

polar liquids such as alcohol and water in terms of molecular properties and dipole moments. Indeed the Mosotti hypothesis on which the expression for the polarization is based is generally supposed to break down entirely in such cases. In view of this it is therefore not without interest to observe that the polarization of the alcohol mixtures, calculated for 20° from the data given above, is so nearly a linear function of the mole fraction of alcohol (water) as shown in Fig. 5. In general, this would, of course, only be expected for non polar liquids.

The writer wishes to express his thanks to Professor E. J. Cohn for the facilities of his laboratory during the course of this investigation.

Summary

Values of the dielectric constant of alcohol-water mixtures from -5 to 40° have been determined for the entire range of composition. The method employed was one recently developed by the author, based on the determination of the natural period of a small all metal circuit completely immersed in the medium. The frequency varied from 2.15×10^8 to 4.10×10^8 ($\lambda = 3.971$ meters and 7.302 meters, respectively). In the case of pure alcohol the dielectric constant was shown to be independent of frequency between $\lambda = 3.972$ meters and $\lambda = 17.005$ meters. A comparison has been given of the author's results with such data in the literature as already existed.

CAMBRIDGE, MASSACHUSETTS

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DISCONTINUITIES IN ADSORPTION ISOTHERMS

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Introduction

In a previous paper² it was shown that the adsorption of hydrogen by nickel at low temperatures increased with pressure in a markedly discontinuous manner. Subsequently the same phenomenon was reported in greater detail³ for another sample of nickel, and also for copper.

Recently Allmand and Burrage⁴ have reported a large number of adsorption isotherms which show discontinuities, observed for the most part with charcoal, and to some extent with silica. They point out that several

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² Benton and White, *THIS JOURNAL*, **52**, 2325 (1930).

³ Benton and White, paper read at the Atlanta meeting of the American Chemical Society, April, 1930.

⁴ Allmand and Burrage, (a) *Proc. Roy. Soc. (London)*, **A130**, 610 (1931); (b) *J. Phys. Chem.*, **35**, 1692 (1931).

other investigators have found more or less irregular isotherms, but have usually attributed the irregularities, either explicitly or implicitly, to experimental error.

Our work in this field has now been extended so as to include measurements of the adsorption of several gases (hydrogen, nitrogen, carbon monoxide) by nickel, copper and iron, at pressures up to one atmosphere and at temperatures which range in most cases from -200 to $+200^{\circ}$. In the course of this investigation, which will shortly be reported in full, we have found additional examples of discontinuities in isotherms, and have studied the effect of altering the conditions of experiment, especially the temperature and the presence or absence of poisons. In the present paper are described such portions of our work as are concerned with these discontinuities. Further, on the basis of the data obtained, we now feel justified in presenting a more complete theoretical treatment than that previously given.² We have been led to a simple hypothesis regarding the nature of the adsorbing areas involved in the discontinuities, and as a result to an entirely new picture of the manner in which the "physical," or "secondary," type of adsorption occurs.

Experimental Method

The apparatus previously described² was used to obtain the data for nickel and iron; for copper a different but similar apparatus was employed. The method was the usual "static" one, in which the adsorption is determined as the difference between the volume of the given gas required to fill a bulb containing the adsorbent at a given pressure and temperature, and the volume of helium required under the same conditions. The measurements with helium were made at a number of temperatures down to -78.5° , but for lower temperatures, where there was danger of a small quantity of helium being adsorbed, the free space was taken as the average of the values calculated from each of these measurements at the higher temperatures, on the basis of the ideal gas law. All volumes have been expressed in cc. at 0° , 760 mm., and all pressures in mm. of mercury at 0° .

Materials.—The nickel sample was obtained by carefully igniting hydrated nickel nitrate up to a final temperature of 400° , and reducing the resulting oxide with hydrogen for about twenty-four hours at each of the temperatures, 200, 250 and 300° . The product weighed 23.03 g. (Nickel III).

Two samples of copper were used, both obtained by reduction of copper oxide by hydrogen, the first for about forty-eight hours at 150 – 170° , the second for one hour at 170° , ten days at 115° and nine days at 130 – 140° . The weights of copper were 71.15 g. and 51.51 g., respectively, for Copper I and Copper II.

