

acids. Analysis of the volatile acids was by Duclaux determinations⁴ on 100-cc. specimens.

Duclaux values of 6.4, 6.9, 7.3 were obtained for the first three 10-cc. portions of distillate collected from the volatile acids from 2-heptene-4-ol. This represents nearly pure acetic acid. The slight deviation may be due to the presence of α -hydroxyvaleric acid, whose influence in this determination is unknown. Confirmation that the volatile acid was acetic was the conversion of 0.5 g. of the sodium salts to 0.5 g. of *p*-bromophenacyl acetate, m. p. 84–85°, by reaction in 50% alcohol with *p*-bromophenacyl bromide.

The volatile acids from the 4-chloro-2-heptene gave a Duclaux value of 23.3 for the first 30 cc. of distillate. From this, these simultaneous equations are applicable: $Ac + Bu = 100\%$; $0.197 Ac + 0.448 Bu = 23.3\%$. Solving, Ac (for acetic) = 86%; Bu (for butyric) = 14%. Hydrolysis of the chloride (3 g.) to the alcohol (1.6 g.; 62% yield), b. p. 60–65° at 23 mm. and subsequent ozonolysis of the alcohol as before gave confirmatory evidence that a mixture was involved. The value for 30 cc. of Duclaux distillate was 22.2, indicative of 90% Ac and 10% Bu .

Duclaux analysis of the volatile acids from α -propylcrotyl phenyl ether (after ozonolysis, etc.) gave 24.7 as the value for 30 cc. of distillate. This represents 80% Ac , 20% Bu and indicates that the ether is a mixture of C and

(4) Virtanen and Pulkki, *THIS JOURNAL.*, **50**, 3143 (1928); McNair, *ibid.*, **55**, 1471 (1933).

G possibly in the ratio of 80:20. The assumption that the volatile acids are exclusively acetic and butyric may not be entirely correct in this case since a small portion of the volatile acid may come from the aromatic part of the molecule. The figures, however, seem fairly reliable.

The product of rearrangement, namely, α -methyl- δ -ethylcrotylphenol, was treated analogously. The Duclaux value for 30 cc. of distillate was 40.3. Calculation gives 18% Ac , 82% Bu , which indicates that the phenol is chiefly D together with a smaller amount of J . The preponderance of butyric acid in the volatile acids was witnessed by converting the acids to dry sodium salts (0.5 g.) and treating the latter with *p*-bromophenacyl bromide. *p*-Bromophenacyl butyrate, m. p. 63°, was formed abundantly.

Summary

Partial allylic rearrangement of 4-chloro-2-heptene into 2-chloro-3-heptene is encountered during synthesis of the former from 2-heptene-4-ol (α -propylcrotyl alcohol). α -Propylcrotyl phenyl ether and its rearrangement product were prepared and their structures determined by ozonolysis. The evidence obtained supports the contention that the allyl group undergoes inversion during rearrangement of allyl phenyl ether into *o*-allylphenol.

EVANSTON, ILL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Adsorption by Dehydrated Chabasite as a Function of the Water Content

BY ARTHUR B. LAMB AND JOHN C. WOODHOUSE

Vom Rath¹ in 1876 demonstrated that crystals of chabasite, a hydrated calcium, sodium, aluminum silicate, on dehydration retain their original form and clarity unchanged even when the loss of water amounts to nearly one-fifth of their original weight and a still larger fraction of their original volume. Friedel² in 1896 found that these dehydrated crystals adsorb gases with marked avidity. Especially interesting is the more recent discovery made independently by several investigators³ that such an adsorption does not take place with gases whose molecules are larger than a certain definite limiting size and so cannot enter the pores of uniform and atomic dimensions characteristic of this adsorbent.

Impressed by the interesting potentialities of

these "crystallogenic"⁴ adsorbents as we have called them, we have now made a careful study of the development of the adsorptive activity of chabasite as it is progressively dehydrated. As a criterion of this activity we have used the adsorptions of hydrogen, oxygen and carbon dioxide upon it, since they represent gases which are, respectively, very slightly, moderately and largely adsorbed.

No similar study, so far as we are aware, has been made.

Apparatus

The samples of chabasite were dehydrated and the adsorption of the resultant product measured in the apparatus shown in Fig. 1.

The manometer C was of the constant-level type. The mercury level on the adsorbent side was kept exactly at (1) by the use of the mercury reservoir B , placed under any de-

(1) G. vom Rath, *Pogg. Ann.*, **158**, 396 (1876).

(2) Friedel, *Bull. Soc. franc. mineral*, **19**, 93–118, 363–384 (1896).

(3) Lamb, U. S. Patent 1,813,174 (Applied for September 25, 1925); McBain, *Colloid Sym. Mon.*, **4**, 1 (1926); *Kolloid Z.*, **40**, 1 (1926); Schmidt, *Z. physik. Chem.*, **133**, 280 (1928).

(4) That is, adsorbents which owe their adsorptive activity to the crystal structure of the parent substance from which they have been prepared.

sired pressure by air supplied from a hand pump. B was connected by a valve to C. The side of C away from the adsorbent was evacuated through the stopcock A by a diffusion pump sealed to the system.

