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Heats of Adsorption of Gases and Vapors upon Crystallogenetic Adsorbents

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The heats of adsorption of many gases and vapors upon amorphous substances and particularly upon charcoal have been measured and a number of relationships affecting them have been discovered.[1] No such measurements have been made, so far as we are aware, upon *crystallogenetic* adsorbents, *i. e.*, adsorbents whose interior architecture retains to a greater or less degree the original structure of the crystalline material from which they have been prepared.[2]

Information on this score is of particular interest not only because of the high adsorptive capacity which certain of these adsorbents exhibit, for instance chabasite, but also because the greater uniformity in the fineness of the porosity of these adsorbents might well lead to heats of adsorption more divergent among themselves, *i. e.*, more specific, but individually less variable with the amount adsorbed than is the case with ordinary amorphous adsorbents.

We have therefore undertaken the measurement of the heats of adsorption of a number of gases and vapors upon three crystallogenetic adsorbents: chabasite, brucite and thomsonite.

Experimental Procedure

The Adsorbed Substances.—Samples of the best commercially available grades of the substances to be adsorbed were tested to ensure the absence of recognized impurities and were then subjected to further appropriate purifications. If the substance was liquid at ordinary temperatures, the final step in every case was distillation through an efficient fractionating column, only the middle fraction, boiling always within a range of 0.05°, being used in our measurements; if it was a gas, it was condensed either to a liquid or a solid and volatile impurities removed by evacuation, after which the condensed gas was allowed to warm up and to evaporate into the apparatus.

The *methyl alcohol* was twice redistilled over sodium. The absolute *ethyl alcohol* was refluxed for several hours over quicklime. The *carbon disulfide* was shaken exhaustively with mercury and distilled over sodium.

The *methyl chloride* was passed through two wash-bottles containing a concentrated solution of potassium hydroxide and then over phosphorus pentoxide. It was thereafter liquefied with carbon dioxide snow, evacuated for some time and then allowed to evaporate into the apparatus. The *ethyl chloride* and the *hydrogen sulfide* were dried over phosphorus pentoxide and repeatedly recrystallized by means of liquid nitrogen and then subjected to a high vacuum. In the case of the ethyl chloride freshly purified samples were employed for each run to avoid the presence of impurities which might have resulted from the action of diffuse light.

The *ethylene* and *nitrous oxide* were passed over phosphorus pentoxide and liquefied. They were then boiled for some time under reduced pressure, frozen with liquid nitrogen and the solid subjected to pumping for some time. The ethylene was further purified by repeated melting and recrystallization. The gas gave no condensate when chilled with solid carbon dioxide. Analysis by absorption in fuming sulfuric acid showed a purity of 99.7%.

The *carbon dioxide* was from a selected cylinder and contained by analysis only 0.12% of impurity. It was dried by passage over phosphorus pentoxide and introduced into the apparatus.

The *methane* was a sample specially purified by Dr. Woodhouse, which is described elsewhere.[3] Analysis by combustion indicated a purity of 99.0–99.4%, but it was probably purer than this.

The Adsorbents

Chabasite.—This was in every case material said to have been collected in the vicinity of Aussig, Bohemia. The clear samples were freed from adventitious material, crushed, sorted to pass a 14- and be retained on a 20-mesh screen, and equilibrated over 24% sulfuric acid for at least two weeks according to the procedure described elsewhere.[3] The activation of the chabasite by dehydration at 500–550° has been described elsewhere. In four representative cases the losses of water were as follows:

Sample no.	9	11	14	16	Average
Loss, %	21.62	21.35	21.37	21.38	21.42

These values agree closely with those obtained by Lamb and Woodhouse with comparable material similarly treated. They found that chabasite dehydrated under these conditions and to this extent had the maximum adsorptive capacity for a variety of gases. Exhaustive dehydration at a higher temperature, accompanied by a marked loss of adsorptive capacity, gave a total water content of 22.3%, so that the activated material can be taken as 96.0% dehydrated.

Brucite.—Our material was all from one lot collected near Cleevelah, Washington. It was cleaned, pulverized, and sorted by the same procedure used with chabasite and was dehydrated at 550° at a pressure of 2–5 mm. Two samples showed a loss of water amounting to 27.33 and 27.15%, average 27.24%, which agrees closely with the values obtained by Lamb and Woodhouse under similar

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(1) For an excellent summary, see "The Sorption of Gases," by J. W. McBain, G. Routledge & Sons, Ltd., London, 1932; and a brief discussion of recent work, "The Adsorption of Gases by Solids," by S. J. Gregg, London, 1934.