The iron adsorbent was prepared from a sample of fused ferro-ferric oxide

containing 0.15% of alumina, which was kindly placed at our disposal by Dr. P. H. Emmett of the Fixed Nitrogen Laboratory in Washington. The sample (Iron I, 54.6 g.) was obtained by reducing the oxide in hydrogen for five days at 375° and for fourteen days at 425–450°.

In all cases reduction was carried out *in situ* and the bulbs sealed off in a stream of hydrogen.

Experimental Results

Nickel.—While the previous results with Nickel I and II definitely showed that hydrogen was adsorbed in a step-wise manner at -183 and -191.5° , the number of experimental points was insufficient to locate the steps with accuracy. A more detailed study of the -183° isotherm for hydrogen on Nickel III gave the results shown in Fig. 1, Curve 1. Here,

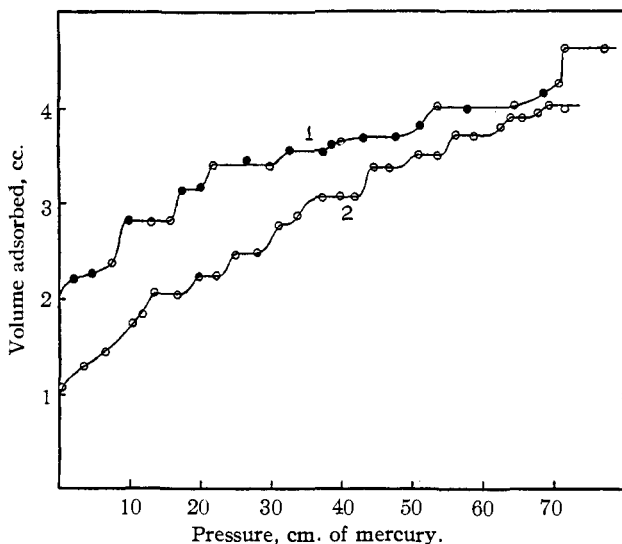


Fig. 1.—Adsorption of hydrogen by nickel at -183° . Curve 1, no CO; Curve 2, 1.0 cc. of CO as poison.

as elsewhere, open circles indicate points obtained by going from lower to higher pressures; full black circles indicate the reverse. Curve 2 was obtained in exactly the same way as Curve 1, except that before any hydrogen was admitted to the bulb, 1.0 cc. of carbon monoxide was introduced at -183° . This carbon monoxide was rapidly and completely absorbed, giving a final pressure of 0.0 mm.; an isotherm at this temperature, carried out with another sample of nickel of approximately the same weight, showed that 10 cc. of carbon monoxide could be taken up at a pressure too small to be read on the mercury manometer.

While there is considerable similarity between Curves 1 and 2, particularly below 250 mm., it is evident that the succession of steps has been

altered by the presence of the carbon monoxide. At low pressures the adsorption of hydrogen is diminished by an amount equal to the 1.0 cc. of monoxide, but the effect produced becomes progressively less at higher pressures.

Copper.—Both samples of copper showed marked discontinuities in the adsorption of hydrogen at temperatures in the neighborhood of -183° . Figure 2 shows the isotherms for hydrogen on Copper II at -195° (Curve 3) and -183° (Curve 2).

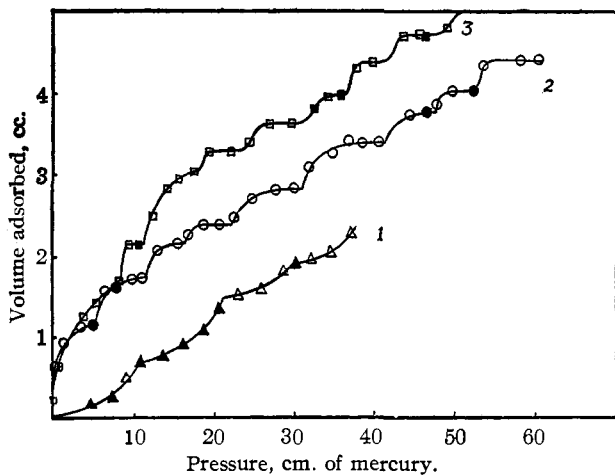


Fig. 2.—Adsorption of hydrogen by copper. Curve 1, on "H-covered" copper; Curve 2, at -183° ; Curve 3, at -195° .