Purified and triply distilled mercury was then admitted to C from B, and as high a vacuum as possible obtained with the diffusion pump. The empty manometer tube had been previously cleaned, and dried, by the passage through the heated tube of dry air for long intervals. The mercury level was gradually raised by pressure from B, with the tube being kept hot, and under the low pressure provided by the diffusion pump. In about two hours it had risen to point (3) where the 7-mm. internal diameter tube joined a capillary tube 800 mm. long, leading downward and ter-

through the 5 mm. tube and this was sealed off flat at (C). Since the residual volume of the small tube could be computed accurately from its linear dimensions, the total volume of the cell could be ascertained to within 0.005 cc. The density of the undehydrated chabasite was determined to the second decimal place and using this value and taking the density of the water in the chabasite as unity, the free space in the cell containing wholly or partially dehydrated adsorbent was computed. The free space in the adsorption apparatus between 1 and 2 was also measured accurately by displacement of mercury. It amounted to only between 1.2 and 1.6 cc. in the several arrangements of apparatus used. The total free space in the apparatus ranged between 1.2 and 1.7 cc. per gram of

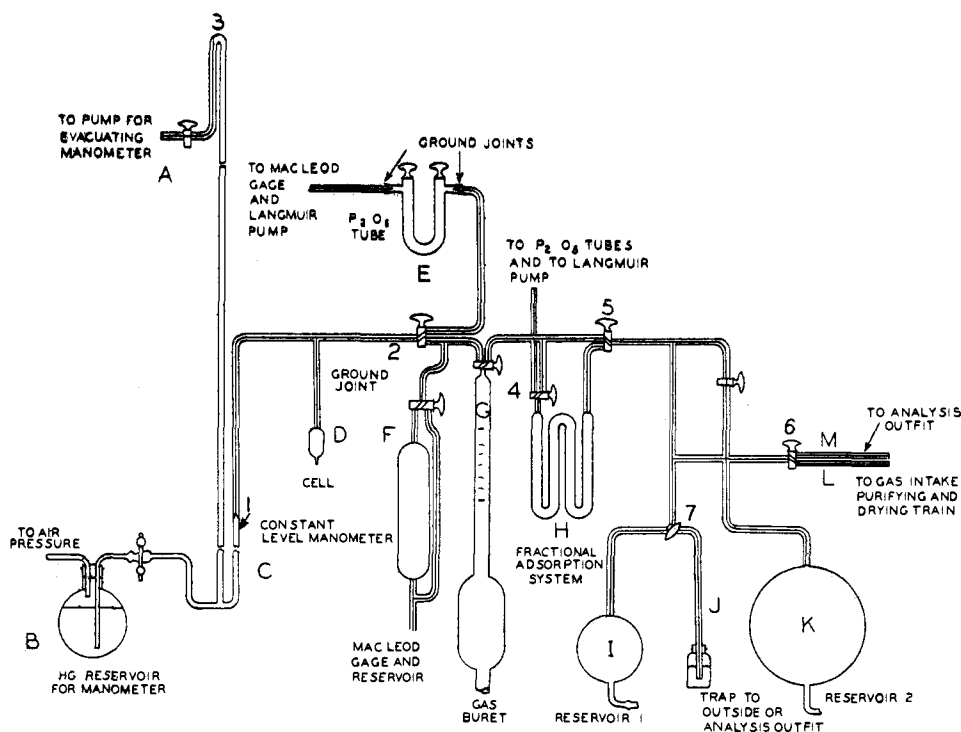


Fig. 1.—Apparatus.

minating in the stopcock. This downward tube was now likewise roasted, still under the low pressure, and any residual adsorbed gases removed. Mercury was boiled over from (3) to fill the heated downward tube with its vapor, the stopcock was closed and the capillary tube filled with mercury. Thus a high vacuum was ensured on this arm of the manometer. The arrangement was such that if by any chance gas entered the evacuated arm, the procedure of evacuation could be conveniently and quickly repeated. Pressures between 1000 and 1950 mm. were read to 1 mm. and between 100 and 1000 to 0.5 mm. on a calibrated millimeter scale. Pressures between 5 and 100 mm. were read to 0.1 mm. and below 5 mm. to 0.02 mm. by means of a cathetometer.

The adsorption cell D shown above in Fig. 2, usually of quartz but sometimes of Pyrex, was attached to the apparatus by interchangeable ground joints. Its volume (5–7 cc.) from (A) to (B) was first determined accurately; this volume was then charged with 10–14 mesh chabasite

anhydrous chabasite with a maximum uncertainty of ± 0.1 cc.

During measurements the cell was surrounded by suitable constant temperature jackets employing transition points, and preferably boiling points of stable substances.

The mercury-operated gas buret, G, had a capacity of 103.47 cc. It was provided with a stirred water jacket and could be read to about ± 0.01 cc., but readings usually were taken only to ± 0.05 cc. Gases were thus measured to within 0.02 cc. or less per gram of anhydrous chabasite. By means of the leveling bulb gas volumes were measured at atmospheric pressure and at the temperature of the jacket. Corrections were made to standard conditions, taking account of individual deviations from the gas laws.

In order to be sure whether water and the several gases employed were really adsorbed reversibly, it was necessary to measure accurately the several temperatures of dehydration and gas adsorption. Up to 356° (the boiling point of mercury) jackets employing vapors from the refluxing of

stable compounds were employed. Above 356° there was used a closed tubular electric furnace.

Below 300°, temperatures were checked by a nitrogen-filled glass thermometer. From 300 to 750° they were measured by a nitrogen-filled quartz thermometer and above that by a thermoelectric pyrometer.

The vapor jackets gave all temperatures identical with the boiling points of the compounds used. When the electric furnace was employed, thermometers and cell were so placed that no part of the adsorbent was subjected to a temperature of more than $\pm 5^\circ$ from that recorded.

At higher temperatures, control was important also in order to prevent injury to the adsorbent through overheating. The observations of earlier experimenters⁵ regarding the reversibility of hydration and dehydration below 600° were checked quantitatively.

Materials

Chabasite.—This consisted of six samples which so far as we know represent collections made in the vicinity of Aussig, Bohemia. The small crystals as received were removed from their rocky matrix, crushed sufficiently to pass a 10- and be retained on a 14-mesh-to-the-inch sieve and the fragments examined individually with a microscope and a polariscope to ensure the absence of any foreign material. Each sample thus secured, usually weighing from 75 to 100 grams, was then exposed in a desiccator over 24% aqueous sulfuric acid at about 20° (aqueous pressure 15 mm.) for at least two weeks, and during the last day as nearly as possible at exactly 20°. After this equilibration samples kept for an additional three months under the same conditions showed no further gain or loss in weight. The water contents of these samples were determined by heating 2-4 g. portions at 900-950° to constant weight. The following results, each representing the mean of two concordant duplicate analyses, were obtained for the six chabasite samples: 22.25, 22.23, 22.34, 22.27, 22.27 and 22.30; average 22.28% H₂O.