(2) The heat of adsorption of water vapor on dehydrated chabasite has recently been measured by Tiselius and Brohult, *Z. physik. Chem.*, **A168**, 248 (1934).

(3) Lamb and Woodhouse, THIS JOURNAL (to appear).

conditions. They found that brucite dehydrated to this extent (88.3% of complete dehydration) exhibited maximum adsorptive capacity.

Thomsonite.—This material came from Table Mountain, Golden, Colorado, and was prepared and activated in the same way as the chabasite. Two samples heated at 550° to constant weight lost 13.17 and 13.20%; average 13.19%. Since the original material contained 13.72% of water, these samples were dehydrated to 96.0 and 96.2% of completion.

Apparatus and Manipulation.—Following the lead of Titoff[4] and many subsequent investigators in this field, we have employed the ice-calorimeter in our measurements. This and the accessory apparatus are shown in Fig. 1.

The adsorption cell L had a volume which never differed greatly from 6.5 cc. and was connected to the buret A and the manometer N·P by capillary tubing of 1 mm. bore. L was surrounded by mercury in the inner tube of the ice-calorimeter proper, F, which was completely covered by a mixture of washed ice and distilled water in the Dewar flask H which in turn was surrounded by ice and water in a large, tall beaker, G. A drop of alcohol was added, as usual, to the water-filling of the ice-calorimeter.

The position of the mercury thread in the capillary tube J was read by means of an attached millimeter scale and a suitable telescope with micrometer eyepiece, to within 0.1 mm. The tube was carefully calibrated throughout its whole length and corrections to within 0.1 mm. were applied when required.

The weight of mercury per centimeter length of thread in this capillary was determined in three successive measurements to be 20.48, 20.51 and 20.47 mg.; average 20.49 mg. Taking 0.01546 g. as the weight of mercury corresponding to one calorie,[5] one centimeter length of thread corresponds to 1.325 cal.

The gas buret was provided with a water jacket which could be stirred with a current of air and was calibrated throughout its length to 0.01 cc. The volume of the capillary tube between the buret and the fiduciary mark in N was 0.24 cc.

The thermometers were calibrated to 0.01°, at the ice-point and at the transition temperature of sodium sulfate decahydrate.

The rate of heat-leak was determined before and after each measurement of the heat of adsorption. Usually it amounted to about 1 mm. per hour, but it was frequently even less. Since the heat evolution accompanying adsorption was usually complete within about fifteen minutes, the heat-leak could often be neglected. The room temperature was usually about 23°; no measurements were carried out when it exceeded 29° or was less than 15°.

The pressure in the system was measured by observing the difference in height of the mercury surfaces in the two limbs of N by means of a cathetometer reading to 0.05 mm. For high pressures the right-hand limb was open to the atmosphere; for low pressures it was exhausted to a negligible pressure as determined by the McLeod gage P. In every case the mercury level in the left-hand limb was brought to the fiduciary mark just below the beginning of the capillary tube.

Preparation of the Adsorbent.—A fresh adsorption cell was used for each new sample of adsorbent. These cells, before they were filled, consisted of a tube about 12 mm. in bore and 60 mm. long sealed on one end to a short length of capillary tubing and on the other to a short length of tubing with a bore of about 3 mm. bearing a mark near the seal. The volume of the cell from the capillary tube to the mark in the other tube was first carefully measured. The cell was then dried, filled with the granular adsorbent, the small tube sealed off sharply at the mark without heating the absorbent, and the capillary tube of the cell sealed onto the capillary tube of the apparatus.

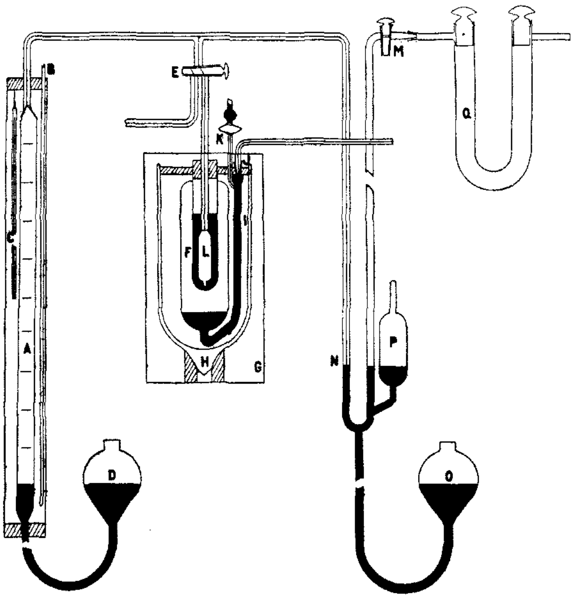

Fig. 1.