Curve 1, Fig. 2, was obtained by admitting hydrogen to Copper II at -78.5° , in which process 9.00 cc. was adsorbed at a pressure of 517.7 mm.; without removing this gas the sample was cooled to -183° and the isotherm was then followed at this temperature. The values shown in Curve 1 are the amounts adsorbed at -183° in excess of the 9.00 cc. originally present. Our measurements of the adsorption of hydrogen over a wide range of temperature show beyond question that copper, like nickel, exhibits a type of adsorption at temperatures above about -100° , which is fundamentally different from the "physical" adsorption occurring at lower temperatures. The 9.0 cc. of hydrogen taken up at -78.5° must be regarded as held to the surface by ordinary valence forces, forming a "surface chemical compound." On cooling to low temperatures, this new surface can adsorb a further quantity of hydrogen. It is this additional, physical adsorption which is shown in Curve 1.

Measurements have also been made of the adsorption of hydrogen at -183° by copper which has been poisoned with varying quantities of carbon monoxide. The sample employed was Copper II, and the carbon

monoxide was introduced and allowed to come to equilibrium at -183° . Three hydrogen isotherms thus obtained are shown in Fig. 3; Curve 1 represents the adsorption of hydrogen in absence of carbon monoxide, while for Curves 2 and 3, 2.0 and 5.3 cc., respectively, of monoxide were used. (Copper II was found to adsorb more than 20 cc. of carbon monoxide at -183° , at apparently zero pressure.) The three curves show a pronounced similarity in shape. It appears remarkable that the adsorption of hydrogen should be so little affected by these relatively large quantities of poison, and we are forced to the conclusion that in this case, as with nickel under similar conditions, hydrogen can be adsorbed not only on the bare metal surface, but also on top of the carbon monoxide.

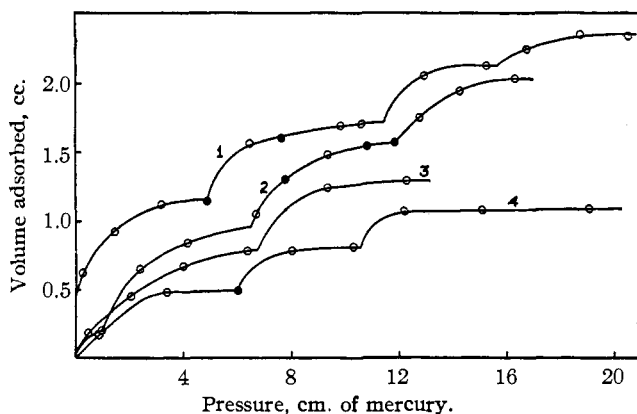


Fig. 3.—Adsorption of hydrogen by copper at -183° . Curve 1, no CO; Curve 2, with 2.0 cc. of CO; Curve 3, with 5.3 cc. of CO; Curve 4, after sintering (no CO).

At the conclusion of the studies on Copper II, this sample was heated in vacuum for one hour and a half at $400-450^{\circ}$ in order to sinter it. After this treatment the adsorption of hydrogen at -183° was again determined, with the results shown in Curve 4, Fig. 3. It appears that while the steps are still present, their height has been decreased.

Iron.—The isotherms for hydrogen on Iron I at -195 , -183 and -78.5° are shown in Curves 1, 2 and 3, respectively, of Fig. 4. In general, the results are similar to those obtained with nickel and copper. The main difference is that iron is the only one of the three metals which gave evidence of discontinuous adsorption of hydrogen at -78.5° . The work as a whole leaves no doubt that this difference is due to the fact that under these conditions the nickel and copper samples show adsorption of the "chemical" type, whereas with the particular sample of iron employed, the rate of this chemical adsorption is immeasurably small at temperatures below about 0° , so that the adsorption of hydrogen at -78.5° is of the physical type.

