

heat capacities of aqueous solutions of lithium chloride, hydrogen chloride and potassium hydroxide at 25°. The solutions have been investigated from a concentration of 0.01 or 0.04 *m* to a concentration of 2 to 2.5 *m*, with a precision of about 0.01%.

The apparent molal heat capacity of the solutes plotted against the square root of the molality shows the important linear relation announced by Randall and Ramage and confirmed by Randall and Rossini: in the case of lithium chloride solutions over the whole concentration range and in the case of the other solutions *above* about 0.2 *m*. In the range *below* this concentration, however, the apparent molal heat capacity shows a sudden *increase* which has not been noted before. This throws some doubt on the validity of extrapolation to infinite dilution. Work is now in progress in this Laboratory to see if this behavior is shown by other solutions.

The partial molal heat capacities of the solute and those of the solvent have been calculated and are presented in graphs and tables.

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THE SORPTION OF GASES BY COPPER

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Introduction

The numerous researches of recent years on the adsorption of gases by solids possessing catalytic activity have brought to light many cases in which gas is extensively and strongly adsorbed at relatively high temperatures and low pressures, where the older idea of adsorption as merely an increased concentration of ordinary molecules at the solid surface would predict that little or no gas would be taken up. These anomalous adsorptions were variously described as "selective," "irreversible," "chemical," etc. Nevertheless the idea persisted that such processes differed only in degree from "physical" adsorption,² and that no sharp distinction could be drawn.

As a result of an extensive investigation of the adsorption of gases by oxide catalysts, Benton³ proposed the view that the two kinds of adsorption could be sharply differentiated, and that the total adsorption by active solids was the sum of the amounts of gas taken up in the two different ways.

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² See, for example, Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 2d ed., p. 193 (1929).

³ Benton, THIS JOURNAL, 45, 887, 900 (1923). This work was carried out in the Princeton Laboratory, with the cooperation and advice of Professor H. S. Taylor.

A simple method was found for estimating these separate quantities, based on a comparison of the adsorption ratios of pairs of gases by a number of surfaces of widely differing catalytic activity.

Definite proof of the separate existence of the two types of adsorption was obtained by Benton and White⁴ in the system nickel-hydrogen. They found that the physical adsorption occurring at low temperatures decreased rapidly from -210 to -183° ; at higher temperatures this type was superseded by "chemical," or "activated" adsorption, characterized by very strong binding forces. Subsequently, the same phenomena were observed in other systems.⁵

Taylor⁶ has recently presented an extensive survey of the available information on activated adsorption, and has particularly emphasized the slow rate of this process and the increase of rate with temperature, as interpreted in terms of an "activation energy" of adsorption. While a slow rate, increasing with temperature, is a very important characteristic of activated adsorption, as distinguished from the physical type, rate alone does not distinguish it from other slow processes, such as compound formation and solubility. Some workers, overlooking the fact that activated adsorption may often be recognized by a characteristic type of equilibrium, high heat of adsorption, etc., independently of rate phenomena, have attempted to interpret all such slow processes as solubility, and have thus been led to question the existence of activated adsorption.⁷

The present paper contains the results of an extended investigation of the adsorption of nitrogen, hydrogen and carbon monoxide by two samples of reduced copper, at pressures up to one atmosphere and at temperatures extending down to 78°K . Although the adsorption of nitrogen under the conditions studied is purely of the physical type, hydrogen exhibits all three of the processes mentioned above, namely, physical adsorption, activated adsorption and solubility. The amounts of hydrogen taken up in each of the three ways have been separately determined. Carbon monoxide also shows three different processes, two of which are readily distinguishable as physical and activated adsorption. The third process is provisionally regarded as solution, but may well be a second type of activated adsorption.

Numerous studies of the sorption of gases by copper have previously been reported, among which may be mentioned the solubility measurements of Sieverts⁸ at high temperatures, and the sorption experiments of

⁴ Benton and White, *THIS JOURNAL*, **52**, 2325 (1930).

⁵ Garner and Kingman, *Nature*, **126**, 352 (1930); Taylor and Williamson, *THIS JOURNAL*, **53**, 2168 (1931); Taylor and McKinney, *ibid.*, **53**, 3604 (1931).

⁶ Taylor, *ibid.*, **53**, 578 (1931).

⁷ Steacie, *J. Phys. Chem.*, **35**, 2112 (1931); Ward, *Proc. Roy. Soc. (London)*, **A133**, 506, 522 (1931).

⁸ Sieverts, *Z. physik. Chem.*, **77**, 591 (1911).

Taylor and Burns,⁹ Pease,¹⁰ Griffin¹¹ and Ward.⁷ None of these investigations has extended to temperatures below 0°.

Experimental Procedure and Materials

The procedure consisted in admitting a known volume of gas to an evacuated bulb containing the adsorbent and noting the pressures produced as a function of time until equilibrium was approximately reached. Then a further quantity of gas was introduced and the process repeated until equilibrium pressures of approximately one atmosphere were reached. Frequently this procedure was reversed, the pressure being observed after withdrawal of a portion of gas from the bulb.

The quantity of gas adsorbed at any time was obtained by subtracting from the total volume admitted the volume of unadsorbed gas in the free space. The latter was determined directly by measurements with carefully purified helium at a series of temperatures down to -78.5°. For temperatures below -78.5° the volume of gas in the free space was obtained by calculation from the experimental values at each of the higher temperatures. The close concordance of the values so calculated shows that helium is not appreciably adsorbed above -78.5°. The apparatus has been previously described.⁴ No stopcocks were employed in the part of the apparatus communicating with the adsorbent.

Two samples of copper were employed. Both were prepared by reduction of the oxide with hydrogen *in situ*, 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 Cu I and Cu II.

