[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Adsorption of Nitrous Oxide on Certain Pseudomorphs

BY ARTHUR B. LAMB AND CUTLER D. WEST

Crystals of chabasite and of certain other zeolites when dehydrated at not too high temperatures lose relatively large amounts of water without any marked change in their outward appearance, their transparency or their crystal lattice. It has been found, particularly in the case of chabasite, that the strong adsorption of gases which these pseudomorphs exhibit reaches a maximum at certain intermediate degrees of dehydration characteristic of the several gases studied.[1] Other crystalline substances are known which, when a volatile component is expelled by heat, although they retain the outward form of the original crystals, acquire a different crystalline structure and in general are no longer transparent. In a number of such instances, X-ray examination has shown that the original crystal gives rise to a great number of small crystallites of the new substance either without any orientation or with orientation along only one or two of the crystal axes of the original substance.[2]

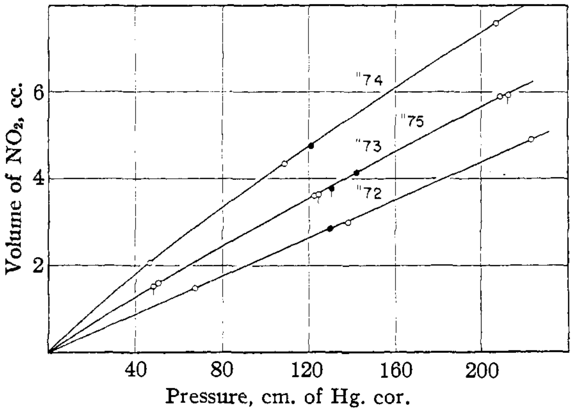

Fig. 1.—Adsorption isotherms of N_2O on $Zn(OH)_2$ (dehydrated) at 0°. Experimental points at decreasing pressures (desorption) shown by solid circles. Dehydration: Expts. 72, 0%; 73, 42.9%; 74, 92.5%; 75, 97.5%. Curve for Expt. 75 not drawn in; points shown as ♀.

It appeared of interest to ascertain whether pseudomorphs of this latter type, retaining little or none of the original crystal lattice, would exhibit adsorptive powers comparable to those of the zeolites and characterized by similar maxima at intermediate degrees of dehydration. We have therefore studied the adsorption of nitrous oxide on a number of pseudomorphs of this class, chiefly oxides formed by the careful dehydration of crystalline metallic hydroxides. Nitrous oxide was selected both because it is adsorbed freely by many substances at 0°, and because it does not react chemically with the adsorbents under investigation.

Procedure.—Adsorption was determined by observing in a constant volume–constant temperature apparatus the variation in pressure when measured volumes of nitrous oxide were admitted to and were removed from the adsorbent at 0°. The apparatus and experimental procedure were similar to those used by Lamb and Woodhouse.[1] In no case was there a troublesome delay in the adjustment of the adsorption equilibrium; that a true equilibrium was reached was shown by the fact that readings made in the directions both of increasing and of decreasing pressures fell closely on a single smooth curve (see Fig. 1).

Because of the small adsorptive power of the materials investigated, and to increase the accuracy, the free space in the apparatus was reduced as far as possible. The water expelled from the crystalline hydrates was determined by collecting and weighing it in a tube containing phosphorus pentoxide. The carbon dioxide expelled from the carbonates was computed from the loss in weight on heating of the detachable adsorption cell provided with a stopcock attached to its stem.

The reported temperatures of dehydration are uncorrected readings of mercury thermometers. The reported pressures have been twice corrected: first, to convert the observed pressures to centimeters of mercury at 0°, and, second, to take account of the departure of nitrous oxide from the laws of a perfect gas. For this latter purpose a in the van der Waals equation was taken as 728×10^{-5} at 0°,[3] giving

$$p = a/76\left(p\frac{273}{T}\right)^2 = 9.58 \times 10^{-5}\,p^2 \text{ cm.}$$

The second correction was positive, opposite in sign and larger than the first correction. The net correction amounted to +0.03 cm. at an observed pressure of 50 cm., and to +3.00 cm. at an observed pressure of 200 cm. Since the gas buret was of the compensating type, its readings gave directly the volume of nitrous oxide delivered at 0° and 76 cm.

With each sample of the undehydrated adsorbent in the cell the initial free space was determined by measurements of the pressure established by a known volume of gas, on the assumption that there was no adsorption. The increase in free space after removal of a measured weight of water was found by assigning to the water a density calcu-

---

(1) Lamb and Woodhouse, THIS JOURNAL, **58**, 2637 (1936).