The adsorptions of nitrogen and of carbon monoxide have also been studied on both copper and iron, but in the majority of these experiments an insufficient number of points was taken to decide definitely whether discontinuities occur. For both metals, however, indications of such dis-

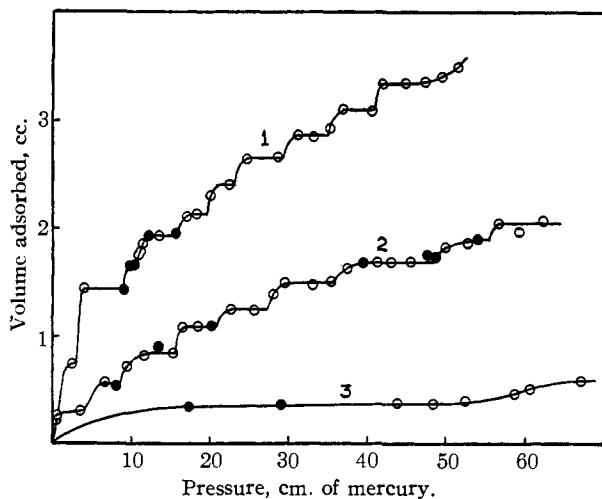


Fig. 4.—Adsorption of hydrogen by iron. Curve 1, at -195° ; Curve 2, at -183° ; Curve 3, at -78.5° .

continuities were found for nitrogen at -78.5° . Subsequently, a more detailed study was made of nitrogen on Iron I at this temperature. The results are shown in Fig. 5. While the maximum deviation of these points

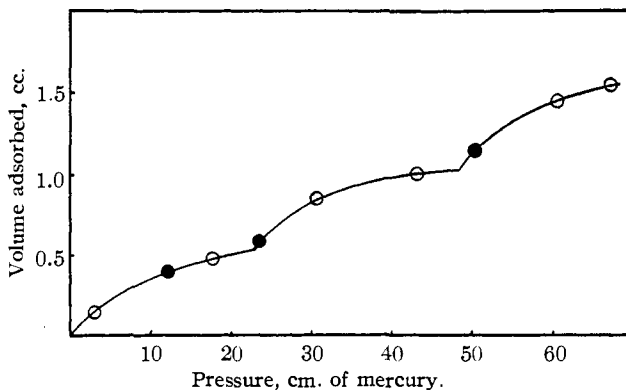


Fig. 5.—Adsorption of nitrogen by iron at -78.5° .

from a single, smooth curve is only about twice the estimated maximum experimental error, 0.05 cc., nevertheless the regularity of the deviations tends to confirm their real existence. As regards the adsorption of carbon monoxide and nitrogen at lower temperatures, it is to be noted that under

these conditions the amounts of gas taken up are so large, even at low pressures, that steps of the order of a few tenths of a cc. could be detected only by taking the experimental points extremely close together. In one or two isotherms for gases near their boiling points, particularly that for nitrogen on Iron I at -191.5° , a single, sharp change in the direction of the curve has been found to occur when an amount of gas of the order of 10 or 15 cc. has been adsorbed. However, we hope to show in a later paper that such a single discontinuity is a somewhat different phenomenon from that of the steps here considered, and represents the point at which the surface becomes completely covered with a layer of adsorbed molecules.

Summary of the Experimental Situation

Absolute values for adsorption of gases are subject to several sources of error, the most serious of which are: (1) failure to attain equilibrium, (2) difficulty in obtaining the exact volume of the free space, all of which error falls on the calculated adsorption, which may be relatively small, (3) errors of calibration in measurements of temperature, pressure and volume and (4) the accidental errors of observation. Errors (2) and (3) result in a displacement of an isotherm as a whole, but cannot lead to irregularities of the kind shown in Figs. 1-5. In these cases Error (1) is also negligible since the steps have been observed to occur only under conditions where the adsorption process was practically instantaneous. Evidence that equilibrium was definitely attained may be seen from the fact that the values obtained from higher and from lower pressures agree closely, and further that no measurable change in adsorption occurred when the system was allowed to stand in one case for seventy-two hours. The remaining source of uncertainty, the accidental errors of observation, is estimated not to exceed 0.05 cc.⁵ Since this is much less than the amount by which many of the points deviate from a smooth curve, and since the deviations occur in a regular, rather than accidental, manner, it appears safe to conclude that the steps have a real existence.