Between successive "runs" the adsorbent was evacuated with a Töpler pump for two hours, at 200° for Cu I, and 170° for Cu II.

A considerable proportion of the experiments consisted of check runs designed to test the reproducibility of the results. No change was found to occur in Cu II, check runs as much as six months apart giving values in close agreement. The reproducibility was less satisfactory for Cu I, and accordingly the data obtained for this sample will be used only in confirmation of the results obtained with Cu II.

All volumes are given in cc. at 0°, 760 mm., and all pressures in mm. of mercury at 0°.

Results with Nitrogen

The isotherms obtained for nitrogen on Cu II are shown in Fig. 1, Curves 1, 2, 3. Curve 1a shows on a reduced scale the complete isotherm at -183°, the first part of which is given in Curve 1. Here as elsewhere in this paper points designated by open circles, triangles, etc., were obtained by proceeding from lower to higher pressures; solid black symbols indicate the reverse process. It was found in all experiments with nitrogen that equilibrium was established practically instantaneously, as shown by the fact that the first pressure reading, taken two to three minutes after admitting the gas, remained unchanged as long as twenty hours. Because of the absence of drift in the work with nitrogen, it was not considered important to approach equilibrium from both sides; where this was done, however, it will be seen that the values are in close agreement.

⁹ Taylor and Burns, *THIS JOURNAL*, **43**, 1273 (1921).

¹⁰ Pease, *ibid.*, **45**, 2296 (1923).

¹¹ Griffin, *ibid.*, **49**, 2136 (1927).

It is evident that the effects of pressure and temperature on the adsorption of nitrogen by copper are qualitatively similar to the results so frequently obtained in the adsorption of gases by charcoal and silica. The observed phenomena are typical of *physical*, or molecular, adsorption. Thus, (1) equilibrium is reached from either side practically instantaneously, (2) the isotherms do not appear to approach a saturation limit, (3) there is no adsorption at "zero" pressure, (4) at temperatures far

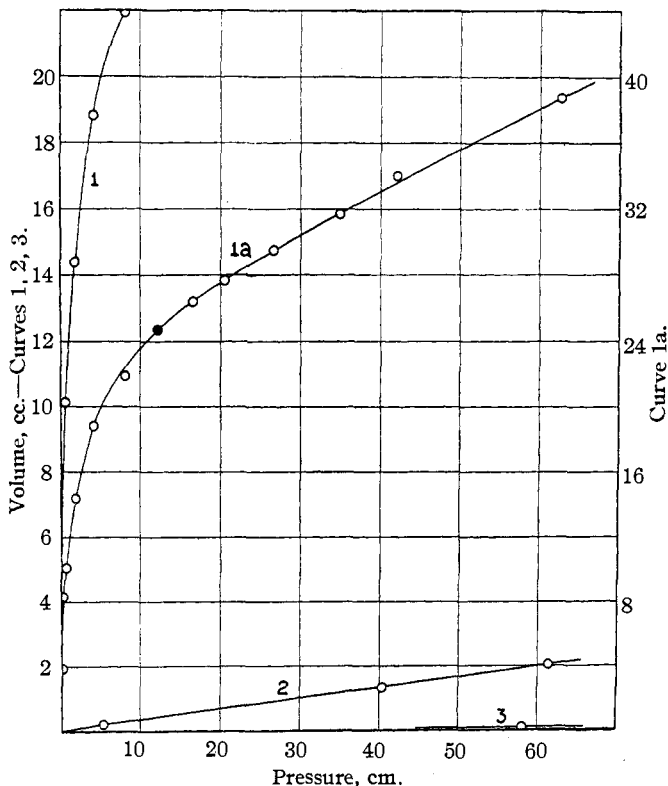


Fig. 1.—Isotherms for nitrogen: Curves 1 and 1a, -183° ; Curve 2, -78.5° ; Curve 3, 0° .

above the boiling point of nitrogen, the adsorption is approximately proportional to the pressure, (5) the adsorption at a given pressure decreases uniformly with rising temperature, (6) the heat of adsorption is relatively small. In the present case rough values of the heat of adsorption have been calculated from the Clausius-Clapeyron equation as follows. From an equation of the form $V = kp^{1/n}$, which agrees well with the data in the low-pressure part of Curve 1a, it was found that an adsorption of 2.0 cc. at -183° corresponds to a pressure of 0.0113 mm. By comparison of this value with the 604 mm. pressure in equilibrium with

2.0 cc. at -78.5° , the heat of adsorption was found to be 3600 cal. per mole. Another value was obtained by extrapolating Curve 2 on the assumption that at -78.5° the volume remains proportional to the pressure up to an adsorption of 10 cc., and comparing the pressures corresponding to this volume at the same two temperatures. The value thus obtained is 2100 cal. It may be concluded that the heats of adsorption on different parts of the copper surface range roughly from 4000 to 2000 cal., values which are, respectively, only three and one and one-half times the latent heat of vaporization of nitrogen at the boiling point (1380 cal.).

