bonate is but slightly more alkaline than tricalcium phosphate, and the titrations above recorded agree with other methods of analysis in indicating that the baking powder reaction stops somewhat short of the complete neutralization of the phosphate to the tricalcium salt stage.

Summary

Graphic representation of both the slow and the rapid electrotitration of phosphoric acid with calcium hydroxide shows that the existence of dicalcium phosphate is transitory so that under equilibrium conditions only the mono- and tricalcium salts are present. The rearrangements involved herein are responsible for part of the difficulty in titrating monocalcium phosphate for its "neutralizing value."

5463 CORNELL AVENUE
CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE ADSORPTION OF GASES BY OXIDE CATALYSTS

BY ARTHUR F. BENTON[1]

Received July 31, 1922

In the adsorption of gases by solid bodies, two more or less distinct phenomena have been observed. Adsorption by inert adsorbents, such as charcoal, mica and silica, has been described as "physical," to distinguish it from the "chemical" type shown by active adsorbents, such as metals. Langmuir,[2] however, considers the adsorption by inert substances due to secondary, and that by active adsorbents due to primary, valence forces. On this basis both types are chemical, and accordingly in the present paper adsorption by active adsorbents will be designated as "primary" and that by inactive adsorbents as "secondary."

The forces involved in primary adsorption are, in general, comparatively strong; "selective" and "irreversible" adsorption are necessarily cases of this type. Here adsorption is determined by chemical affinity in its usual sense. The residual valence forces to which secondary adsorption is due are weaker and less specific. The tendency of different gases to be held by secondary adsorption is measured by their relative boiling or melting points. The tendency of different adsorbents to hold a given gas by secondary adsorption may perhaps, in a similar way, be measured by the melting points, or related properties, of the adsorbents.

The two types of adsorption[3] may be further differentiated in respect to

---

[1] National Research Fellow in Chemistry.

[2] Langmuir, (a) THIS JOURNAL, **40**, 1400 (1918); (b) **38**, 2267 (1916).

[3] A third type, that in which actual liquid condensation occurs, will not be discussed in this paper.

the effect of temperature and pressure. Secondary adsorption decreases rapidly and continuously with increasing temperature, whereas primary adsorption usually first increases, then decreases, as the temperature is raised. In the former type the amount of gas adsorbed increases gradually with increasing pressure, and the surface does not become saturated until comparatively high pressures are reached. Primary adsorption, on the other hand, increases very rapidly with increasing pressure, at low pressures, but soon reaches a saturation value, constant for a given temperature, beyond which the quantity adsorbed remains independent of further pressure increase. Langmuir's measurements[4] on mica, glass and platinum show how sharply the two kinds of adsorption may often be differentiated in these respects, especially when low pressures are used.

Under suitable conditions, however, there can be no doubt that both types of adsorption may occur simultaneously. Charcoal adsorbs gases for which it shows a specific affinity more extensively than would be predicted[5] from their melting or boiling points, and the same applies to mica and glass.[4] The rare gases on quartz might be regarded as the limiting case of secondary adsorption, following definite laws of variation with temperature and pressure. Oxygen on tungsten[6] at high temperatures and low pressures is an example of purely primary adsorption, following quite different laws. Many previous adsorption measurements lie somewhere between these two extremes, so that two distinct phenomena may have often been measured at the same time. In these circumstances it does not appear strange that general laws covering all cases have not been found. That charcoal has given results which are partly amenable to a single method of treatment is due simply to the fact that charcoal is rather inactive chemically toward many of the gases used.

The present investigation of the adsorption of gases by solid oxides, though undertaken primarily in an effort to trace the relation between adsorption and catalysis, has materially increased the number and variety of adsorbents for which data are available, and has thrown some new light on the relation between primary and secondary adsorption.

Experimental Part

Apparatus.—The apparatus operated on the principle of the constant-pressure gas thermometer, and consisted essentially of a glass bulb containing the oxide to be examined, connected through a 3-way cock to a Töpler pump and a compensated gas buret, fused glass joints being used throughout. The various gas generators, with their accompanying purifying trains, were connected with the buret through 3-way cocks.

---

[4] Langmuir, This Journal, 40, 1361 (1918).

[5] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 6.

[6] Langmuir, *ibid.*, **37**, 1148 (1915).