It remains to consider the conditions under which the steps occur, since only a minority of the 118 isotherms we have studied give evidence of irregularities. In general, with a given gas and metal, the steps appear at the lower temperatures, and in no case above 0° . More specifically, it may be stated that they occur only where the adsorption is of the physical type. We cannot be certain that the isotherms obtained for adsorption of the chemical, or "activated," type are perfectly smooth, but no evidence to the contrary has been found. In every case where the adsorption was of the physical type, provided only that the quantity of gas taken up was not too large, definite evidence of steps appeared; more detailed investigation of the very large adsorptions occurring at temperatures approaching the

⁵ See description of apparatus given in Ref. 2.

boiling point would in all probability reveal the same phenomenon. The correctness of this view receives support from the fact that Allmand and Burrage,⁴ working with the physical adsorption of vapors by charcoal and silica gel, obtained definite evidence of discontinuities only when an extremely large number of points was taken. It is presumably for this reason that other investigators who have studied adsorption of gases and vapors by solids have not reported discontinuities. The data now existing strongly favor the view that the occurrence of steps is a general characteristic of the process of physical adsorption.

Theoretical Significance of the Discontinuities

Nature of Areas Concerned.—The reduced metals employed in the present work consist of granules of assorted sizes, with an upper limit of 2–3 mm. Microscopic and x-ray analyses have shown that such a granule is an aggregate of minute crystallites. It is obvious that the surface area of such a crystallite, or even of an entire granule, is so small that it is out of the question to ascribe the occurrence of a step, that is, a sudden increase in adsorption of the order of 0.2–0.3 cc., to a single, individual particle. On the contrary, it is necessary to suppose that when a step occurs, a very large number of the particles, probably all of them, take up each a small quantity of gas, abruptly and nearly simultaneously. For if a sudden increase of adsorption occurred at different pressures for different granules, the resulting steps in the isotherm would be immeasurably small, and an apparently smooth curve would result.

Allmand and Burrage⁴ have suggested a tentative explanation of their results in terms of a sudden, local formation of liquid "pools," or of a two-dimensional liquid film. Such an hypothesis might be tenable if it can be shown that these sudden changes from gaseous film to liquid film would each occur at the same pressure for every granule. Nevertheless, the idea of liquid films cannot be a general explanation of step-wise adsorption, since we find steps occurring at temperatures far above the critical temperature of the gas used.

The possibility that the steps represent the successive formation of complete layers over the whole surface of the adsorbent can also be eliminated, because we have definite evidence that our metal surfaces were still incompletely covered with a unimolecular layer of gas even after ten or more steps had occurred. For example, the adsorption of hydrogen by nickel or copper at 0° and one atmosphere, which, being of the chemical type, cannot exceed a unimolecular layer, is far greater than the amount taken up at –183°, although the latter comprises a large number of individual steps.

The occurrence of steps would thus seem to imply the existence of areas of different adsorptive activity. It is now well recognized that the surface

of a solid catalyst exhibits marked variations in catalytic activity and, therefore, probably also in adsorptive activity. The regions of especially high activity have been variously pictured as corners and edges of crystals, as crystal faces with a particular set of indices, as "filamentary projections" from the surface, or as "amorphous patches." However, it appears that none of these suggestions is capable of accounting for the steps, primarily because of the large number and fairly regular sequence of the steps observed. It may also be noted that since catalytic activity is related to the chemical rather than the physical type of adsorption, the catalytically active spots are not necessarily important in physical adsorption.

The Hypothesis of Concentric Rows.—We are thus led to propose a new picture of physical adsorption, which may be called the hypothesis of concentric rows. We believe that the surfaces of the metallic adsorbents employed are composed essentially of plane crystal faces, however fragmentary and intergrown, and that all the faces of given indices are alike in their properties, but differ in size. For a given kind of face, such as cube faces, a step is considered to represent the nearly simultaneous completion, on all such faces, of a row of adsorbed molecules parallel to the edges. The first row formed is thought to be at the edges themselves; thereafter, additional rows form inside and adjacent to one another, until finally the succession of rows reaches the center and the face becomes completely covered.