Results with Hydrogen

Isotherms at Low Temperatures.—The values obtained for hydrogen on Cu II. at low temperatures are shown in Fig. 2. If we omit from consideration the discontinuities in the adsorptions at -195 and -183° , a

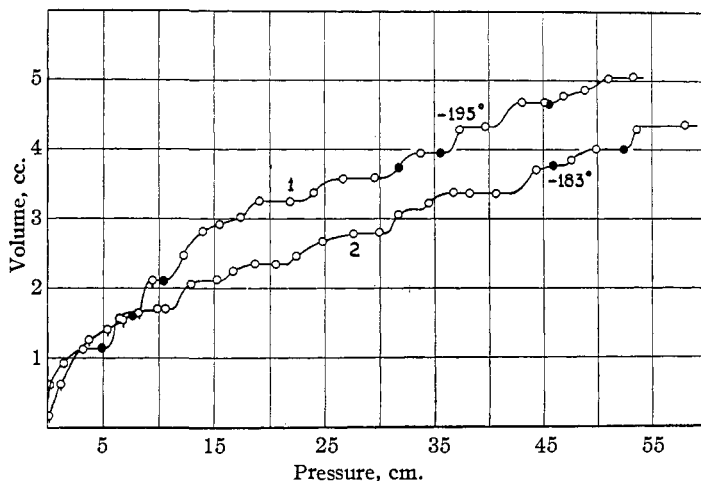


Fig. 2.—Isotherms for hydrogen at low temperatures.

detailed discussion of which has already been presented,¹² the curves at these two temperatures show all the ordinary characteristics of the physical type of adsorption. In both cases equilibrium was established practically instantaneously, and the values obtained were completely reversible, as may be seen from the close agreement of points obtained from higher and from lower pressures. Also, the adsorptions continue to increase rapidly with increasing pressure, without giving evidence of any approach to a saturation limit; at -183° the volume is nearly a linear function of the pressure. In general, the adsorption decreases with rising temperature, giving a heat of adsorption, as already reported,¹² of about 800 cal. for an adsorption of 2.5 cc., which falls to about 400 cal. as the volume

¹² Benton and White, *THIS JOURNAL*, **53**, 2807, 3301 (1931).

taken up increases to 4.25 cc. Heats calculated for the first 1 or 2 cc. have no significance, since at -183° a slight adsorption, about 0.5 cc., occurs at "zero" pressure; this 0.5 cc., as will be shown below, is definitely to be attributed to adsorption of the chemical, or activated type, and hence is not comparable with the purely physical adsorption at -195° .

In an earlier experiment at -183° an isotherm was obtained which shows no adsorption at zero pressure, and which lies quite uniformly 0.5 cc. below Curve 2 of Fig. 2. It appears that for some reason the 0.5 cc. of activated adsorption did not occur in this case. The explanation is probably found in the fact that here the evacuated adsorbent was cooled for a longer period at -183° before the first admission of gas. While too few points were taken to trace out the detailed course of the isotherm, a heat of adsorption can be calculated from each observed point in conjunction with the corresponding point at -195° , as interpolated from Curve 1. The values thus obtained are listed in Table I.

TABLE I

HEAT OF PHYSICAL ADSORPTION OF HYDROGEN BY COPPER II			
Vol. adsorbed	p at -195°	p at -183°	Q
0.56	9	27.1	1280
.83	18	64.7	1490
1.46	60	133.6	930
1.70	85	168.7	800
2.29	114	265.4	980
2.58	125	332.6	1140
3.33	229	421.4	710
3.54	255	486.6	750
3.68	315	508.7	560

It may be concluded that the heat of adsorption for the first few cc. of hydrogen is not far from 1000 cal. per mole. The latent heat of vaporization of hydrogen is about 220 cal. at the boiling point.

Isotherms at Higher Temperatures.—The adsorptions of hydrogen by Cu II at -78.5 and 0° are shown in Fig. 3, Curves 1 and 2. One of the most striking differences between these results and those given in the last section is that here equilibrium is approached with great slowness. In spite of the fact that for each point the pressure appeared to become constant after six to eight hours, it is clear that final equilibrium was not attained, since points obtained from the side of higher pressure give larger adsorptions than those obtained from the side of lower pressure. Nevertheless, the differences are not so great as to leave the general course of the isotherms in doubt. The curve at -78.5° is made up from all the points obtained in different runs; it was found that the longer the time of observation, the more closely Curve 1 was approached.

It is obvious that the process occurring at these temperatures differs

markedly from that at low temperatures. In addition to the great difference in rate, it is to be noted that here the isotherms tend to become comparatively flat at higher pressures, and that there is a large adsorption at zero pressure. Much more gas is taken up than at the low temperatures.

The results with Cu I completely paralleled those obtained with Cu II, except that in the former case the adsorptions were always smaller by a factor of about four.

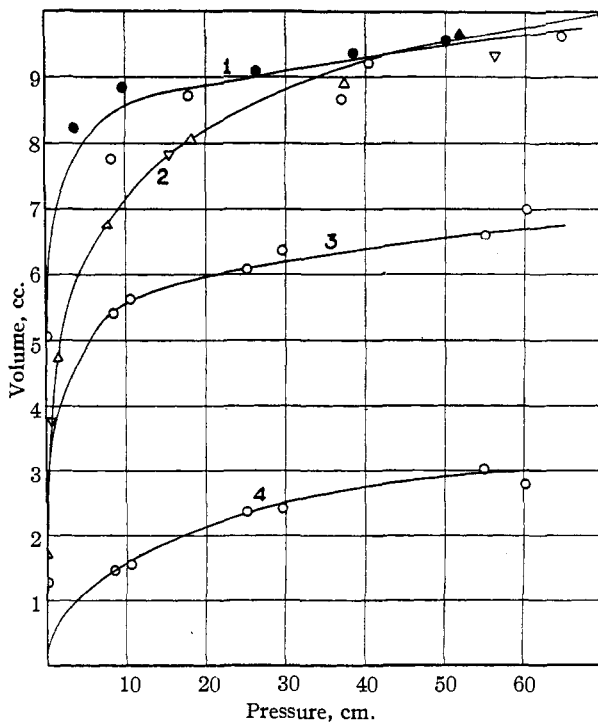


Fig. 3.—Isotherms for hydrogen: Curve 1, total sorption at -78.5° ; Curve 2, total sorption at 0° ; Curve 3, activated adsorption at 0° ; Curve 4, solution at 0° .