(2) C. D. West, *Am. Mineral.*, **21**, 245–9 (1936); J. Boehm, *Z. Krist.*, **68**, 567 (1928); Büssem and Köberich, *Z. physik. Chem.*, **17**, 310 (1932).

(3) Landolt and Börnstein, "Tabellen," 5th ed., p. 262.

lated from the known densities of the undehydrated adsorbent and its final dehydration product.

Materials.—The crystalline adsorbent materials were crushed carefully and granules of approximately uniform size, namely, passing a 20 and caught on an 80 mesh sieve were used. The *magnesium hydroxide* was massive natural brucite. Ignition of two different lots gave H_2O = 30.8 and 31.4%; calculated, 30.9%. The *calcium hydroxide* was in the form of small, clear, hexagonal prisms artificially prepared by C. Grove[4] and kindly furnished us by Dr. John Johnston. Analysis by conversion to sulfate gave Ca = 54.3 and 54.5%; calculated, 54.1%. The *zinc hydroxide* was prepared by the slow diffusion process described by Dietrich and Johnston[5] as small, well-formed, orthorhombic crystals. Titration gave Zn = 65.65 and 64.77%; calculated, 65.78%. The optical characteristics of this crystalline substance, which have not heretofore been reported, are: biaxial negative; principal indices 1.570, 1.578, 1.580, all ±0.002; 2E greater than 111°; dispersion *r* greater than *v*. The *zinc carbonate* was natural, massive smithsonite; heating above 500° gave ZnO = 65.0%; calculated, 64.9%. The *calcium sulfate dihydrate* was natural, single crystalline, gypsum; heating above 400° gave H_2O = 21.2%; calculated, 20.9%.

TABLE I

ADSORPTION ISOTHERMS OF NITROUS OXIDE ON PARTIALLY DEHYDRATED ZINC HYDROXIDE AT 0°

Weight, 1.6119 g.; H_2O, 18.14%

Volume of NO_2, cc.		Pressure of NO_2 in cell, cm.	
Buret	Cell	Obs.	Corr.
Expt. 72, no dehydration			
6.34	..	...	...
4.87	1.47	67.5	67.7
3.34	3.00	136.8	138.0
1.42	4.92	219.8	223.4
3.49	2.85	128.9	129.9
Expt. 73, evacuated two hours at 135°; loss H_2O = 0.1255 g. = 42.9%			
8.95	..	...	...
7.35	1.60	50.8	50.8
5.35	3.60	121.7	122.6
3.05	5.90	205.4	208.5
4.80	4.15	141.0	142.3
Expt. 74, evacuated three hours at 145°; loss H_2O = 0.2712 g. = 92.5%			
9.91	..	...	...
7.85	2.06	46.8	46.8
5.55	4.36	108.0	108.7
2.31	7.60	203.9	207.0
5.14	4.77	120.3	121.2
Expt. 75, evacuated two hours at 365°; loss H_2O = 0.2866 g. = 97.5%			
7.15	..	...	...
5.64	1.51	48.2	48.2
3.52	3.63	123.3	124.2
1.21	5.94	209.1	212.4
3.36	3.79	129.4	130.5

The *nitrous oxide* (S. S. White Dental Supply Company) after passage over solid potassium hydroxide and phosphorus pentoxide was used without further treatment.

Results.—To illustrate the measurements made, typical data obtained with a single sample of zinc hydroxide, first without any dehydration and then after three successive dehydrations, are given in Table I and are shown graphically in Fig. 1. Similar data were obtained for all the substances studied and from these isotherms for each stage of dehydration were constructed. These data are too extensive for reproduction here but are available in tabular form as American Documentation Institute Document No. 1435.[6]

From these data the volumes of nitrous oxide adsorbed at 200 cm. pressure per gram of pseudomorph and per gram of water (or carbon dioxide) expelled were computed as illustrated for a few cases by the data in Table II. The results are collected in Table III (A) and are plotted in Fig. 2.