Before discussing the mechanism by which such a formation of rows could occur, we may examine the data to see how far they support the hypothesis. If each crystal was composed of only one kind of face and if all the faces were of the same size, then the volumes of gas corresponding to successive steps should be nearly, but not quite, equal. A sample made up of large crystals would show a very large number of very small steps, whose magnitude would decrease slowly. A sample of equal weight composed of very minute crystals would exhibit a small number of relatively large steps, and the magnitude of successive steps would decrease more rapidly. Thus for a cubic crystal capable of adsorbing 1000 molecules along an edge, there would be 500 rows, and the number of molecules adsorbed per row would decrease by about 0.4% for successive rows.

Tables I and II give the observed volumes adsorbed for each step that appeared to be definitely completed before the next began. It is evident that for each isotherm the interval between the majority of the clearly defined steps is very nearly constant. Inspection of Figs. 1-5 shows that in a number of cases, especially at low pressures, the experimental points have not been taken sufficiently close together to define the position of all the steps. In such cases, however, the interval between the steps that could be definitely recognized proves to be a simple multiple of the unit step.

TABLE I
 VOLUMES ADSORBED PER STEP BY IRON I

Hydrogen at -195°		Hydrogen at -183°		Nitrogen at -78.5°	
Total vol.	Diff.	Total vol.	Diff.	Total vol.	Diff.
1.44	6×0.24	0.30	(0.30)	0.53	0.53
1.66	.22	0.56	.26	1.02	.49
1.93	.27	0.84 ?	.28	1.56	.54
2.13	.20	1.09	.25		
2.40	.27	1.25	.16		Av., .52
2.66	.26	1.50	.25		
2.86	.20	1.69	.19		
3.10	.24	1.87	.18		
3.36	.26	2.06 ?	.19		
	Av., .24		Av., .23		

 TABLE II
 VOLUMES OF HYDROGEN ADSORBED PER STEP BY Cu II AND Ni III

Cu at -195°		Cu at -183°		Ni at -183°	
Total vol.	Diff.	Total vol.	Diff.	Total vol.	Diff.
2.11	6×0.35	1.12	(3×0.37)	2.83	(9×0.32)
3.25	3×0.38	1.70	2×0.29	3.16	.33
3.59	.34	2.35	$2 \times .33$	3.41	.25
3.95	.36	2.80 ?	} $3 \times .34$	3.70	.29
4.33	.38	3.36		4.02	.32
4.68	.35	3.76 ?	} $2 \times .32$	4.63	$2 \times .31$
5.05	.37	4.00			
	Av., .36	4.39	Av., .39		Av., .30
		Av., .33			

In the case of both copper and nickel at -183° (Table II), the evidence that the steps are uniform is somewhat doubtful, particularly at the lower pressures. The reason is probably to be found in the fact that in both cases the adsorption is not entirely of the physical type. At somewhat higher temperatures chemical adsorption of hydrogen by both metals readily takes place, and even at -183° a slight adsorption of this type occurs on the most reactive parts of the surface. At -195° the adsorption appears to be entirely of the physical type in all cases, and here the evidence that the steps represent equal increments of volume is especially strong.

It may readily be shown that the magnitude of the steps observed, as well as the negligible decrease in successive steps, requires that the individual crystals be of a size which existing information indicates to be probable. Thus, if l represents the length of the edge of a cubic crystal, and d the effective diameter of an adsorbed molecule, then the volume of gas adsorbed by the six faces of this crystal in a single step is $6 \times 4 \times (l/d) \times 22400/(6.06 \times 10^{23})$. If the crystals are assumed to be uniform in size, the number in a sample of adsorbent of weight W and density ρ is $W/\rho l^3$. Hence, the total adsorption per step is $(24 \times 22400l)/(6.06 \times 10^{23}d) \times$

$(W/\rho l^3)$. Since W and ρ are of the same order of magnitude for all three metals, we may take Iron I as a typical example, for which $W = 54.6$ and $\rho = 7.90$. The effective diameter, d , of a hydrogen molecule may be taken to be approximately the same as the average separation of the molecules in liquid hydrogen, namely, 3.6×10^{-8} cm. Employing these values, and taking the observed adsorption per step as 0.24 cc., we find for the length of the cube edge, $l = 0.27\mu$. This means 750 molecules adsorbed along a cube edge. It is evident from this that for the first ten or fifteen steps, no measurable decrease in adsorption per step would be observed.