Experiments with Temperature Variation.—With the adsorbent at -78.5° hydrogen was admitted and allowed to reach approximate equilibrium, 9.00 cc. being taken up at a pressure of 517.7 mm. In this condition the system was then cooled to -183° and an isotherm obtained at the latter temperature. It was found that the adsorption showed no tendency to decrease to the ordinary values at -183° , but on the contrary an immediate increase occurred. The excess over the 9 cc. originally present was nearly as great as the entire adsorption obtained directly at the low temperature. This experiment further shows that hydrogen is held at the higher temperature in a way fundamentally different from the physical

adsorption at -183° , and that the physical adsorptive capacity of the copper is somewhat, but not greatly, decreased by the presence of the large adsorption of the high temperature type, which remains on the surface upon cooling to the low temperature.

Similar experiments carried out between -78.5 and 0° reveal an entirely new situation. The procedure employed was as follows. The adsorbent was brought to approximate equilibrium with hydrogen at a given pressure at -78.5° , and the system was then brought to 0° as rapidly as possible. In this process it was observed that the pressure increased to an extent greater than could be accounted for by the change in temperature of the gas in the free space, indicating a considerable desorption of gas from the copper. In fact, the amount remaining adsorbed was much less than the equilibrium value at 0° . However, this large increase of pressure was followed by a slow decrease, which continued until the amount of gas taken up was approximately equal to the amount taken up in an ordinary experiment at 0° . On then cooling to -78.5° it was found that the adsorption increased to a value considerably higher than the original adsorption at this temperature, and this increase over the original value at -78.5° was approximately equal to the amount which had been slowly taken up at 0° . On again warming to 0° , the adsorption did not again pass through a minimum, but returned to approximately the usual value at 0° .

The results of this series of experiments are collected in Table II. The values given in Rows (3) and (7) are taken directly from Curves 2 and 1, Fig. 3.

TABLE II
EFFECT OF CHANGING TEMPERATURE ON SORPTION OF HYDROGEN BY CU II

	Run no.	30	34	32
(1) Gas taken up at -78.5°	Pressure	35.9	178.4	403.7
	Volume	8.23	8.72	9.21
(2) Initial values after warming to 0°	Pressure	105.0	295.6	602.3
	Volume	5.64	6.37	7.00
(3) Total sorption at 0° at pressures given in (2)		7.20	8.80	9.80
(4) Difference of (2) and (3)		1.56	2.43	2.80
(5) Final values reached at 0°	Pressure	84.5	251.3	550.2
	Volume	6.59	8.40	9.40
(6) After cooling to -78.5°	Pressure	22.5	139.7	355.3
	Volume	9.07	11.18	12.23
(7) Direct values at -78.5° at press. given in (6)		7.60	8.80	9.20
(8) Difference of (6) and (7)		1.47	2.38	3.03

Solubility of Hydrogen.—In interpreting the facts shown in Table II it is necessary first to establish the source of the gas evolved in passing from -78.5 to 0° . The obvious possibility that this represents the normal decrease in the amount of gas *physically* adsorbed at -78.5° may be eliminated by the following reasoning. From the heat of physical ad-

sorption of hydrogen by Cu II, which was found above to be roughly 1000 cal. per mole, it is possible to calculate from each observed point at the low temperatures the pressure which would be in equilibrium with the same physical adsorption at -78.5 and at 0° . In this manner an isotherm can be constructed for the physical adsorption at each of these temperatures. The following values were thus obtained: for $p = 600$ mm., $V = 0.66$ cc. at -78.5° and 0.44 cc. at 0° ; for $p = 300$ mm., $V = 0.44$ cc. at -78.5° and 0.31 cc. at 0° . Thus, at the highest pressure shown in Table II, the maximum amount of physically adsorbed gas which could be evolved in passing from -78.5 to 0° would be 0.22 cc., an amount which is almost negligible in comparison with the 2.8 cc. which was found actually to be evolved.

The assumption is justified, therefore, that the gas given up on warming to 0° is almost entirely composed of gas which was adsorbed in the activated form at -78.5° . The fact that after reaching 0° gas ceased to be evolved and resorption occurred, *shows clearly that a third kind of process takes place*. There can be little doubt that this represents a slow transfer of hydrogen into the interior of the copper. On cooling to -78.5° this dissolved gas is unable to escape and remains "frozen" in the solid. At the same time, however, the activated adsorption on the surface resumes its normal value at -78.5° , so that the total "sorption" is greater than that originally obtained at this temperature.

If we assume for the moment that no solution occurs in an experiment carried out wholly at -78.5° , then the values shown in Row (2) of Table II represent the actual adsorptions at 0° , while the differences in Row (4) are the volumes of gas dissolved at 0° at the pressures shown in Row (2). Similarly, the differences in Row (8) represent the volumes dissolved at 0° at the pressures given in Row (5). The values in Rows (3) and (5) are the sums of the adsorption and solution at 0° .

The amounts of gas dissolved at 0° , as given in Rows (4) and (8), have been plotted as Curve 4 of Fig. 3. It is not surprising to find that the volumes dissolved are approximately proportional to the square root of the pressure, a rule which has been found to hold for practically all measurements of the solubility of gases in solids.

When the dissolved gas is subtracted from the total taken up at 0° , Curve 3 of Fig. 3 is obtained, representing the actual adsorption at 0° plus any slight solution which may occur at -78.5° . The fact that Curves 1 and 3 are parallel to each other strongly suggests that there is in fact a slight solution at -78.5° . It is most probable that if this slight solubility, in amounts proportional to the square root of the pressure, were subtracted from Curves 1 and 3 to give the true adsorptions at -78.5 and 0° , both isotherms would reach definite saturation limits at pressures of 100 – 200 mm.