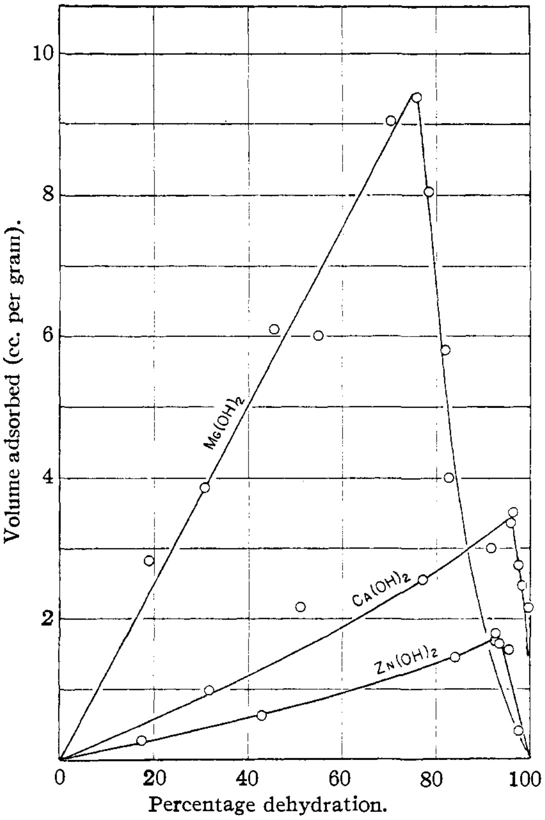

Fig. 2.—Activity of pseudomorphs at different stages of dehydration.

---

[4] J. Johnston and C. Grove, THIS JOURNAL, **53**, 3976 (1931).

[5] H. G. Dietrich and J. Johnston, *ibid.*, **49**, 1419 (1927).

[6] For detailed paper order Document 1435 from American Documentation Institute, Offices of Science Service, 2101 Constitution Ave., Washington, D. C., remitting 23¢ for microfilm form or 50¢ for photocopies readable without optical aid.

TABLE II

CALCULATION OF ADSORPTION OF NITROUS OXIDE ON PARTIALLY DEHYDRATED ZINC HYDROXIDE AT 0°

Expt.	Vol. H_2O expd. cc.	Free space cc.	Volume of NO_2 Adsorbed at 200 cm. pressure, cc. Obs.	Free	Absorbed	Per gram of pseudomorph	Per gram of expd. H_2O
72	0	1.672	4.40	4.40	0	0	0
73	.126	1.798	5.67	4.73	0.94	0.63$_3$	7.50
74	.271	1.943	7.38	5.12	2.27	1.69$_2$	8.37
75	.287	1.959	5.63	5.15	0.48	0.36$_2$	1.67

TABLE III

ACTIVITY OF PSEUDOMORPHS AT DIFFERENT STAGES OF DEHYDRATION

A

Dehydration %	Max. temp.	Adsorption, cc. per g. Pseudomorph	H_2O expelled
$Ca(OH)_2$: 24.35% H_2O of density 1.1			
31.6	395	0.98	11.8
91.5	400	3.00	10.3
95.8	412	3.36	11.1
96.2		3.51	11.5
97.4	500	2.75	8.8*
98.2	450	2.47	7.9*
(100)	550	2.16	6.7*
$Mg(OH)_2$: 30.9% H_2O of density 1.3			
19.0	310	2.83	45.5
30.7	331	3.87	36.0
46.5	310	6.09	36.1
55.0	326	6.01	29.5
70.2	315	9.04	32.5
75.9	348	9.38	30.6
78.4	330	8.04	25.1
81.9	512	5.80	17.1*
82.7	512	4.00	11.7*
$Zn(OH)_2$: 18.14% H_2O of density 1.0			
17.4	109	0.27	8.2
42.9	133	0.63	7.4
84.0	111	1.46	8.1
92.5	121	1.80	9.0
92.5	145	1.69	8.4
93.4	163	1.66	8.1*
95.6	227	1.58	7.5*
97.5	398	0.42	2.0*
97.5	365	.36	1.7*

B

Dehydration %	Max. temp.	Adsorption, cc. per g. Pseudomorph	H_2O expelled
$CaSO_4 \cdot 2H_2O$: 20.95% H_2O of density 1.4			
97.6	175	6.71	25.6
(100)	275	4.08	15.4*
(100)	400	1.67	6.3*
$ZnCO_3$: 35.05% CO_2 of density 2.91			
51.0	300	2.16	9.9
77.0	300	2.56	6.9
89.0	350	6.75	15.1
(100)	500	0.11	0.2*
$MgCO_3$ (natural, massive): 52.2% CO_2 of density 2.66			
(100)	480	18.41	16.9
(100)	520	16.85	15.4
$CuSO_4 \cdot 5H_2O$: 36.1% H_2O of density 1.40			
80.0	80	3.24	8.0
(100)	290	2.89	5.1*
$KAl(SO_4)_2 \cdot 12H_2O$: 45.6% H_2O of density 1.25			
57.8	78	.39	1.09
79.7	93	.71	1.25
97.5	213	.99	1.24
(100)	317	1.26	1.50*
$Al_2O_3 \cdot H_2O$ (activated alumina): 13.13% H_2O of density 1.42			
?	25	5.94	?
26.3	173	12.2	16.6
68.9	450	16.7	16.8

* Past the maximum.