Hydrogen, Oxygen and Carbon Dioxide.—Selected samples of the compressed or liquefied commercial gases were analyzed carefully and found to be, respectively, 99.0-99.25, 99.5 and 99.88% pure as drawn from the cylinders. The gases were then dried over phosphorus pentoxide and introduced into the adsorption apparatus where they were further purified by means of fractional adsorption.

For this purpose they were allowed to enter the apparatus through L and to escape through J until the voided gas showed a constant and high degree of purity. Tube H charged with 50 g. of activated chabasite and highly evacuated was now chilled to -192° for hydrogen, -182° for oxygen and -78° for carbon dioxide and the gas adsorbed in it up to a pressure of about 1900 mm. A portion of this gas was then discarded, a large fraction of the remainder was drawn into the reservoirs I or K and the residue removed from H by evacuation at room temperature. This procedure was repeated one or more times and the finally purified gas stored in I or K. In the case of

(5) The most pertinent previous information appears to be the observations of Rothmund [*Rec. Trav. Chim.*, **44**, 329 (1925)] that chabasite dehydrated at a temperature of 400-600° loses most of its water but can regain it fully on exposure to water vapor at room temperature. At higher temperatures this reversibility becomes less complete and at 800° is wholly lost.

carbon dioxide the purification was also frequently carried out using the dehydrated chabasite itself in D. When enough of the gas had been added to raise the pressure there to the maximum desired, a small measured portion containing practically all of the impurities was removed and replaced by an equal volume of the pure original gas (99.88%). This was repeated (usually two repetitions were ample) until the first sample withdrawn showed a purity of 99.88%. We could then be certain that the residual gas was of a considerably higher purity.

Procedure

The water vapor was drawn off from the sample through stopcock 2 into the phosphorus pentoxide tube E, by means of a mercury diffusion pump backed by an oil pump. After suitable intervals of heating and pumping, tube E was disconnected and weighed. By the use of an identical counterpoise and by careful control of the humidity this could be done with an accuracy of ± 0.2 mg. which corresponds to an uncertainty of only about 0.004% with the usual 5-g. sample of chabasite.

Adsorption Measurements.—The gas after final purification was transferred to the buret F and from there measured volumes of it were admitted to the evacuated cell D containing the suitably dehydrated adsorbent. Pressure readings were taken until no further change could be detected. This was usually the case within at most twenty minutes. Additional amounts of gas were then introduced until the limit of the manometer had been reached. The points thus obtained gave an "in-going" isotherm. The process was now reversed, measured volumes of gas being removed and an "out-going" isotherm obtained.



Fig. 2.—Adsorption cell.

Experimental Results

A typical set of experimental data as obtained for a single "out-going" point on an oxygen isotherm is given in Table I in order to illustrate the application of the corrections and the methods of calculation.

TABLE I

OXYGEN ISOTHERM AT 0° ON AUSSIG CHABASITE		
Run 120: 78.4% dehydrated at 255°; 2.775 g. anhydrous chabasite; 5.88 cc. free space		
Time: -1:30-2:30 P.M., Dec. 17		
		Volume gas
Barometer, corr., mm.	750.5	Removed, cc. 11.00
Manometer, mm.	768.0	Removed, corr., cc. 10.10
Manometer, mm.	10.0	Total in system, cc. 23.95
Pressure, mm.	758.0	Free, cc. 5.85
Pressure, corr., mm.	755.4	Adsorbed, cc. 18.10
Temperature buret, °C.	19.9	Adsorbed cc. per g. 6.52

Our experimental data are collected in Tables II-V and are shown graphically in Figs. 3-9.

TABLE II
HYDROGEN ADSORPTION ISOTHERMS AT 0° ON CHABASITE DEHYDRATED TO VARIOUS DEGREES

Chabasite Sample											
9		9		9		9		10		7	
61.4		78.4		91.3		96.3		96.7		97.5	
				380		630		634		640	
Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.
1833	0.25	1796	1.0	1850	1.9	1918	5.6	1802	5.8	1870	5.2
857.8	.10	1193	0.8	1203	1.4	1276	4.0	1225	4.2	605.7	2.1
364.7	< .05	722.5	.5	671.7	0.9	906.8	3.0	780.7	2.8	276.7	0.9
		366.4	.3	279.0	.4	542.1	1.9	432.2	1.6	45.0	.4
		137.1	.1	101.6	< .1	366.8	1.4	168.4	0.6		
						188.4	0.8				
						52.8	.3				
						13.0	.1				

TABLE III
ADSORPTION ISOTHERMS AT 0° OF OXYGEN ON CHABASITE DEHYDRATED TO VARIOUS DEGREES

Chabasite Sample													
8		8		10		9		10		10		8	
40.0		74.0		90.7		94.5		95.5		96.3		97.8	
250		306		390		460		575		635		730	
Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.
822.5	1.3	927.0	7.3	1962	19.8	1864	25.9	1950	33.2	1847	36.3	1894	33.0
575.8	0.8	554.7	4.1	1615	18.2	1545	23.4	1484	29.0	1441	33.3	1510	30.4
298.5	.3	356.5	2.8	1235	14.4	1260	20.8	1016	24.5	1144	31.0	1153	27.2
10.0	.0	10.5	0.1	876.7	11.1	999.8	18.2	647.6	19.9	906.4	28.6	832.3	23.9
				514.0	6.7	779.5	15.6	302.8	13.7	740.4	26.5	462.6	18.9
				259.3	3.4	580.9	12.8	169.4	10.0	551.5	23.8		
				133.5	1.6	390.7	9.8	79.7	6.3	391.8	20.9		
				70.8	0.7	239.2	7.1	58.8	5.1	269.1	17.6		
						138.6	4.7			172.4	14.7		
						52.8	2.1			64.8	8.9		
										25.9	5.5		

Since however a total of 30 isotherms for oxygen and 15 for carbon dioxide were measured at 0°, be-