Materials.—All the gases used in the experiments were carefully purified by well-known methods and check analyses at intervals indicated less than 0.1% of total impurity in each. The helium was very kindly furnished by the United States Bureau of Mines, through the courtesy of Dr. R. B. Moore.

The oxides were prepared as follows. Cupric oxide I was a commercial product which had been obtained by strong ignition of metallic copper. The sample used was 8-mesh. Cupric oxide II was prepared by calcination of evaporated copper nitrate at 400°, and was 10–30 mesh. Cupric oxide III was prepared by precipitation of hot sodium hydroxide solution by hot copper sulfate solution; the apparent density (app. d.) of product after final drying was 1.0. The manganese dioxide was a commercial product of high purity, prepared by precipitation; app. d., 0.3. Cobalt sesquioxide was obtained by precipitation from cobalt sulfate solution with a mixture of sodium hydroxide and sodium hypochlorite solutions; app. d., 0.86. Ferric oxide was prepared by precipitation with ammonia solution from hot ferric ammonium sulfate solution; app. d., 0.94. Vanadium pentoxide was prepared from a purified sample of ammonium metavanadate.[7] The material was heated at 250° in a current of dry oxygen until completely transformed to the pentoxide; app. d., 0.60. Hopcalite,[8] a 60:40 mixture of manganese dioxide and copper oxide, was prepared by thoroughly mixing a suspension in water of the proper proportions by weight of manganese dioxide and cupric oxide III similar to the samples previously described. Each of the separate components had been dried for several hours at 100° before mixing; app. d., 0.45. Silica was obtained by thoroughly washing a commercial sample of precipitated silica; app. d., 0.25.

The precipitated oxides were washed repeatedly for several weeks by decantation with distilled water, until they began to be colloidal and until tests for impurities were negative. They were then dried for several hours on a water-bath, ground to a fine powder and preserved in glass-stoppered bottles. The final drying immediately preceding the adsorption tests was carried out at 200° in all cases except cupric oxides I and II (400°) and vanadium pentoxide (250°). The temperatures used in this final drying were always the same as those subsequently employed in removing the adsorbed gases in each case, except with vanadium pentoxide (200°) and cobalt sesquioxide (125°). The latter temperature was found to be the highest at which dissociation of the cobalt sesquioxide in a vacuum was negligible. Carnelley and Walker[9] found the following hydrate contents for oxides prepared and dried by processes similar to the above: $(5SiO_2).H_2O$; $(2Fe_2O_3).H_2O$;$(4Co_2O_3).5H_2O$.

Procedure.—The bulb containing the oxide was supported in an electric furnace and heated in a current of dry air to the temperatures given above, until appreciable quantities of water vapor ceased to be evolved. This process generally required 10 or 12 hours, and minimizes the danger of subsequent change in the oxides during the comparatively short periods of heating to remove the adsorbed gas after each measurement. The bulb was then sealed at one end, fused to the apparatus and evacuated at the temperature already given for the various oxides. It was next brought to the desired temperature by immersion in a suitable bath. The buret containing a measured volume of one of the gases to be examined was then put in communication with the evacuated bulb. Buret readings were taken at frequent intervals, while the pressure was kept close to 760 mm. The gas was finally removed through the pump, the last traces removed from the bulb by heating, and its volume determined in a second cali-

---

[7] Kindly furnished by Dr. R. M. Burns of the Barret Co.

[8] Frazer and Scalione, U. S. pat. 1,345,323, June 29, 1920.

[9] Carnelley and Walker, *J. Chem. Soc.*, **53**, 59 (1888).

brated buret. In this way any loss of gas due to chemical reaction or other cause could readily be estimated. This procedure supplied the volume of gas necessary to form the adsorbed film, plus the volume in the free space and connecting tubing. The latter was determined from the helium measurements on the assumption that only negligible amounts of this gas would be adsorbed at the temperatures in question.[10] The small correction was applied for the variations in temperature of that part of the free space (about 1 cc.) at room temperature. Another small correction was necessitated by the fact that, owing to the use of a compensated gas buret, the pressures at which the measurements were made depended on the temperature of the water-jacket. The corrections for these pressure differences in different runs were made on the assumption that the volume of gas adsorbed was proportional to the pressure. In spite of the fact that this relation is almost certainly not the true one, the error involved in its use was negligibly small, since tests were never made at pressures differing from 760 by more than a few millimeters.