A few less complete measurements of the adsorption of nitrous oxide on other pseudomorphs were made and they are given in Table III (B). Duplicate measurements were not made with these substances. Maxima were not obtained with the last two materials but the data are too few to justify any special conclusions.

It can be seen from these data that these pseudomorphs differ considerably among themselves in their adsorptive activity, but even the most active adsorbent of those studied ($Mg(OH)_2 - H_2O$) certainly does not approach dehydrated chabasite in this respect, for, under these conditions, chabasite adsorbs about 133 cc. of carbon dioxide per gram[1] and would therefore probably adsorb an equal volume of nitrous oxide. However, these pseudomorphs do show a sharp maximum of adsorption in the range of 80–95% dehydration similar to that found for dehydrated chabasite.[1] While curves for different experiments with the same materials do not always coincide within the experimental error, nevertheless they have the same shape and reach maxima at the same per cent. dehydration.

The interpretation given in the case of chabasite for the general course of these curves connecting adsorption and dehydration appears to apply here as well. As water is removed the porosity of the adsorbent, and hence its inner surface and its adsorptive capacity, steadily increase so long as the residual oxide groups retain their positions in the crystal lattice. At the higher temperatures required to remove the last amounts of water, coalescence and perhaps recrystallization of these finest constituent particles ensue with a consequent decrease in the inner surface and hence in the adsorptive capacity. The drop from the maximum can thus be attributed to a sintering or growth of the finest crystallites.

This explanation is, of course, in line with many observations showing the enhanced activity of substances formed at low temperatures as compared with their activity when heated to higher temperatures. Thus Hüttig,[7] for instance, showed that zinc oxide prepared by heating zinc carbonate at low temperatures is more effective in catalyzing the decomposition of methanol than the same material heated to higher temperatures.

The adsorption of the nitrous oxide per gram of expelled water as given in the final column of Table III (A) shows some features of interest. The values for calcium oxide and zinc oxide pseudomorphs are quite constant over the whole range of dehydration up to the maximum. Those for magnesium oxide are much larger, but they diminish quite regularly to about two-thirds of the initial value at a dehydration corresponding to the maximum adsorption. They all drop sharply when the maximum is passed.

The crystalline hydroxides in which the water has the higher apparent density as computed from the observed densities of the crystalline hydroxides and oxides show the higher adsorption per gram of expelled water. At first glance this appears surprising, for in the case where the water has the higher density there would be less volume available for adsorption of the nitrous oxide per gram of water expelled. However, even in the most extreme case ($Mg(OH)_2$) the volume of nitrous oxide adsorbed, as a liquid, is only perhaps 10% of the available volume, so this factor cannot be very important. On the other hand, in the hydroxides where the water has the greater density the oxides evidently hold this water more tenaciously and should on this score adsorb the nitrous oxide in larger amounts. This latter factor would be expected to outweigh the former so that the net effect would be an increased adsorption with increasing density of expelled water, as observed.

X-Ray Examination.—Powder photographs were taken of brucite at progressive stages of dehydration to see whether any structural changes accompanied the changes in adsorptive activity. For this purpose a small amount of the pseudomorph was removed from its adsorption cell after its activity had been determined and was photographed in MoK radiation in cameras of 20 cm. focus. Precautions were taken to avoid exposure to the atmosphere. Similar photographs were taken of the initial brucite and of the final ignition product and of known mechanical mixtures of the two. The films were read visually so that only qualitative comparison could be made; for more exact results it would be necessary to standardize the procedure carefully and to photometer the films.

With this reservation some conclusions may be drawn. First, at its maximum activity at about 80% dehydration the brucite gives almost exclusively the powder lines of the MgO structure, and there is no perceptible difference in the photographs of material at its maximum activity and of the same material after half of its activity has been destroyed by further heating. For example, the adsorbent of the sixth experiment listed under $Mg(OH)_2$ in Table IIIA is indistinguishable from that of the eighth by visual examination of the photographs, and similarly for the seventh and the ninth. Second, photographs of a pseudomorph of a given composition differ from those of a mechanical mixture of the initial brucite and its ignition product MgO having the same composition. The differences consist in the extreme diffuseness of the MgO lines on their first appearance in the pseudomorph, and also in the premature disappearance of the $Mg(OH)_2$ lines in the pseudomorph, relative to the mechanical mixture, as the water content decreases. For example, in the mechanical mixture corresponding to 80 or even 90% dehydration the first five or six lines of $Mg(OH)_2$ are distinct though weak, whereas they are absent in the pseudomorph. From this one would conclude that the physical states of the $Mg(OH)_2$ and MgO are different in the pseudomorph from what they are in the initial and final materials. Presumably the crystallites of both these components of the pseudomorphs are extremely small.