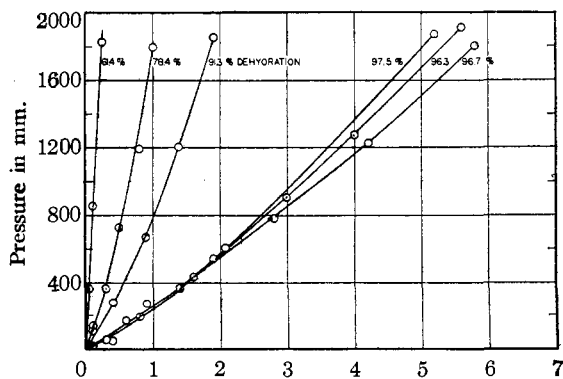


Fig. 3.—Adsorption isotherms at 0° of hydrogen by chabasite at various degrees of dehydration.

cause of limitations of space only a part of these have been included in the tables.⁶ The tempera-

(6) All of these data in tabular form are available as Science Service Document No. 1003 (9 pages, 25 cents in microfilm form or 55 cents in photoprint form; payable in advance by check or money order to Science Service, 2101 Constitution Avenue, Washington, D. C.).

tures of dehydration given in the tables are the respective maximum temperatures attained during the dehydration which was usually continued for four to ten hours until no appreciable amount of water came off at pressures less than 0.1 mm. The volumes of gas adsorbed as given in the tables represent the number of cubic centimeters, corrected to standard temperature and pressure, adsorbed at the given pressure, per gram of anhydrous adsorbent.

Incomplete results with ammonia, which so far as we know is the most highly adsorbed of all gases upon these adsorbents, show that it is somewhat adsorbed upon chabasite when even less than 5% of the total water is removed; and there is some evidence that ammonia actually drives water out of partially dehydrated chabasite. Moreover, ammonia when once adsorbed is held with extreme tenacity. It was found, for example, that all of the ammonia adsorbed on 90% dehydrated chabasite could only be removed by prolonged heating of the adsorbent above 400° at vacua obtainable by mercury diffusion pumps.

TABLE IV
CARBON DIOXIDE ADSORPTION ISOTHERMS AT 0° ON CHABASITE DEHYDRATED TO VARIOUS DEGREES

10		10		10		10		10		10		10		9					
Chabasite Sample																			
Dehydration %																			
Temperature of dehydration, °C.																			
120		180		250		890		90.7		91.3		380		512		608		635	
Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.
605.5*	32.3	149.6*	65.9	1010*	105.0	2.0*	78.7	684.1*	128.1	373.5*	112.1	109.6*	103.9	25.0*	75.8				
1405*	34.9	1202*	79.0	1741	108.1	20.0*	105.8	1559	132.8	1922	125.1	1518*	123.1	597.7*	114.0				
1972	35.1	1574	80.6	1315	106.3	762.0*	128.0	1051	130.6	1260	123.2	1901	125.0	1700	123.0				
1372	34.6	1259	79.5	924.3	104.6	1892	133.1	683.0	128.4	686.2	117.8	1224	122.0	501.0	114.2				
1092	33.7	916.4	77.9	570.7	101.9	1304	131.1	391.6	125.2	411.2	113.3	833.4	119.6	148.7	103.5				
657.2	32.7	586.6	75.8	368.5	99.2	749.8	127.9	236.2	122.1	249.0	108.7	415.8	116.3						
523.8	32.0	358.5	72.9	207.1	95.0	402.3	124.5	114.7	118.3	194.3	106.0	240.2	110.8						
388.3	31.1	147.5	66.3	115.4	89.4	203.2	120.3	57.3	113.7	74.8	95.8	167.4	107.8						
103.7	26.4	74.7	61.7	38.8	82.1	97.7	115.1	33.8	109.3	39.9	89.8	81.7	102.0						
20.8	19.4	33.9	54.2	19.9	74.1	38.8	109.6	14.9	103.0	14.0	77.5	47.8	96.3						
		14.5	46.1	12.5	66.1	12.0	101.7	8.0	94.6	4.3	61.3								
				5.0	49.9	2.4	85.8			1.6	45.0								
										1.2	37.4								

Under these conditions there was actual decomposition of the ammonia, and very probably a

The displacement of water by ammonia and the subsequent removal of the latter by evacuation at these relatively low temperatures does, however, facilitate the preparation of highly active adsorbents.

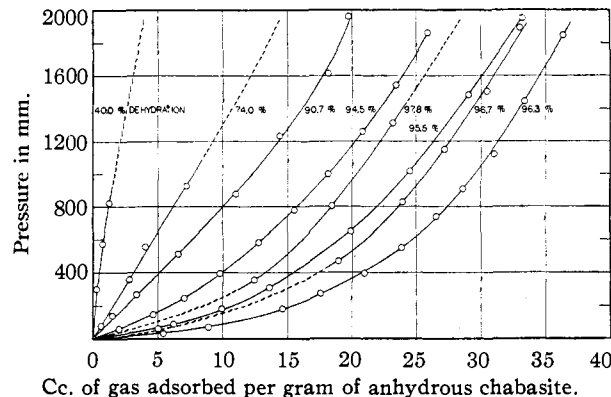


Fig. 4.—Adsorption isotherms at 0° of oxygen by chabasite at various degrees of dehydration.