Activated Adsorption of Hydrogen.—The foregoing results show that when the solubility of hydrogen is subtracted from the total sorption, there remains an activated adsorption at -78.5 and at 0° , in comparison with which the physical adsorptions are almost negligibly small. The isotherms for activated adsorption are characterized by a large adsorption at very low pressures, and by a tendency to approach an early saturation limit.

A further distinguishing feature of activated adsorption is the comparatively slow rate at which equilibrium is established. In illustrating this point it is essential to select data obtained under conditions where the activated adsorption is not accompanied by the slow process of solution. Such conditions exist in the case of values obtained at very low pressures, and for the observations made after reaching equilibrium at 0° and then cooling to -78.5° . As representative of the rates observed under these conditions, Table III shows the rate data for (a) a low-pressure point at -78.5° , (b) a low-pressure point at 0° and (c) a point obtained at -78.5° after cooling from 0° . The values shown for zero time are the amounts taken up at the preceding point.

TABLE III
RATE OF ACTIVATED ADSORPTION OF HYDROGEN

(a) -78.5°			(b) 0°			(c) -78.5°		
Time, hrs.	P , mm.	V , cc.	Time, hrs.	P , mm.	V , cc.	Time, hrs.	P , mm.	V , cc.
0	..	1.27	0	..	1.70	0	...	9.40
0.05	30.0	3.27	0.03	25.0	4.18	0.05	362.1	11.80
0.10	20.0	3.90	0.45	18.3	4.49	0.30	360.3	11.91
0.72	7.5	4.69	4.03	14.8	4.65	1.88	358.8	12.01
2.97	3.9	4.91	5.03	14.0	4.69	6.38	355.6	12.21
4.63	2.7	4.99	5.70	14.0	4.69	8.05	355.3	12.23
5.80	2.0	5.03				9.63	355.3	12.23

It is evident that at -78.5° activated adsorption is a very slow process. At comparable pressures the rate is much faster at 0° , all but a few tenths of a cc. being taken up almost instantaneously. Comparison of (c) with (a) indicates that for values not too near equilibrium the rate at -78.5° is greater at higher pressures.

In Fig. 4 are shown a few of the data obtained for rates at higher pressures, both at -78.5° (Curves 1 and 2) and at 0° (Curves 3, 4, 5). The values given for zero time are the volumes taken up at the previous point. It is seen that in certain ranges hydrogen appears to be taken up *much more slowly at 0 than at -78.5°* . Closer observation shows, however, that the curves at -78.5° give a gradual and uniform decrease of rate, indicative of the single process of activated adsorption (solubility being practically negligible at this temperature), whereas at 0° two different processes are clearly disclosed, a very rapid activated adsorption, and a slow solution.

No attempt will be made in this paper to determine the various rates

as functions of pressure, temperature, amounts already sorbed, etc. It may be remarked, however, that when volume is plotted against the square root of the time, as in Fig. 4, the solution process yields lines which are nearly straight over a considerable range.

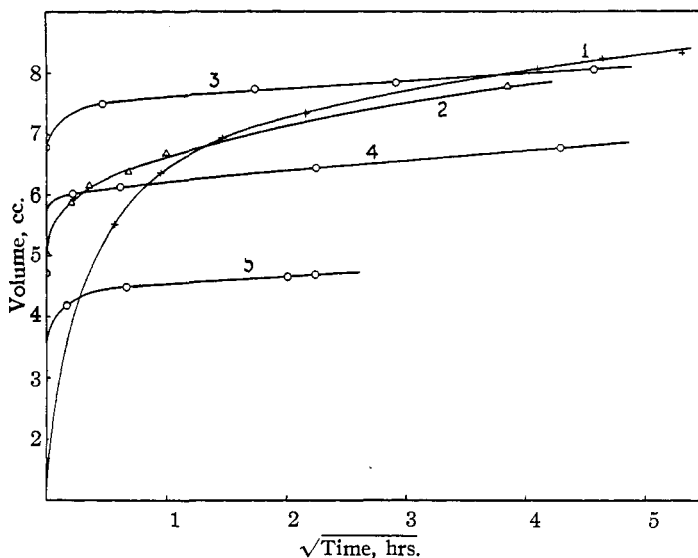


Fig. 4.—Rate of sorption of hydrogen: Curves 1 and 2, -78.5° ; Curves 3, 4 and 5, 0° .

Isobars for Hydrogen.—The interrelationship of the solution process and the two types of adsorption on Cu II is brought out by Fig. 5, which represents the 500 mm. isobars for physical adsorption (Curve 2), for activated adsorption (Curve 3), and for the amount of solution which actually occurred in these experiments (Curve 4), which probably does not represent equilibrium. Curve 1, which is the sum of Curves 2, 3 and 4, gives the total sorptions observed experimentally.

Results with Carbon Monoxide

Isotherms.—The data obtained for the isothermal adsorption of carbon monoxide by Cu II are plotted in Fig. 6, Curves 1, 2, 3, 4. Curve 1a shows on a reduced scale (at the right of the figure) the complete isotherm at -183° , the first part of which is given in Curve 1. The rate of adsorption at -183° was very rapid, a constant pressure being obtained within a few minutes after the admission of gas. Points approached from higher pressures agree well with those obtained from the side of lower pressure. At -78.5° (Curve 2) the rate was also rapid, and the points for adsorption and desorption are in satisfactory agreement. At 0° the major part of the

gas was adsorbed almost instantaneously, but this was followed by an extremely slow process in which small additional quantities of gas were taken up. The sum total of these small quantities for all the points amounted to 0.4 cc. Seven days were needed to complete the isotherm as shown in Curve 3. Although the final pressure at each point remained apparently constant for four to six hours, and the points obtained from