Interpretation of data.—When a gas comes in contact with a solid at least three things may happen, adsorption, absorption (solution) and ordinary chemical reaction. The lack of a suitable method of distinguishing clearly between the first two of these phenomena has frequently led to great confusion, which is still reflected in the use of the word "occlusion."[11] Nevertheless, it has been shown that the time factor[12] offers a satisfactory method of differentiating between the two effects. At comparatively low temperatures gases diffuse into, or through, most solids only slowly, if at all, whereas adsorption equilibria are established extremely rapidly. At higher temperatures, the rate of solution increases, while the extent of adsorption usually decreases, so that it becomes increasingly difficult to distinguish between the two phenomena. In the range of temperatures in which adsorption measurements are ordinarily made, however, the distinction is generally simple. From this standpoint, ordinary chemical reaction between the gas and the adsorbent has an effect similar to that of solution. At lower temperatures, where the reaction rate is slow, attention to the time factor makes possible accurate adsorption measurements, but at higher temperatures the experimental difficulties become increasingly great.

Accordingly, in these experiments buret readings were plotted as ordinates against time elapsed after introducing the gas. In this way curves were obtained which consisted in general of a rapidly rising or falling portion at the beginning, corresponding to the establishment of thermal equilibrium in the bulb, followed by a gradually rising portion which was

---

[10] That this assumption is legitimate appears from the fact that coconut charcoal, though a better adsorbent for other gases than these oxides, takes up scarcely any helium at these temperatures. [Compare Dewar, *Proc. Roy. Soc.*, **74**, 124 (1904)].

[11] Besides meaning ad- and ab-sorption, and possible compound formation, this elastic word is used also in referring to mechanical inclusions.

[12] Compare Holt, Edgar and Firth, *Z. physik. Chem.*, **82**, 513 (1913). Firth, *J. Chem. Soc.*, 119, 1120 (1921). McBain [*Trans. Faraday Soc.*, 14, 203 (1918)] mentions other references to published articles bearing on this question.

nearly straight, or slightly convex upward. In most cases this nearly straight line could be extrapolated back to zero time with considerable confidence, but it was usually found impracticable to attempt measurements of the adsorption of hydrogen or carbon monoxide at temperatures above 0°. To insure the rapid attainment of thermal equilibrium, the evacuated bulb was maintained at the temperature at which the measurement was to be made for a considerable period of time before the gas was introduced. By this means the time required to reach the nearly horizontal part of the curve was reduced to about 10 minutes in cases where large adsorptions occurred, and to about 5 minutes for helium and hydrogen.

There is perhaps a possibility that the shape of the curves for oxygen and carbon dioxide can be ascribed to a slow penetration into pores. As opposed to this view may be cited the facts that helium and nitrogen always gave horizontal lines, and that the oxides whose oxygen curves were steepest did not always give the steepest carbon dioxide curves. But the main argument against the idea of penetration into pores is found in the sharpness with which the first part of the time-curves bends around into the later portion. Nor can the observations with carbon dioxide be accounted for by reaction with possible traces of alkali in the oxides, because nearly the highest rate of disappearance occurred with ferric oxide which was precipitated with ammonia, and also because in all cases all of the carbon dioxide introduced could be recovered by sufficiently long-continued evacuation at 200°. The solution of carbon dioxide in these oxides is no doubt facilitated by the presence of the water which they contain even after drying at 200°; but even if they contained no water, there would be nothing extraordinary in their ability to dissolve this gas, since it has long been known that oxygen can diffuse through metallic oxides at comparatively low temperatures.[13]

The inclination of the volume-time curves for hydrogen probably represents the true initial rate of reaction, since at the low temperatures employed practically all the water formed would be adsorbed. Similarly, in the carbon monoxide measurements most of the carbon dioxide would be adsorbed, but perhaps not all, so that the true rate of reaction in these cases might be slightly greater than the slope of the curves would indicate. Further information on the extent of reaction was obtained by measuring and analyzing the gases pumped off, thus estimating the loss of hydrogen or the quantity of carbon dioxide formed. However, experiments with reducing gases were made only at temperatures at which the rate of reaction was very slow.