Reproducibility of the Measurements

In the measurements upon samples of chabasite which were only slightly dehydrated the adsorption equilibria adjusted themselves slowly, but in the measurements made with samples considerably dehydrated, for instance 50% or more, equilibrium was attained rapidly, usually in less than twenty minutes.

further removal of water. For these reasons no attempt has been made to treat the ammonia

Hysteresis was also substantially absent, the "in-going" points corresponding closely to the "out-going." This has been indicated in the case of the data for the adsorption of carbon dioxide at 0° by labeling the "in-going" points in

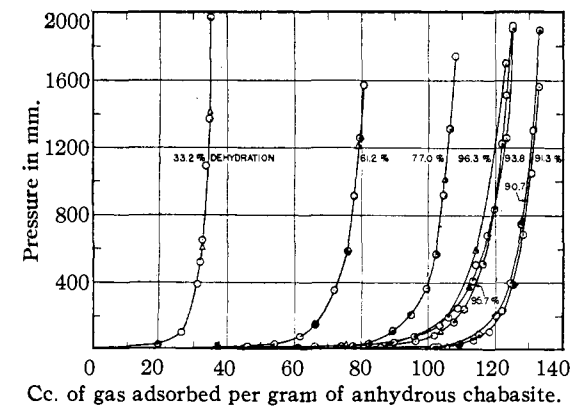


Fig. 5.—Adsorption isotherms at 0° of carbon dioxide by chabasite at various degrees of dehydration. Triangles represent "in-going" values.

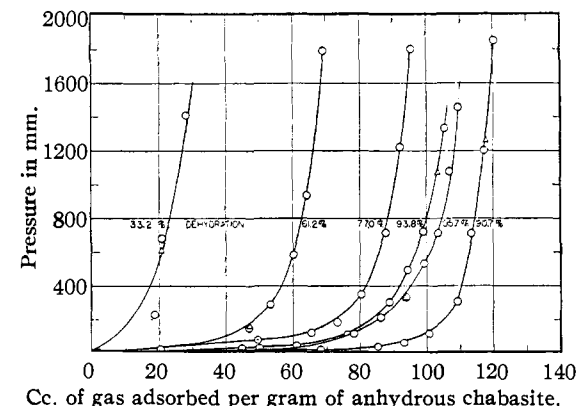


Fig. 6.—Adsorption isotherms at 34.5° of carbon dioxide by chabasite at various degrees of dehydration. Triangles represent "in-going" values.

results quantitatively as has been done with hydrogen, oxygen and carbon dioxide.

the Tables with a * and in the figures with a Δ. It can be seen that they agree closely with corre-

TABLE V
CARBON DIOXIDE ISOTHERMS AT TEMPERATURES OF 34.5 TO 306° ON CHABASITE DEHYDRATED TO VARIOUS DEGREES
Chabasite Sample 10

33.2		61.2		77.0		90.7		93.8		95.5		95.7	
Dehydration, %													
120		180		250		390		512		575		608	
Temperature of dehydration, °C.													
Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.
34.5°													
597.7*	20.8	150.1*	47.4	1798	95.8	1250*	118.1	1064*	103.8			314.4*	94.0
1398	28.3	1778	69.5	1210	92.5	1840	120.8	1321	105.9			1444	109.9
665.8	21.2	926.2	64.5	707.2	88.1	1195	117.8	716.9	99.6			1067	107.4
219.0	19.0	572.5	60.5	338.9	80.9	652.3	113.7	483.0	94.7			755.2	103.9
		278.9	53.6	174.3	73.7	294.8	109.7	288.8	89.1			527.9	99.7
		139.6	47.2	111.7	65.9	107.6	101.2	104.7	77.3			324.7	94.2
				65.0	49.8	47.8	93.6	32.9	61.4			204.2	86.8
						27.9	85.8	14.0	45.0			109.6	78.6
						7.5	68.6	6.9	37.4			17.0	50.2
												0.5	20.8
61.2°													
2020	22.3	1763	56.8	1943	85.2	1593	111.5	1270	93.0	876.5	94.8	1793	102.0
981.0	17.3	970.9	52.2	1041	79.7	926.0	107.4	871.3	87.8	498.0	88.1	1331	99.9
		482.9	45.0	577.8	72.8	378.4	100.8	332.6	76.8	328.7	82.5	941.2	96.7
				370.6	65.3	169.2	93.1	115.6	61.1	214.2	76.1	632.5	92.9
				165.5	49.6	99.7	85.6	43.8	44.9	159.5	71.8	400.5	87.6
						25.9	68.6	23.0	37.4			206.2	79.2
												110.6	66.2
												56.8	50.0
												1.6	20.8
100.0°													
		1991	40.7	1516	62.8	1548	98.3	1900	79.8	796.7	70.4	1803	82.0
				1031	55.8	826.7	91.7	1297	74.7	488.1	62.9	1444	7.2
				718.0	48.4	527.8	84.6	808.4	67.7	323.7	56.1	1056	75.3
						209.0	68.0	499.8	60.2	219.2	50.5	757.0	70.8
						49.4	46.1	320.6	52.7	149.5	44.4	456.3	64.1
								211.2	45.0			219.2	52.7
								121.6	37.2			86.2	36.5
218°													
		1949	25.6	1919	32.0	1909	38.1						
		1111	19.8	1327	28.0	1591	35.9						
		585.4	14.6	885.2	24.4	1193	28.9						
		219.0	9.0	404.5	18.5	804.7	25.2						
		144.4	7.4	237.4	15.6	438.1	20.5						
		66.7	5.0			189.2	15.5						
						61.8	11.6						
						28.9	8.6						
						18.0	7.5						
306°													
		748.1	7.9			1842	19.1						
		398.2	5.1			1190	16.2						
		225.0	3.2			695.2	12.6						
		119.5	2.2			388.4	10.2						
		73.8	1.7			154.5	7.3						
		24.9	1.0			17.0	4.3						

sponding "out-going" points. A similar reproducibility was obtained in the other measurements with carbon dioxide, oxygen and hydrogen.

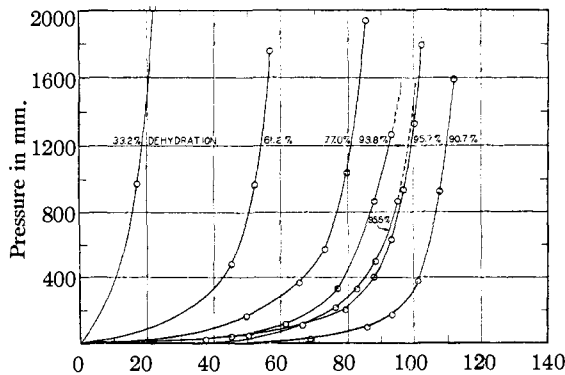


Fig. 7.—Adsorption isotherms for carbon dioxide at 61.2° by chabasite at various degrees of dehydration.