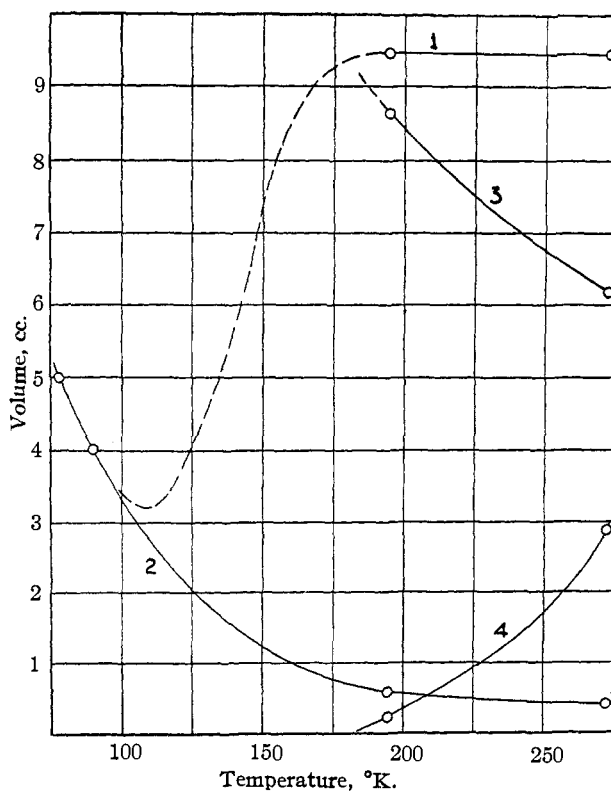


Fig. 5.—Isobars for hydrogen at 500 mm.: Curve 1, total sorption; Curve 2, physical adsorption; Curve 3, activated adsorption; Curve 4, solution.

higher and lower pressures agree well, it is possible that further sorption would have occurred if the times of observation had been greatly extended. At 110° there was again an almost instantaneous sorption, followed by a slow process. Here the slow process was considerably more rapid than at 0°, it involved much larger quantities of gas and equilibrium was definitely not reached even, in one case, after 280 hours. Of the 14.4 cc. taken up at the highest point in Curve 4, Fig. 6, about 7.0 cc. is accounted for by the slow process. The amounts taken up rapidly at 110° are plotted in Curve 5. Typical rate data are given in Table IV for some of the points at 0

and 110°. The values given for zero time are the final amounts taken up at the previous point.

TABLE IV
RATE OF SORPTION OF CARBON MONOXIDE

0°				110°			
Time, hr.	P, mm.	V, cc.	Rate, cc./hr.	Time, hr.	P, mm.	V, cc.	Rate, cc./hr.
0	...	0	..	0	...	0	..
0.05	0	1.23	..	0.05	2.0	1.82	36
0	...	4.98	..	0.80	1.3	1.84	0.03
0.03	26.0	9.23	140	1.9	1.3	1.84	0.00
0.82	25.0	9.28	0.064				
3.83	24.0	9.33	.017				
20.0	23.5	9.35	.001	0	...	1.84	..
27.0	23.0	9.37	.003	0.02	50.6	4.68	140
33.0	23.0	9.37	.000	0.92	43.0	4.94	0.29
0	...	10.69	..	17.2	16.5	5.81	.053
0.08	377.0	11.36	8	25.2	12.5	5.95	.018
16.7	376.0	11.41	0.003	39.9	8.5	6.08	.009
24.4	375.0	11.46	.006	63.7	6.0	6.16	.003
36.2	374.8	11.47	.000	72.7	5.0	6.19	.003
41.4	374.9	11.46	.000	90.7	4.3	6.22	.002
				95.9	4.0	6.23	.002
110°							
0	...	6.23	..	117.3	212.5	12.95	0.013
0.05	300.0	10.05	76	144.3	203.5	13.25	.011
0.97	295.0	10.22	0.19	168.3	196.0	13.50	.010
15.8	272.0	10.98	.051	193.3	188.5	13.74	.010
26.4	261.8	11.32	.031	216.3	183.2	13.93	.008
40.3	251.0	11.68	.026	239.5	179.0	14.06	.006
48.3	245.0	11.87	.024	255.8	172.3	14.28	.013
63.8	233.0	12.27	.026	279.8	168.0	14.43	.006
90.8	223.0	12.60	.012				

When 14.43 cc. had been taken up at 110°, the system was heated to 210°. In this process the sorption was found to have *decreased* to 10.82 cc. at 343 mm. pressure. In sixteen hours a further decrease to 10.13 cc. at 369 mm. occurred. On then returning to 110° resorption took place, giving 14.79 cc. at 157 mm., a value not greatly different from the original 14.43 cc. The pressure thereafter continued to fall slowly, and three hours later the sorption had risen to 15.00 cc.

The results with Cu I were very similar to those for Cu II, both as to rates and relative amounts adsorbed under different conditions. Since, however, the absolute quantities taken up were much smaller (again, as with hydrogen, by a factor of three or four), and since measurements were not made above 20°, the results for Cu I will not be detailed here.