It was found that after any considerable amount of reduction had occurred, succeeding adsorption experiments did not check those made

---

[13] Schutzenberger, *Compt. rend.*, **98**, 1520 (1884). Richards and Rogers, *Am. Chem. J.*, **15**, 567 (1893).

previously, but when the oxide was heated for some time in oxygen at 200°, the surface was restored approximately to its original adsorbing power. Accordingly, whenever more than 1 or 2 cc. of carbon monoxide or hydrogen reacted, the surface of the adsorbent was reoxidized before further measurements were made. In only one or two cases, however, was it necessary to resort to this procedure, since of all the tests made, only carbon monoxide at 0° reacted at all rapidly, and this test was accordingly the last made on each adsorbent. The usual order of gases measured was helium, carbon dioxide, oxygen, hydrogen, carbon monoxide.

Data.—The results of the adsorption measurements are given in the accompanying tables (I to IX). The volumes listed have been calculated

ADSORPTION EXPERIMENTS

TABLE I

MANGANESE DIOXIDE, 14.27 G.

	Volume required to fill bulb					Volume adsorbed per gram				
Gas	−79°	0°	25°	110°	184°	−79°	0°	25°	110°	184°
He..	66.67	47.11	43.18	33.73	28.33	..	..	..	..	..
N_2....	..	..	47.47	34.89	28.88	..	..	0.301	0.081	0.038
CO_2.	..	170.5	131.3	50.9	30.1	..	8.66	6.17	1.20	0.12
O_2...	..	..	46.51	34.94	..	..	..	0.234	0.085	..
H_2....	67.63	48.7	43.74	..	..	0.070	0.11	0.039	..	..
CO..	165.5	74.3	61.2	..	..	6.92	1.90	1.26	..	..

TABLE II

COBALT SESQUIOXIDE, 14.44 G.

	Volume required to fill bulb				Volume adsorbed per gram			
Gas	−79°	0°	56.5°	110°	−79°	0°	56.5°	110°
He............	23.99	16.98	14.06	12.04	..	..	..	..
CO_2...........	..	164.7	87.6	47.5	..	10.21	5.09	2.46
O_2............	..	20.80	15.74	13.10	..	0.264	0.116	0.073
H_2............	28.71	..	..	..	0.325	..	..	..
CO............	110.7	..	..	..	6.00	..	..	..

TABLE III

HOPCALITE, 9.437 G.

	Volume required to fill bulb				Volume adsorbed per gram			
Gas	−79°	0°	110°	184°	−79°	0°	110°	184°
He...............	29.74	21.40	15.45	13.09	..	..	..	..
CO_2..............	...	79.76	22.1	15.6	..	6.18	0.70	0.26
O_2...............	...	23.73	16.05	13.46	..	0.247	0.064	0.039
H_2...............	31.07	22.2	...	...	0.141	0.08	..	..
CO...............	73.86	63.1	...	...	4.68	4.42	..	..

TABLE IV

FERRIC OXIDE, 15.22 G.

	Volume required to fill bulb					Volume adsorbed per gram				
Gas	−79°	−40°	0°	110°	184°	−79°	−40°	0°	110°	184°
He..	26.17	21.70	18.46	13.09	10.95	..	..	..	..	..
CO_2.	..	...	289.1	57.5	27.9	..	..	17.79	2.92	1.11
O_2...	..	...	25.83	14.96	11.95	..	..	0.484	0.123	0.066
H_2....	30.41	...	19.81	..	..	0.279	..	0.089	..	..
CO..	174.3	84.3	43.15	..	..	9.73	4.11	1.62	..	..

TABLE V

VANADIUM PENTOXIDE, 12.08 G.

Gas	Volume required to fill bulb				Volume adsorbed per gram			
	−79°	0°	110°	184°	−79°	0°	110°	184°
He	25.86	18.64	13.52	11.47	...	...	...	...
CO_2	...	23.18	14.13	11.66	...	0.376	0.051	0.016
O_2	...	19.01	13.70	11.61	...	0.031	0.015	0.012
H_2	26.08	18.63	...	...	0.018	0.000	...	..
CO	29.60	19.28	...	...	0.310	0.053	...	...

TABLE VI

CUPRIC OXIDE III, 12.54 G.

Gas	Volume required to fill bulb					Volume adsorbed per gram				
	−79°	0°	25°	110°	184°	−79°	0°	25°	110°	184°
He	20.11	14.26	13.06	10.15	8.50	..	..	..	..	...
CO_2	...	71.02	47.0	16.5	9.64	..	4.53	2.70	0.50	0.091
O_2	...	15.86	...	10.62	8.72	..	0.128	..	0.037	0.018
H_2	21.20	15.33	...	...	..	0.087	0.085	..	..	...
CO	56.91	35.13	...	...	..	2.94	1.66	..	..	...