---

[7] G. Hüttig and others, *Z. anorg. allgem. Chem.*, **198**, 214, 219 (1931); Ivannikov, Frost and Shapiro, *Chem. Abs.*, **28**, 1595 (1934).

Summary

The adsorption of nitrous oxide upon pseudomorphs formed by partially dehydrating the crystalline hydroxides of magnesium, calcium and zinc and by partially decarbonating zinc carbonate at 0° has been measured. It is found that although these pseudomorphs exhibit considerable adsorptive activity they are far inferior in this respect to the zeolites, for instance, to chabasite. However, as with the zeolites, the adsorptive activity increases to a maximum at 80–95% dehydration and then diminishes rapidly to almost zero at complete dehydration. This behavior is explained as due to the formation of exceedingly minute crystallites of the metallic oxides and of the metallic hydroxides during the dehydration.

The progress of the dehydration was also followed in the case of brucite by means of X-ray powder photographs and the results were found to be consonant with those obtained in the adsorption measurements.

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 23, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Interatomic Distances in Cobalt Diselenide

BY BURTON LEWIS AND NORMAN ELLIOTT

The crystal structure of cobalt diselenide has been reported twice in the literature, by de Jong and Willems[1] in 1928, and by Tengner[2] in 1938. The substance has the pyrite structure and is based on a unit cell 5.845 = 0.005 Å.[3] on an edge. The value 0.375 has been assigned to the parameter which fixes the atomic positions of selenium.

It was noted by Pauling and Huggins[4] that the distance between two selenium atoms in cobalt diselenide was 0.24 Å. larger than that found in crystalline selenium, the discrepancy being either unaccounted for by the theory of the additivity of covalent radii or due to an error in the parameter determination. The crystal structure of cobalt diselenide has therefore been reinvestigated using a shorter X-ray wave length than was used by previous experimenters. In this way more reflections have been observed than before. The results are reported in this paper.

The preparation of cobalt diselenide and the analysis of its powder photographs were the same as have been described in a previous paper.[5] The X-ray data are listed in Table I.

The observations (421) > (333) + (115), (423) + (502) = (333) + (115), (601) = (604), (425) + (603) > (116) + (532), (640)α_1 > (444)α_1, (640)α_2 < (444)α_1, and (640) > (600) + (442) limit the parameter to the range of values 0.375–

TABLE I

Copper K_α radiation. $\lambda = 1.539$ Å. Camera radius = 5.005 cm.

Sin Θ	*hkl*	*I*, obsd.	*I*, calcd.
0.2599	200	195	195
.2913	201	800	845
.3193	112	700	645
.3682	220	155	125
.4327	113	600	580
.4522	222	40	45
.4711	203	250	210
.4886	132	350	360
.5232	400	60	55
.5844	420	20	25
.5994	421	180	175
.6129	332	80	80
.6407	422	40	35
.6795	333 511	160	160
.7042	205 423	160	165
.7175	512	100	105
.7399	440	160	180
.7848	600 442 α_1	30	25
.7860	600 442 α_2		
.7960	601 α_1	40	45
.7973	601 α_2		
.8065	116 532 α_1	150	140
.8076	116 532 α_2		
.8588	533 α_1	90	90
.8598	533 α_2		
.8784	425 603 α_1	130	145
.8794	425 603 α_2		
.8877	136 α_1	100	100
.8891	136 α_2		
.9070	444 α_1	20	20
.9087	444 α_2		
.9462	640 α_1	40	40
.9478	640 α_2		
.9554	207 641 α_1	240	220
.9574	207 641 α_2		
.9647	336 172 552 α_1	300	330

---

[1] De Jong and Willems, *Z. anorg. allgem. Chem.*, **170**, 241 (1928).

[2] Tengner, *ibid.*, **239**, 126 (1938).

[3] De Jong and Willems report the edge of the unit cell to be 5.854 Å. This is probably a mistake caused by interchange of the last two numbers.

[4] Linus Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[5] Norman Elliott, THIS JOURNAL, **59**, 1958 (1937).