Isotherms obtained from different samples of chabasite of nearly the same degree of dehydra-

tion were also usually quite concordant. This is evidence not only of a still broader reproducibility of the phenomenon, but also of the absence of any displacement of water from the partially dehydrated chabasite during the adsorption and

desorption of the gases within the range of temperatures and pressures employed. This fixity of the residual water was confirmed by passing the desorbed gases through weighed tubes containing phosphorus pentoxide and ascertaining that there was no increase in weight.

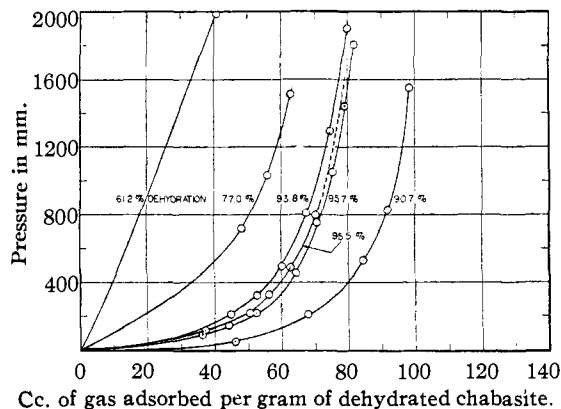


Fig. 8.—Adsorption isotherms of carbon dioxide at 100° by chabasite at various degrees of dehydration.

Utilizing large-scale plots for these isotherms, isobars were now constructed where the amounts adsorbed per gram of anhydrous chabasite were plotted against percentages of water removed. The resulting curves for hydrogen and oxygen on the same scale and for carbon dioxide on a four times smaller scale all at 0° are shown in Fig. 10. Those for carbon dioxide at successively higher temperatures are shown in Fig. 11.

These isobars are also indicative of the reproducibility of our results. The isotherms from which they are derived were obtained in some instances from as many as six different samples of chabasite. These samples not only were independent at the start but were independently dehydrated at somewhat different temperatures and pressures and according to different schedules. In spite of this, the resultant individual points lie smoothly on the isobaric curves. This shows that the adsorptive capacity of this variety of chabasite at a given degree of dehydration is definite and independent, within the limits tried, of the mode of dehydration.

It is also of interest that the adsorptive capacity of a highly dehydrated chabasite remains undiminished after repeated adsorptions and desorptions have occurred both with the same gas and other gases. Thus for example, using chabasite Sample 1, where 19.05% of water of the total of 22.25% originally present had been re-

moved, a later isotherm with carbon dioxide checked closely an earlier isotherm made with this gas, although in the interim several other isotherms at other temperatures had been measured upon the same sample. Similarly chabasite Sample 11, where 21.41% of water had been removed, gave an isotherm substantially identical with an earlier one although in the meantime a dozen isotherms at other temperatures and with other gases had been measured upon it.

Discussion

It can be seen from Figs. 10-11 that the adsorption increases steadily as water is removed from the chabasite, but that ultimately a sharp maximum is reached at a point where only a little water remains. From there on the adsorption diminishes rapidly until at complete dehydration practically no gas is adsorbed. It should be pointed out also that while the adsorption equilibria up to the maximum are reversible, as noted above, after the maximum is passed the reversibility diminishes, and when the water has been largely removed, the equilibria are only slowly attained and are of somewhat doubtful reproducibility. Continued heating after the maximum activity has been developed lessens the activity even when no measurable loss of water occurs.

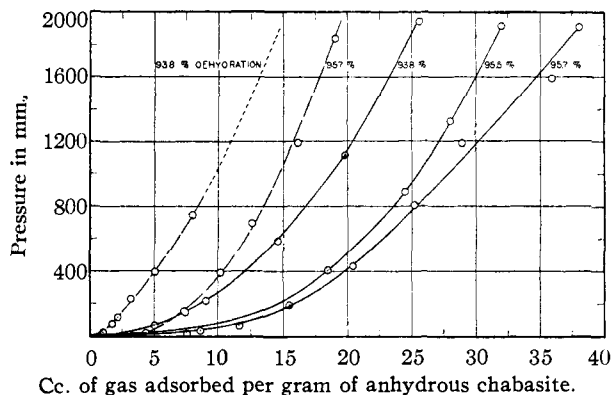


Fig. 9.—Adsorption isotherms at 218 and 306° of carbon dioxide by chabasite at various degrees of dehydration: broken lines, 306°; solid lines, -218°.

From Fig. 11 it can be seen that the same characteristic maximum adsorption at 93% dehydration observed at 0° persists at the higher temperatures. There is also a secondary maximum which is barely suggested in the curve for adsorption at 0° but becomes well marked in the curves for 34.5, 61.2 and 100°. Incomplete results at 218

and 300° show that this secondary maximum is also well marked at these temperatures. It is noteworthy that this secondary maximum occurs at nearly the same percentage dehydration (96%)

sites dehydrated by these amounts exhibit an astonishing specificity in their behavior toward these gases. Our data in this range are too meager and too inaccurate to fix the exact ratios between