TABLE VII

SILICA, 6.112 G.

Gas	Volume required to fill bulb				Volume adsorbed per gram			
	−79°	0°	110°	184°	−79°	0°	110°	184°
He	33.56	24.04	17.33	14.68	..	..	...	...
N_2	107.9	33.99	19.21	15.66	12.17	1.628	0.308	0.160
CO_2	..	227.7	36.46	19.90	..	33.32	3.130	0.854
O_2	101.6	33.25	19.20	15.67	11.13	1.507	0.306	0.162
H_2	38.22	25.47	17.94	15.09	0.762	0.234	0.099	0.067
CO	162.4	40.31	19.81	15.82	21.09	2.662	0.406	0.187

TABLE VIII

CUPRIC OXIDE I, 66.06 G.

Gas	Volume required to fill bulb		Volume adsorbed per gram	
	25°	218°	25°	218°
N_2	41.2	27.7	...	...
CO_2	41.85	27.7	0.010	0.000
O_2	41.4	27.7	0.003	0.000
CO	41.75	..	0.008	...

TABLE IX

CUPRIC OXIDE II, 28.70 G.

Gas	Volume required to fill bulb						Volume adsorbed per gram					
	−79°	−15°	25°	110°	218°	300°	−79°	−15°	25°	110°	218°	300°
N_2	52.8	39.7	34.5	26.9	21.1	18.6	...	...	...	...	...	...
CO_2	..	..	35.6	27.5	21.5	18.8	...	...	0.038	0.021	0.014	0.007
O_2	52.9	..	34.5	26.9	..	..	0.003	...	0.000	0.000	...	...
H_2	52.8	39.6	34.5	..	..	..	0.000	0.000	0.000	...	...	...
CO	54.3	41.3	36.0	..	..	..	0.052	0.055	0.052	...	...	...
2 vols. CO 1 vol. CO_2		..	36.2	..	..	..	...	...	0.059	...	...	...
1 vol. CO_2 9 vols. N_2		..	34.9	..	..	..	...	...	0.014	...	...	...

to normal conditions (cc. at 0°, 760 mm.), and represent the volumes required to fill the bulb, and the volume adsorbed by 1 g. of adsorbent, at a pressure of 760 mm. and at the temperatures indicated.

Discussion of Results

Order of Gases.—It will be observed that the order of adsorption of the different gases is the same on each of the oxides. Carbon dioxide is most extensively adsorbed, carbon monoxide is next, followed by nitrogen, then oxygen, while hydrogen is least adsorbed. The order of decreasing boiling points is carbon dioxide, oxygen, carbon monoxide, nitrogen, hydrogen. The corresponding order for melting points is carbon dioxide, carbon monoxide, nitrogen, oxygen, hydrogen; in other words, the same as the order of adsorption. This relation holds because the adsorptions are largely of the secondary valence type. A glance at the tables will show *that for active oxides, the adsorption of carbon monoxide is abnormally* large, and this abnormality increases at higher temperatures. Thus at 0° and above, carbon monoxide is held on active oxides mainly by primary adsorption, while at low temperatures the adsorption is largely secondary.

Although the effective surface areas of these oxides are unknown, so that it is not possible to compare them in terms of adsorptions per unit area, yet this difficulty may be overcome to some extent by using ratios of the volumes of different gases adsorbed by each oxide. Table X contains some ratios of this kind, the figures in parentheses in the first column referring to the temperatures at which the adsorption measurements under consideration were made.

TABLE X

ADSORPTION RATIOS FOR DIFFERENT GASES

Ratio	Co_2O_3	Hopcalite	CuO III	MnO_2	F_2O_3	V_2O_5	SiO_2
CO (−79°):CO_2 (0°)	0.59	0.76	0.65	0.80	0.55	0.82	0.63
CO_2 (0°): O_2 (0°)	39	25	35	25	37	12	22
CO (−79°): O_2 (0°)	23	19	23	20	20	10	14
CO (0°):CO_2 (0°)	?	0.72	0.37	0.22	0.09	0.14	0.08
CO (0°): O_2 (0°)	?	18	13	5.6	3.3	1.7	1.77