As to the effect of temperature on the magnitude of the steps, it might be expected that a slight decrease would be observed as the temperature was raised. The data shown in Tables I and II, while covering only a narrow range of temperature, tend to support this expectation.

It is significant that steps were still present after sintering Copper II (Fig. 3, Curve 4), although the treatment given is known⁶ to eliminate the catalytic activity almost completely. However, the height of the steps actually observed was decreased, as would be the case if sintering has the effect of increasing the average size of the crystals.

For adsorbents in general it must be expected that the relations will not always be so simple as those here observed. Thus the presence of more than one kind of crystal face will give rise to steps of different magnitudes. Again, a wide variation in crystal size will produce complications because the larger crystals could continue adsorbing gas after the smaller ones had taken up enough rows to cover their entire surface. Because of the intrusion of this latter effect at higher pressures, it does not appear profitable to attempt to calculate from the size of an individual step the total adsorption corresponding to a unimolecular layer.

It may be that these complications are responsible for the failure of Allmand and Burrage to note any definite sequence in the volumes corresponding to the successive breaks in their curves. A further difficulty is that in many cases the formation of a particular step began before the previous one was complete. Nevertheless, if the numerous minor irregularities in their curves are disregarded, as possibly due to experimental error, and only the major, definite breaks considered, a number of their isotherms may be seen to give marked evidence of a uniform succession of steps.⁷

Mechanism of Adsorption in Rows.—It is clear that the ordinary exchange of condensation and evaporation on a uniform surface could lead to adsorption in steps only in case neighboring adsorbed molecules evaporate less readily than those which are isolated from one another. In this case a row of molecules once formed around the edges, adjacent to rows

⁶ Pease, *THIS JOURNAL*, **45**, 2298 (1923).

⁷ See, for example, Ref. 4(a), Figs. 2, 5, 7.

previously formed, would be more stable than the same molecules distributed at random over the surface. However, unless the difference in stability is very great, or unless additional factors are involved, sharp discontinuities in adsorption would not be anticipated. An additional factor of great importance is to be found in the mobility of adsorbed molecules in the plane of the surface. While there is good evidence that in adsorption of the chemical type such mobility is frequently absent, the experiments of Volmer and others,⁸ as well as the accepted view of the forces involved, indicate that this property is a general characteristic of adsorption of the physical type. As a result of this mobility, molecules condensing at random on the surface can quickly find the most stable location available. When the pressure is gradually increased after a given row has been completed, there is at first no appreciable increase in adsorption, because the molecules entering the last completed row either themselves evaporate or take the place of those which were previously members of the row, but which also evaporate from time to time. Finally, at a given pressure, a sufficient number of molecules collect at some point to start the nucleus of another row, which is then rapidly completed over a short range of pressure.

It appears that our hypothesis, in fact any hypothesis capable of accounting for a regular progression of steps in the volumes adsorbed, would involve some regularity also in the pressures at which successive steps occur. Figures 1-5 indicate that in general the differences between these "critical" pressures increase somewhat uniformly with increasing adsorption. It must be recognized that these pressures have not been located with certainty, and the curves between steps have necessarily been drawn in a rather arbitrary manner. Nevertheless, in a few cases it is obvious that the sequence of pressures is not regular. It is possible that these irregularities are due to the presence of more than a single kind of crystal face.

Heat of Adsorption.—From the Clausius-Clapeyron equation it is possible to calculate from our data rough values of the heat of adsorption corresponding to some of the various steps. Tables III and IV give the results of such calculations for hydrogen on Iron I and Copper II, respectively. Here p_1 and p_2 are the pressures in equilibrium with V cc. of adsorbed gas at -195 and -183° , respectively, and Q is the differential heat of adsorption in calories per mole, when V cc. has already been adsorbed. These values may be contrasted on the one hand, with the heat of vaporization of hydrogen at the boiling point, which is about 230 cal., and on the

⁸ Volmer and Estermann, *Z. Physik*, **7**, 13 (1921); Volmer, *Z. physik. Chem.*, **102**, 267 (1922); **115**, 253 (1925); Volmer and Adhikari, *ibid.*, **119**, 46 (1926); Adhikari and Felman, *ibid.*, **131**, 347 (1928). Allmand and Burrage⁴ have included the concept of mobility in their discussion of discontinuous adsorption.