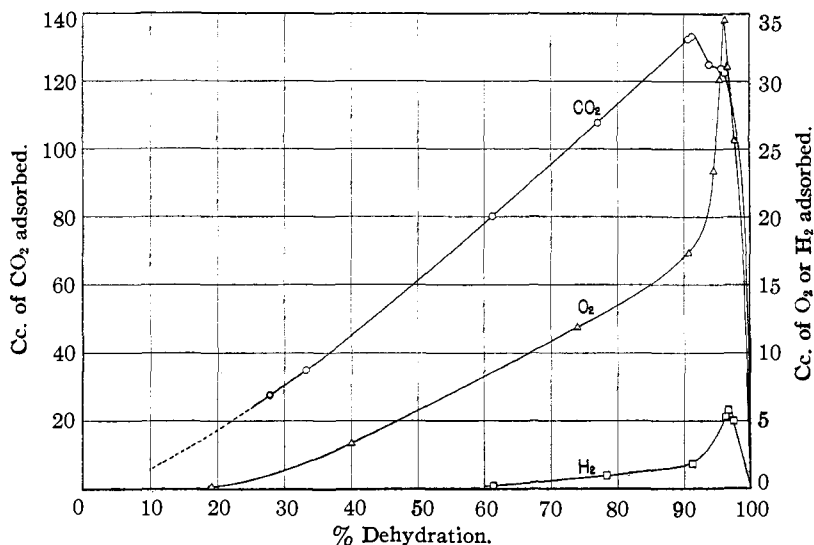


Fig. 10.—Adsorption at 0° and 1600 mm. of CO₂, O₂ and H₂ by chabasite at various degrees of dehydration: ○ = CO₂; △ = O₂; □ = H₂.

the adsorptions of these gases under these conditions, but at 17% dehydration 15 cc. of carbon dioxide and less than 0.2 cc. of oxygen are adsorbed and at 50% dehydration 6 cc. of oxygen and less than 0.1 cc. of hydrogen are adsorbed. These amounts correspond to ratios at least of the order of 75:1 and 60:1, whereas the ratios between the volumes of these gases adsorbed under the same conditions on active charcoal are approximately 3:1 and 4:1, respectively. This remarkable specificity makes possible a simple and effective separation of such gases out of their mixtures.

where the primary and sole maxima occur for oxygen and for hydrogen.

A reasonable interpretation of the general course of these curves is that the porosity of the adsorbent, and hence its inner surface and its adsorptive capacity, steadily increase as water is removed, so long as the original crystal lattice persists. At the high temperatures required to remove the last traces of water, the crystal lattice begins to collapse, with a consequent decrease in the adsorptive capacity. The sharp drop from the maximum is then to be attributed to a sintering that takes place at the high temperatures of dehydration.

Another feature of these curves is of great interest. They do not run linearly from the origin (no water removed), but appear to approach the horizontal axis rather abruptly at points at some distance to the right of the origin. In other words, significant quantities of the carbon dioxide, oxygen and hydrogen only appear to be adsorbed when, respectively, 5, 17 and 50% of the total water have been removed. It follows that chaba-

A reasonable explanation of the negligible adsorption of these gases at and below these critical degrees of dehydration is as follows: The first 5% of the water removed appears to come from

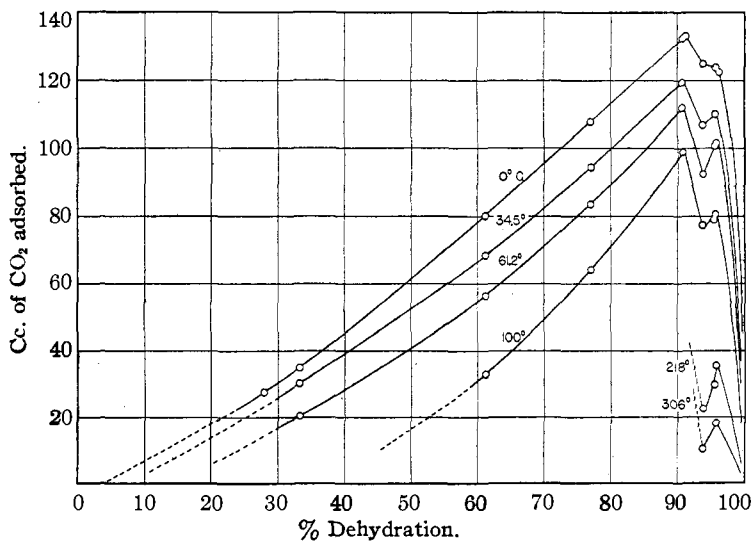


Fig. 11.—Adsorption isobars at 1600 mm. of carbon dioxide by chabasite at various degrees of dehydration.

the "outer" surface of the crystals or crystallites and its removal provides only an insignificant increase in surface and a consequent insignificant increase in adsorption. The next water removed

(up to 17%) opens up relatively coarse pores into which all three gases readily penetrate. The surface thus developed is sufficient to adsorb carbon dioxide largely but oxygen and hydrogen only in negligible amounts. When more water is removed (up to 50%), some additional coarse pores are produced into which carbon dioxide can enter, but the chief effect is to open up a great number of smaller pores into which only oxygen and hydrogen can enter. The resultant inner surface is sufficiently large to adsorb a significant amount of oxygen but is not large enough to adsorb more than a negligible amount of hydrogen. The removal of still more water (50-95%) not only increases the number of coarser and finer pores and thus increases the adsorption of carbon dioxide and oxygen, but it opens up a multitude of the very finest pores into which hydrogen alone can enter. This finest porosity provides a correspondingly great surface with a consequent considerable adsorption even of hydrogen.

This explanation does not, on first thought, seem to help in understanding the marked specificity exhibited by the chabasite dehydrated to 17 and 50% as compared, for instance, with the adsorption of these gases on active charcoal. The negligible adsorption of oxygen compared with that of carbon dioxide at 17% dehydration (1:60), or of hydrogen compared with that of oxygen, cannot be due to any difficulty in the access of the oxygen or the hydrogen, respectively, to the inner surface of the adsorbent, for the oxygen molecule is smaller than the carbon dioxide molecule and the hydrogen molecule in turn is smaller than the oxygen molecule.

On further thought, however, it is clear that this disparity between the ratio of 60:1 for these partially dehydrated chabasites and of 4:1 for charcoal is due to the marked difference in the nature of the porosity of the two types of adsorbent. Whereas in the former at this degree of dehydration the two gases compared both have ready access to all the porosity, in the latter there is a considerable porosity into which only the smaller and less adsorbable of the two gases can enter. Charcoal therefore appears to be a relatively better adsorbent for the less adsorbable gas than would otherwise be the case.

Stated somewhat differently, it may be said that since the same area of adsorbent surface in these specially dehydrated chabasites is available to both gases, the observed ratio between the

amount of each gas adsorbed, though extreme, is nevertheless presumably normal.