Nature of Sorption of Carbon Monoxide.—From the relative sorption at different temperatures, and especially from the rate measurements, it is obvious that at least two different processes take place. At first glance it

might seem that the very rapid process is simply physical adsorption, and that the slow process, the rate of which increases with temperature, represents the activated adsorption. However, this view is at variance with the facts in several particulars. In the first place, the large adsorptions at low pressures obtained at -78.5 and 0° are indicative of activated adsorption. Second, the decrease in adsorption from -183 to -78.5 to 0° is far less than would be expected for purely physical adsorption. Carbon monoxide and nitrogen are closely alike in physical properties, and their physical adsorptions would be expected to vary with temperature in much the same way, yet comparison of Figs. 1 and 6 shows that the relative

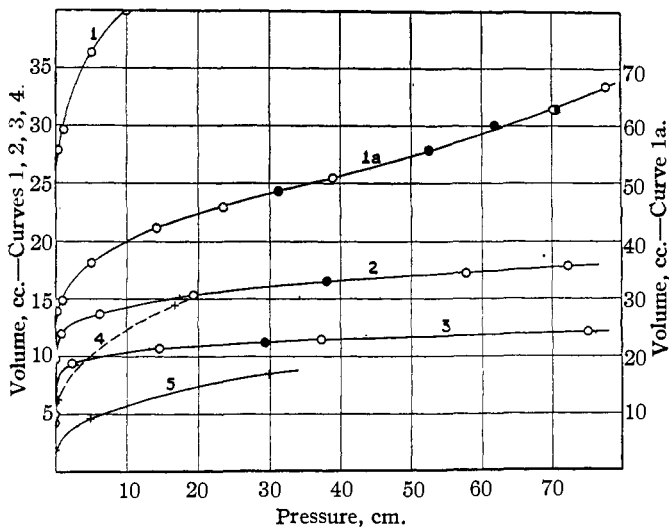


Fig. 6.—Isotherms for carbon monoxide: Curves 1 and 1a, -183° ; Curve 2, -78.5° ; Curve 3, 0° ; Curve 4, final values at 110° ; Curve 5, immediate adsorption at 110° .

adsorption of these two gases changes rapidly with increasing temperature. Thus the ratio of carbon monoxide to nitrogen adsorbed at 600 mm. is 1.54 at -183° , 8.7 at -78.5° and 110 at 0° ; at 100 mm. the ratios for the same temperatures are 1.69, 38 and 410. Data in the literature for charcoal¹³ and silica,³ where the adsorptions are certainly of the physical type, give values for the $\text{CO}:\text{N}_2$ ratio which vary only between 1.2 and 1.8 in this range of temperature and pressure. A large part of the adsorption by Cu II at -78.5 and 0° must, therefore, be of the activated type, even though the gas was taken up with great rapidity. Finally, the data in Table IV show that after about 5 cc. had been taken up at 110° , the sorption of the next 1 cc. was very slow, whereas at 0 and -78.5° this sixth cc. was taken up practically instantaneously at very low pressures. Since

¹³ Homfray, *Z. physik. Chem.*, **74**, 129 (1910).

the rate of a given type of adsorption cannot decrease with rising temperature, the slow process at 110° cannot represent either the physical or the activated adsorption. The evidence suggests that it is a process of solution, though an alternative possibility will be mentioned below.

While the data obtained do not permit a quantitative estimation of the separate amounts of gas taken up in each of the three ways, the situation seems to be qualitatively as follows. At -183° the major part of the adsorption is of the physical type, though the large adsorption at very low pressures, as compared with nitrogen, suggests that even at this temperature activated adsorption occurs. That the latter view is probably

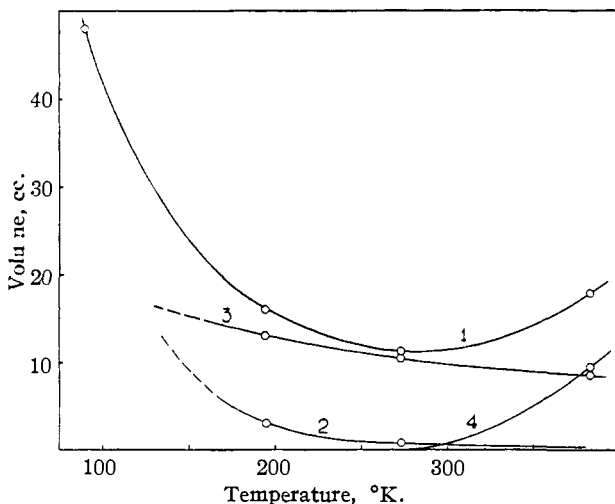


Fig. 7.—Isobars for carbon monoxide at 300 mm.: Curve 1, total sorption; Curve 2, physical adsorption; Curve 3, activated adsorption; Curve 4, solution.

correct is further indicated by the fact that at -78.5° the rate of activated adsorption of carbon monoxide is enormously greater than that of hydrogen; since at -183° there is a detectable activated adsorption of hydrogen, it would be expected that here carbon monoxide would be readily adsorbed in this form. At -78.5° the total adsorption of 16 cc. at 300 mm. consists of about 13 cc. of the activated type, and about 3 cc. of the physical type. At 0° the activated adsorption has decreased to about 10–11 cc., while the physical adsorption has fallen to less than 1 cc., and the process of solution has just begun to have an appreciable rate. At 110° and 300 mm. the physical type has become negligible, the activated type has decreased to about 8.5 cc. (Curve 5, Fig. 6), while the slow solution process accounts for about 9 cc., which is still short of equilibrium. This analysis is illustrated by the isobars for 300 mm. shown in Fig. 7, where Curve 2 represents the physical adsorption, Curve 3 the activated

adsorption, and Curve 4 shows the amount of solution which actually occurred though not of course the equilibrium value. Curve 1 represents the observed total sorption, and is the sum of Curves 2, 3 and 4.

It must be mentioned that there is no decisive evidence that the third process occurring is necessarily a process of solution. A second type of activated adsorption would be an alternative possibility. If this is the case, and if it can be shown that in this process the monoxide is adsorbed in such a way as to *decrease*, rather than increase, its chemical reactivity, a simple explanation would be thus provided for the well-known ineffectiveness of copper as a catalyst for many reactions involving carbon monoxide. However, since there is at present no convincing evidence for the occurrence in other systems of more than a single type of activated adsorption, it has seemed best to assume provisionally that we are dealing with a process of solution.