TABLE III

HEAT OF ADSORPTION OF HYDROGEN BY IRON I IN THE TEMPERATURE RANGE, -195 TO -183°

V	p_1	p_2	Q
1.60	94	370	1590
1.80	110	490	1740
2.00	165	550	1400

TABLE IV

HEAT OF ADSORPTION OF HYDROGEN BY COPPER II IN THE TEMPERATURE RANGE, -195 TO -183°

V	p_1	p_2	Q
1.50	65	60	-90
2.00	90	125	380
2.50	113	228	820
3.10	180	320	670
3.50	245	420	630
3.85	320	480	470
4.25	370	530	420

other, with the heats of chemical adsorption of hydrogen by these metals near room temperature, which are of the order of 10,000-20,000 cal.⁹

The low values of Q obtained for the first part of the adsorption on Copper II are believed to be connected with the fact already mentioned, that at -183° some of the adsorption of hydrogen by this sample is of the chemical type and, therefore, not comparable with the purely physical adsorption at -195° . The falling off of Q when the amount of adsorption is larger seems to be a real effect, since here the values are probably correct to about 100 cal.

Adsorption in Presence of Poisons.—Since carbon monoxide is held by these metals at -183° by adsorption of the physical type, it is assumed that in the experiments in which this gas was used as a "poison," the monoxide formed a series of rows adjacent to the crystal edges. The hydrogen which was subsequently admitted would be expected to continue this row formation where the monoxide left off. Thus the curve for the poisoned adsorption would be very similar to that for hydrogen alone, but with a certain number of steps eliminated, depending on the amount of poison used. Our curves lend considerable support to this view, but it appears necessary to make the assumption that hydrogen can also be adsorbed on top of the monoxide. This would account for the fact that the curves tend to approach one another at the higher pressures. A more detailed consideration of the effects produced by carbon monoxide does not seem justified, in view of the complications which may arise from the slight chemical adsorption of hydrogen at -183° . It has previously been shown¹⁰ that at

⁹ See, for example, Beebe and Taylor, *THIS JOURNAL*, **46**, 43 (1924); Kistiakowsky, Flösdorf and Taylor, *ibid.*, **49**, 2200 (1927).

¹⁰ Griffin, *THIS JOURNAL*, **49**, 2136 (1927); White and Benton, *J. Phys. Chem.*, **35**, 1784 (1931).

0°, where the adsorption of hydrogen by reduced nickel and copper is practically entirely of the chemical type, small quantities of carbon monoxide actually increase the adsorption of hydrogen.

When hydrogen is physically adsorbed at low temperatures on a copper surface which has previously been largely covered with a layer of chemically adsorbed hydrogen (Fig. 2, Curve 3), steps are obtained, but in this case they are convex downward. Whatever may prove to be the explanation of this altered flexure, it is possible that it is a general characteristic of adsorption in multimolecular layers, since our isotherms for nitrogen and carbon monoxide at -183° , although showing no clear evidence of steps, nevertheless tend to become convex downward when the adsorptions are large.

Summary

In a study of the adsorption of gases by nickel, copper and iron, a considerable number of new examples of discontinuous isotherms have been found. The effects on the discontinuities of temperature, poisons, and heat treatment of the adsorbent have been investigated.

Evidence is presented to show that a step-wise increase of adsorption with pressure is a general characteristic of the physical type of adsorption. It is shown that the steps may occur under conditions which preclude the existence of liquid films or even of multimolecular layers of gas and, further, that the phenomenon has no direct relation to the "active spots" of catalytic theory.

A new hypothesis of physical adsorption is proposed, according to which the observed steps represent the formation of concentric rows of adsorbed molecules, first at the edges of each crystal face, and building up successively toward the center. The hypothesis is shown to be supported by the known facts. The mechanism of adsorption in rows offers no difficulty if it is assumed that neighboring adsorbed molecules evaporate from the surface less readily than isolated molecules, and that physically adsorbed molecules possess mobility in the plane of the surface.

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