 to 800 times faster than the net rate of adsorption as measured by Strother at atmospheric pressure. The adsorption process effective in the exchange reaction was identified with the fast initial adsorption of gas observed by Strother with zinc oxide and, in the case of chromium oxide, by Burwell and Taylor already cited. The argument developed by E. A. Smith and Taylor was dependent on the postulate that the slow step in the exchange reaction was the desorption of chemisorbed hydrogen deuteride, HD, from the surface. This postulate has been challenged by others[17,18] as a result of parallel studies of the same exchange on other surfaces. Hence, the argument for heterogeneity of the zinc oxide surface thus advanced by E. A. Smith and Taylor could always be discounted. The present research which reveals this same heterogeneity by methods entirely free from any postulate as to reaction mechanism fortifies the earlier conclusions and, at the same time, exhibits an experimental technique whereby the heterogeneity of a catalyst surface can be rigorously revealed.

Summary

A new experimental technique for determining isobars of adsorption on zinc oxide at various temperatures has been developed.

The technique reveals desorption of chemisorbed hydrogen from a surface on raising the temperature through certain temperature ranges at constant pressure; the desorption is then followed by further chemisorption of the gas.

Chemisorption of hydrogen, in addition to van der Waals adsorption, is indicated at a temperature of 80°K. on the zinc oxide preparations studied.

The data indicate a marked heterogeneity of the surface in the chemisorption of hydrogen.

Analysis of earlier literature reveals the generality of the phenomenon; its consequences in the determination of activation energies of chemisorption and its significance in catalysis at surfaces has been emphasized.

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[15] Ref. 5, see Tables IV, X and XIII.

[16] E. A. Smith and Taylor, THIS JOURNAL, **60**, 362 (1938).

[17] Eley and Rideal, *Nature*, **146**, 401 (1940); Eley, *Proc. Roy. Soc.* (London), **A178**, 452 (1941).

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

Active Magnesia. II. Adsorption of Fluoride from Aqueous Solution

BY ALBERT C. ZETTLEMOYER, EARL A. ZETTLEMOYER[1] AND WILLIAM C. WALKER

Observations have shown that the fluoride content of drinking water is a very important factor in dental health. Small amounts cause the teeth to be exceptionally healthy, but in high concentrations fluoride causes severe mottling. In several areas of the United States the fluoride content of drinking water exceeds the limit of safety. For this reason many substances have been studied as adsorbents for the reduction of fluoride concentration of drinking water. As a result of these studies Elvove[1a] has recommended active magnesia as the least expensive and most efficient adsorbent for the purpose. This author has reported a study of fluoride adsorption by active magnesia, but only for one grade at concentrations below 0.5 millimole per liter (10 p. p. m.).

The present paper is the second in a series[2] describing the properties of active magnesia. It is devoted to the presentation of fluoride adsorp-

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[1a] E. Elvove, *Public Health Reports*, **52**, 1308 (1937).

[2] Zettlemoyer and Walker, *Ind. Eng. Chem.*, **39**, 69 (1947).