The ratio of carbon monoxide adsorbed at —79° to carbon dioxide adsorbed at 0° is nearly the same for each adsorbent. This suggests that both of these cases involve mainly secondary adsorption. The second and third rows show that for acidic oxides either the adsorption of oxygen is abnormally great, or that of carbon dioxide is abnormally small. Ordinary chemical considerations suggest that the latter alternative is the correct one. This would also account for the high value in Row 1 for vanadium pentoxide. Silica in Row 1 would then be only apparently normal, the low value for carbon dioxide being balanced by an exceptionally low value for carbon monoxide due to the weakness of the affinity of carbon monoxide for silica. Obviously, however, the adsorptions in these cases are principally of the secondary valence type. The deviations from complete uniformity could perhaps be attributed merely to quantitative, rather than qualitative differences in the forces involved, yet there is no reason why certain of these oxides should not adsorb carbon dioxide or oxygen to some extent by primary valence forces.

The large differences in the ratios of carbon monoxide at 0° to carbon dioxide at 0°, or of the monoxide at 0° to oxygen at 0°, show the specific nature of carbon monoxide adsorption at this temperature. If the assumption be made that with adsorption by silica primary valence forces do not enter the process appreciably, these ratios furnish a means of distinguishing quantitatively between the primary and secondary adsorptions. On this basis the secondary adsorptions of carbon monoxide at 0° should in all cases be 1.77 times as great as the oxygen adsorptions, or 0.08 times as great as the carbon dioxide adsorptions. In Table XI are given the secondary carbon monoxide adsorptions at 0°, calculated in this way, together with the observed total adsorption. The last two rows contain the primary adsorptions, obtained by subtracting the secondary adsorptions from the total.

TABLE XI

PRIMARY AND SECONDARY ADSORPTION OF CARBON MONOXIDE

		Co_2O_3	Hopcalite	CuO III	MnO_2	Fe_2O_3	V_2O_5	SiO_2
Total CO at 0°		?	4.42	1.66	1.90	1.62	0.053	2.662
Secondary, calc. from	O_2 at 0°	0.47	0.44	0.23	0.60	0.85	0.055	(2.662)
	CO_2 at 0°	0.82	0.49	0.36	0.69	1.42	0.030	(2.662)
Primary, from	O_2 at 0°	?	3.98	1.43	1.30	0.77	0.00	(0.0)
	CO_2 at 0°	?	3.93	1.30	1.21	0.20	0.023	(0.0)

The two methods of calculation do not give identical results because, as already mentioned, the adsorptions of carbon dioxide and of oxygen by certain of these oxides cannot be regarded as purely secondary. The two methods do, however, place the oxides in the same order with respect to the primary adsorption of carbon monoxide. Similar results are obtained for hydrogen, but since the adsorptions of this gas are very small, the relative precision of the measurements is much less than with carbon monoxide. It should be noted that these calculations are quite independent of any assumptions with regard to the relative effective surface areas. It has, however, been tacitly assumed that a large primary adsorption has no effect on the secondary adsorptive capacity. If, as seems likely, this is not strictly true, all the secondary adsorptions in Table XI should be diminished, and the primary adsorptions therefore increased, by a certain small fraction of the calculated primary adsorptions. Obviously this correction could not alter the order of the oxides with respect to primary adsorption.

The order of chemical reactivity of these oxides toward hydrogen and carbon monoxide[14] is the same as the order in which they are listed in Tables X and XI and, therefore, the same as that of the primary adsorption, with the exception of manganese dioxide and cupric oxide, which are reversed. This parallelism suggests that primary adsorption is an intermediate stage in the reduction of these oxides, at least at comparatively low temperatures. In other words, carbon monoxide, on coming in contact with a readily reducible oxide, is almost instantly adsorbed by primary valence forces, forming a surface complex which can decompose either into the original substances or into the reduction products, depending on the conditions. At higher temperatures the rate of decomposition of the surface complex into the reaction products is extremely rapid, but at comparatively low temperatures it becomes so slow that at any instant a large fraction of the surface is covered with this adsorbed layer of carbon monoxide molecules. At still lower temperatures carbon monoxide is adsorbed less and less by primary valence, and more and more by secondary. The latter, however, is not a preliminary stage in the reduction, except in so far as a primary valence union results from the secondary type by a shift of electrons. These matters will be considered in greater detail in a later paper.