General Discussion

Physical versus Activated Adsorption.—At low temperatures all three gases studied show typical physical adsorptions, and these are much greater for nitrogen and carbon monoxide than for hydrogen, as would be expected from the relative boiling points. With nitrogen no activated adsorption occurs within the range investigated, and accordingly increased temperature brings about a uniform decrease of adsorption to very small values. With hydrogen the rate of activated adsorption on the most active parts of the surface begins to be appreciable just above -183° . At -78.5° a large fraction of the activated adsorption occurs rapidly, but the less active areas still give a slow rate, which is very much faster at 0° . At these latter temperatures the physical adsorption has become practically negligible. In the case of carbon monoxide the rate of activated adsorption is very great even at 183° , with the result that over a considerable range of temperature a pronounced overlapping of the two types of adsorption occurs. This last case is analogous to the situation observed in the earlier studies of the adsorption of the monoxide by oxide catalysts.³

Thickness of Adsorbed Films.—At first glance the points obtained for the adsorption of nitrogen and carbon monoxide at -183° (Fig. 1, Curve 1a, Fig. 6, Curve 1a) appear to lie on fairly smooth curves. When the scale of these plots is taken into consideration, however, it will be realized that large deviations occasionally occur, amounting in some cases to more than 1 cc. In view of the great constancy of temperature and rapid rate of adsorption prevailing in these runs, the accidental errors of measurement are estimated not to exceed 0.05 cc. The irregularities, therefore, are apparently real. If the curves are drawn through the experimental points within the limit of error, a number of "breaks" appear. For nitrogen these occur at adsorptions of about 22 and 32 cc., for carbon

monoxide at about 30, 47 and possibly 60 cc. There may be other undetected breaks at smaller volumes.

The large intervals between breaks make it unlikely that this phenomenon is the same as the very small discontinuities previously referred to in connection with Fig. 2. The breaks here considered are believed to represent the volumes corresponding to the formation of successive adsorbed layers on the surface. If so, the adsorptions at -183° and atmospheric pressure represent four or five molecular layers. This would certainly not be surprising in view of the fact that the temperature is only 12 and 7° , respectively, above the boiling points of nitrogen and carbon monoxide. Further discussion of this question will be reserved for a later paper in which the much more pronounced breaks observed with iron under similar conditions will be considered.

Solubility.—Fortunately there is little danger of confusing physical adsorption with solubility because in the cases so far studied the sorption due to the former process has become extremely small even at temperatures where the rate of solution is scarcely detectable. Our results show, however, that rate alone will not in general distinguish between activated adsorption and solution. Nevertheless, it is found that such a distinction is possible when all available data, including both rates and equilibria, are utilized. In this connection, experiments "with temperature variation," in the sense described above, furnish a most powerful tool, since under suitably chosen conditions they permit an approach to the two simultaneous equilibria from opposite sides.

The solubility of hydrogen in reduced copper at 0° , as observed in this investigation, is much greater than would be expected from an extrapolation of the solubilities obtained by Sieverts³ for massive copper at temperatures above 400° . Previous experiments in this Laboratory by Griffin,¹¹ on the effect of small quantities of carbon monoxide on the sorption of hydrogen by copper at 0 and 20° , lead to the same conclusion. The recent results of Ward⁷ seem also to point in the same direction, although the solubilities he has reported may be too high, particularly at the lower temperatures, because of his disregard of activated adsorption. While these results at lower temperatures are not necessarily in conflict with Sieverts' data, Ward has advanced the suggestive idea that the low-temperature solubilities represent intergranular penetration rather than actual solubility in the crystal lattice.

Summary

1. The sorptions of nitrogen, hydrogen and carbon monoxide by two samples of reduced copper have been measured at pressures to one atmosphere and at temperatures down to 78°K .
2. It is shown that in general three definitely distinguishable processes

occur, (a) surface adsorption of the physical type, (b) surface adsorption of the activated type, and (c) solubility. Under certain conditions one process may predominate, while under other conditions two or more of these phenomena may occur simultaneously, so that the total observed sorption is the sum of the amounts taken up in the several ways.

3. Within the range investigated, nitrogen shows only physical adsorption, characterized by a rapid rate and a small heat of adsorption.

4. Hydrogen exhibits all three processes. At the lowest temperatures only physical adsorption occurs, at -78.5° activated adsorption is the predominating process, while at 0° both activated adsorption and solution occur. The amounts of hydrogen taken up in each of the three ways have been determined.

5. In the case of carbon monoxide three different processes also are found. Two of these are shown to be physical and activated adsorption, while the third is either solubility or a second kind of activated adsorption.

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AN APPARATUS FOR MEASURING PARTIAL VAPOR PRESSURES OF BINARY LIQUID SYSTEMS

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One of the commonest methods used in the determination of partial vapor pressure of binary mixtures is the so-called dynamic method. This method consists essentially in distilling off a small portion from a large volume of mixture, and then analyzing the distillate obtained. That this method is open to rather serious objections is admitted by many investigators. Zawidski¹ has pointed out that the volume of the mixture used is often too small, and as a result the composition and boiling point vary too much during the distillation. Kuenen² stated that the temperature of the vapor varied considerably, and that there was often an appreciable difference in temperature between the liquid mixture and the vapor, due probably to superheating of the liquid or cooling of the vapors. Another drawback to this method according to Rosanoff and co-workers³ is the fact that only relatively small quantities of the distillate are available for analysis. Other methods might be discussed, but the reader is referred to the article by Rosanoff³ for more complete criticisms of methods available.

¹ Zawidski, *Z. physik. Chem.*, **35**, 129 (1901).

² Kuenen, "Verdampfung und Verflüssigung von Gemischen," Leipzig, 1906.

³ Rosanoff and co-workers, *THIS JOURNAL*, **31**, 451 (1909).