Another interesting feature of these curves is the relative location of the point of maximum adsorption as disclosed by the data in Table VI.

TABLE VI
LOCATION OF THE MAXIMA

	Water removed	Percentages	
		residual water	Dehydration
Hydrogen	21.6	0.48	97.8
Oxygen	21.4	.68	96.9
Carbon dioxide	20.5	1.58	92.9

The maxima for hydrogen and oxygen are displaced slightly in the direction of more complete dehydration, the maximum for hydrogen being displaced somewhat farther than that for oxygen. These maxima clearly represent the resultant of two opposing effects of the dehydration, namely, the continuing exposure of additional inner surface which increases, and the accelerating collapse of the crystal structure which decreases the adsorption. If the second porosity to be developed is finer than the first and impenetrable by carbon dioxide while the third porosity is still finer and impenetrable by oxygen and if these porosities are correspondingly more extensive, it would be expected that with oxygen and even more with hydrogen the effect of the increase in porosity and inner surface would prevail over the progressive collapse of the crystal lattice to higher degrees of dehydration than in the case with carbon dioxide. This displacement then of the maxima is in full accord with the inference drawn from the other parts of the curves.

A final point of interest with regard to these curves is the very considerable volumes of gases adsorbed at the maxima as compared, for instance, with corresponding volumes for charcoal. Thus the most highly activated coconut charcoal adsorbs at 0° and under atmospheric pressure about 1.5 cc. H₂, 20 cc. O₂ and 87 cc. CO₂, while as can be seen from the above curves, dehydrated chabasite at the several maxima adsorbs, respectively, 2.7 cc. H₂, 27 cc. O₂ and 130 cc. CO₂.

Summary

Chabasite shows a maximum adsorption of hydrogen, oxygen and carbon dioxide at 0°, when 97.8, 96.9 and 92.9%, respectively, of its original water has been removed at suitable temperatures. It shows a similar maximum adsorp-

tion of carbon dioxide at the same percentage dehydration at temperatures of 34.5, 61.2 and 100°. This behavior is explained as due to the collapse of the crystal skeleton when the last fractions of the water are removed.

Slightly dehydrated chabasite exhibits a pro-

nounced specificity of adsorption toward hydrogen, oxygen and carbon dioxide. This behavior is explained on the assumption of several limiting pore sizes and of differing extents of the corresponding inner surfaces.

CAMBRIDGE, MASS.

RECEIVED AUGUST 19, 1936

NOTES

The Ethyl Esters of Triiodophenoxyacetic Acids and Potassium Triiodophenoxyacetate

BY T. C. DANIELS AND R. E. LYONS

Several hitherto undescribed triiodophenoxy substitution products of ethyl acetate have been prepared because of their possible opacity to x-rays. The procedure followed was similar to that used by Hewett, Johnson and Pope¹ in preparing tribromophenoxyacetic esters. A mixture of 0.05 mole of triiodophenol, with equivalent quantities of sodium and of ethyl mono-, di- or trichloroacetate, dissolved in 50 cc. of absolute alcohol, was heated on a water-bath for two, three and one-half, or seven hours, respectively, and then poured into 250 cc. of cold water. The monophenoxy derivative, after two recrystallizations from alcohol, was obtained in 40% yield as colorless silky crystals; the diphenoxy, after two recrystallizations from chloroform (in which iodine was liberated slowly) as colorless needles. Attempts to secure the triphenoxy derivative in crystalline form were unavailing, only a yellow, amorphous mass being obtained.

The mono-substituted ester was hydrolyzed incompletely by heating with 30% aqueous potas-

sium hydroxide for several hours. The reaction mixture was poured into water, filtered and the free acid precipitated by dilute hydrochloric acid. Saponification of the di- and tri-substituted esters does not occur under similar conditions.

INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

RECEIVED OCTOBER 12, 1936

The Effect of Helium on the Kinetics of the Thermal Decomposition of Acetaldehyde

BY C. J. M. FLETCHER

The extent to which organic molecules decompose by way of a free radical and chain mechanism, or by a simple rearrangement, has been a matter of considerable debate. Although there is an increasing body of experimental evidence which indicates that free radicals and chain processes do exist in the decomposition of such molecules, there is still the alternative that molecular rearrangement can compete with the chain mechanism often to its virtual exclusion. Acetaldehyde is a substance for which a chain mechanism has been proposed,¹ and it has been suggested that the kinetics of its chain decomposition in the presence of free radicals produced either photochemically,² or by the thermal decomposition of azomethane,³ support such a mechanism. However, the concentration of free radicals present,⁴ the influence of small amounts of nitric oxide,⁵ and the catalysis of acetaldehyde by diethyl ether⁶ do not support this hypothesis.

- (1) F. O. Rice and Herzfeld, *THIS JOURNAL*, **56**, 284 (1934).
- (2) Leermakers, *ibid.*, **56**, 1537 (1934).
- (3) Allen and Sickman, *ibid.*, **56**, 2031 (1934).
- (4) Patet, *Z. physik. Chem.*, **B32**, 294 (1936).
- (5) Staveley and Hinshelwood, *J. Chem. Soc.*, 812 (1936).
- (6) Fletcher and Rollefson, *THIS JOURNAL*, **58**, 2129 (1936).

TABLE I

Phenoxyacetate	M. p., °C.	Formula	Iodine, %	
			Calcd.	Found
Ethyl triiodo-	128.5	C ₁₀ H ₉ O ₃ I ₃	68.27	67.98
Ethyl di- iodo-	160.0	C ₁₀ H ₁₀ O ₄ I ₂	74.02	73.77
Ethyl tri- iodo-	208-211 ^a	C ₂₂ H ₁₁ O ₅ I ₃	76.23	76.06
Potassium triiodo-	211 (free acid)	C ₈ H ₅ O ₃ I ₃ K	67.07	66.63

^a Decomposition point.

(1) Hewett, Johnson and Pope, *J. Chem. Soc.*, **103**, 1630 (1913).