Order of Adsorbents.—Comparison of different adsorbents is rendered difficult by the lack of knowledge concerning the effective surface areas of these oxides. However, it is probably not unreasonable to assume that they are roughly of the same order of magnitude, since analogous methods of preparation and drying were used. The fact that the primary adsorption so closely parallels chemical reactivity lends further support to this conclusion.

It will be observed that the best adsorbent for any one gas is, in general, the best adsorbent for all the gases, except where primary adsorption is mainly involved. The order of decreasing secondary adsorption, per gram of material, is silica, ferric oxide, manganese dioxide, cobalt sesquioxide, Hopcalite, cupric oxide, vanadium pentoxide. This should accordingly be the order of intensity of the surface fields of force of these oxides, and consequently their melting points and related properties should be in the same order. Unfortunately, owing to dissociation, the melting points of manganese dioxide, cobalt sesquioxide and Hopcalite are not available, but those of the other 4 oxides are in fact in the same order as that of secondary adsorption. Charcoal, with the highest melting point, is a better adsorbent than any of these oxides.

Variation of Adsorption with Temperature.—If the adsorptions are plotted as ordinates against the temperatures as abscissas, curves are obtained which, in general, rise very rapidly at lower temperatures.

---

[14] As determined in these experiments from the slope of the volume-time curves, previously described. Cf. Wright and Luff, *J. Chem. Soc.*, **33**, 1, 504 (1878).

When, however, the logarithms of the volumes adsorbed are plotted against the logarithms of the corresponding temperatures, the resulting curves in the majority of cases do not deviate greatly from straight lines. The slope of the carbon dioxide curves is roughly the same for all the oxides, and the same applies to those for oxygen and for nitrogen. Striking differences are observed, however, in the curves for carbon monoxide and hydrogen. With carbon monoxide, silica, ferric oxide and vanadium pentoxide give curves with slopes approximately equal to each other and to those for carbon dioxide, but in the cases of cupric oxide, manganese dioxide and Hopcalite, the slopes of the curves for carbon monoxide are considerably less. For example, Hopcalite adsorbs nearly as much carbon monoxide at 0° as at —79°. Similar relations hold for hydrogen. These abnormal slopes, in the cases of carbon monoxide and hydrogen on active oxides, are due of course to the fact that here the adsorption is mainly secondary at lower temperatures, and primary at higher temperatures.

Variation of Adsorption with Pressure.—Although measurements have been made only at a pressure of 1 atmosphere, the behavior of the gases on evacuation permits qualitative conclusions to be drawn concerning the variation of adsorption with pressure. If, for convenience, one assumes that the adsorption varies as p^n, then the value of n will be the smaller, the greater the difficulty of removing the gas. With active adsorbents, carbon dioxide could always be more readily pumped off than carbon monoxide. In such cases also, carbon monoxide could be much more easily removed after a measurement at —79° than at 0°. Some observations with cupric oxide III may be cited by way of illustration. At the conclusion of each adsorption measurement, the Töpler pump was operated at 5-minute intervals, until the pressure was reduced to 0.05 mm., before resorting to heating. At this point, after a measurement with carbon dioxide at 0°, 3.5 cc. (0°, 760 mm.) remained adsorbed, or 6.5% of the amount adsorbed at 1 atmosphere pressure. The corresponding figures for carbon monoxide at —79° were 4.0 cc. and 11%. After a carbon monoxide measurement at 0°, 14.5 cc. remained adsorbed at this pressure, or 70% of the quantity adsorbed at 760 mm.[15] It is obvious therefore that the shape of the isotherms must be very different for primary and secondary adsorption, the value of the exponent, n, being much smaller in the former case.

Effect of Partial Reduction.—This effect was tested by making successive adsorption measurements with carbon monoxide at the same temperature, without re-oxidizing the surface between measurements. With

---

[15] These volumes probably represent the true adsorptions at a pressure greater than 0.05 mm., since equilibrium is not reached when the pump is operated at such short intervals. But the values given here were all obtained in the same way, and are therefore comparable among themselves.

ferric oxide at 0° and cupric oxide at —79°, these successive small reductions (3–8 cc. of carbon dioxide were formed in each test)[16] resulted in corresponding increases in the amount of carbon monoxide adsorbed, and the same was true of an adsorption measurement at 0°, following partial reduction at —79°. With cupric oxide III and II at 0°, however, successive reductions (10–15 cc. of CO_2)[16] resulted in greatly decreased adsorption of carbon monoxide. In all cases the quantity of carbon dioxide adsorbed was substantially unaffected by partial reduction.

The effects noted seem to depend on the temperature at which the partial reduction occurred rather than that at which the succeeding adsorption measurement was made. If this is so, the reduction of these oxides probably takes place in two different ways, depending on the conditions. The two possible ways in which a heterogeneous reaction can take place have been discussed by Langmuir,[17] and may be differentiated as interfacial and non-interfacial. In the former case the reaction occurs most readily at the boundary between the two solid phases; in the latter, the reaction does not occur more readily at the boundary than elsewhere, and consequently solid solutions may be formed. Ferric oxide and ferro-ferric oxide[18] actually form solid solutions, but cupric and cuprous oxides[19] do not; however, since the stability of a solid solution would be comparatively great at low temperatures, it may be that the reduction of cupric oxide to copper by carbon monoxide at —79° is non-interfacial.

When the reduction is non-interfacial and is not carried too far, the resulting surface will contain oxygen atoms (or ions) and spaces free from oxygen in an irregular arrangement. This is assumed to be the case with ferric oxide at 0° and with cupric oxide at —79°. The results indicate then that such a surface adsorbs more carbon monoxide than the unreduced oxides. If the reduction of copper oxide by carbon monoxide at 0° is an interface reaction, succeeding adsorptions are diminished because copper adsorbs less carbon monoxide than copper oxide;[20] but if it is not an interface reaction, it may be assumed that, since the reduction proceeded much further in these cases, most of the surface oxygen atoms were removed, producing a decrease in adsorptive capacity.

Adsorption and Method of Preparation.—The adsorptions by cupric oxide prepared by ignition of metallic copper (Table VIII) or evaporated copper nitrate (Table IX) are very much smaller than those observed for precipitated cupric oxide. This is no doubt largely a question of surface area, but sintering probably also plays a part. When copper oxide is

---

[16] Each of these tests extended over a considerable time, so that here reduction proceeded very much further than in the regular adsorption measurements.

[17] Ref. 2b, p. 2263.

[18] Sosman and Hostetter, This Journal, **38**, 807 (1916).

[19] Smyth and Roberts, *ibid.*, 42, 2582 (1920).

[20] Compare Taylor and Burns, *ibid.*, **43**, 1273 (1921).

prepared by removing water from the hydroxide at a comparatively low temperature, the direction of the free valence bonds remains fixed, so that the oxide has a strong surface field of force, and shows a high adsorptive capacity, reactivity and catalytic power; but at higher temperatures, more and more rearrangement becomes possible, with consequent reduction in surface energy.

Summary

The adsorption of carbon dioxide, oxygen, hydrogen and carbon monoxide by copper oxide, manganese dioxide, cobalt sesquioxide, ferric oxide, vanadium pentoxide, silica and Hopcalite (60% of manganese dioxide to 40% of cupric oxide), prepared by as nearly as possible analogous processes, has been measured at 1 atmosphere pressure and temperatures from —79° to 184° (—79° to 0° for hydrogen and carbon monoxide). In order to obtain the true adsorptions, a method was devised to correct for the absorption (solution) which occurs in some cases, and for the progressive chemical reaction with hydrogen and carbon monoxide.

Two different types of adsorption, designated as "primary" and "secondary," are discussed in connection with these and other measurements. Secondary adsorption is the type which occurs with inert adsorbents, and depends on secondary valence. The melting points of the adsorbent and of the adsorbed substance are a measure of the forces involved. Primary adsorption, on the other hand, occurs with active adsorbents, and depends on primary valence forces. In common with other manifestations of chemical affinity, it is specific. The forms of the isotherms and isobars are very different for the two types.

In certain of the present measurements, both kinds of adsorption occur simultaneously. A method has been devised for distinguishing between the two types and estimating the extent of each, in such cases.

The adsorption data may be summarized in the three following statements: (1) the secondary adsorption of different gases is in the order of their melting points; (2) the secondary adsorption by different adsorbents is in the order of their melting points; (3) the primary adsorption of carbon monoxide is approximately in the order of the relative reducibility of the different oxides.

The relation of the adsorption results to the catalytic behavior of these oxides will be the subject of a later paper.

In conclusion the author wishes to express his indebtedness to Prof. H. S. Taylor for his constant interest and many helpful suggestions during the course of this research.

PRINCETON, NEW JERSEY