The phosphorus pentoxide tube Q was then attached and the whole system evacuated through it with a mercury diffusion pump. A cylindrical furnace was placed around the adsorption cell and its temperature raised gradually to 300° and then more rapidly to 500–550° as indicated by a mercury-in-quartz, nitrogen-filled thermometer with its bulb beside the cell. The pressure was maintained at 0.03 mm. After a suitable interval the stopcocks were closed, the furnace was removed and the tube Q disconnected and weighed.

Calorimetric Measurements.—The ice-calorimeter assembly was now raised by a jack so as to surround the adsorption cell, the position of the mercury thread was adjusted by means of the stopcock K and the measurement of the initial heat-leak was commenced. The tube Q was re-

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[4] Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

[5] Ostwald-Luther, "Physiko-chemische Messungen," 1925, p. 397.

placed, the system exhausted, the mercury in N brought to the fiduciary mark, the buret charged with gas and its temperature and pressure accurately ascertained.

After a constant heat-leak had been maintained for at least twenty minutes, gas was introduced into L and G, the stopcock E was closed and the pressure and volume in the buret were measured. A constant heat-leak was in general reestablished in about fifteen minutes, but observations were usually continued for an additional half hour.

After one such determination of the heat of adsorption, an additional amount of gas was admitted to the adsorbent and the resultant heat evolution again measured. This procedure was repeated until the rate of the adsorption became unduly slow.

Computation of the Results.—The observed pressures of the gases before and after adsorption were corrected to 0° by the usual formula applicable to mercury and a brass scale. They were also corrected for molecular attraction by means of the values of the term a in the van der Waals equation as listed in the Landolt–Börnstein tables. From these corrected pressures and the observed temperatures the volumes under standard conditions of the gas in the buret were computed by means of the simple gas law. Their difference, corrected for the dead space, gave the volume of gas actually taken up by the adsorbent.

The total excursion of the mercury thread corrected for the heat-leak and for any inaccuracies in the bore of the capillary multiplied by the above mentioned factor gave the apparent heat of adsorption. From this was subtracted the relatively small amount of heat given off by the gas in cooling from the observed room temperature to zero degrees as computed from the known specific heat of the gas. Finally, dividing by the weight of the adsorbent, the heat of adsorption per gram of adsorbent was obtained.

Reliability of the Measurements.—The volume of gas taken up by the adsorbent could be ascertained to within about 0.02 cc. and since volumes of 10 cc. or more were usually involved, the error on this score would amount to about 0.2%. Usually the uncertainty due to the unknown volumes created by the removal of water from the adsorbent was considerably less than this, but in some instances where the saturation pressure was high and the amount adsorbed small, an additional error of about the same magnitude was introduced. The thermal measurements were subject to an experimental uncertainty of about 0.02–0.03 cal., and since heats of 5–10 cal. were usually evolved, the error here was about 0.3%. The over-all error attached to a typical measurement of the heat of adsorption can therefore be estimated as about 0.5%. An examination of the plotted results (see Fig. 3) indicates that the average deviation from a smooth curve of the measurements within the above ranges is no greater than this estimate.

Results

Heats of Adsorption.—The experimental data and the results computed therefrom for a single measurement of the heat of adsorption of carbon dioxide upon chabasite are given in full in Table I in order to illustrate the procedure followed in all of our measurements and in the computations based upon them.

TABLE I

HEAT OF ADSORPTION OF CARBON DIOXIDE ON DEHYDRATED CHABASITE

Sample $16B_3$; weight 1.4922 g.

Movement Hg, cm.	11.85
Heat, gross cal.	15.70
Heat capacity, cal.	0.22
Heat, net cal.	15.48
Heat, cal. per gram	10.37
Initial temperature, °C.	24.1
Initial pressure	
Observed, mm. Hg	564.2
Correction (a) mm. Hg	+2.6
Corrected, mm. Hg	566.8
Initial volume, cc.	48.20
Initial volume, S. T. P., cc.	33.04
Final temperature, °C.	23.6
Final pressure	
Observed, mm. Hg	27.89
Correction (a) mm. Hg	0.00
Corrected, mm. Hg	27.89
Final volume, cc.	48.20
Final volume, S. T. P., cc.	1.62
Volume adsorbed	
Gross, cc.	31.42
Correction dead space, cc.	−0.11
Corrected, cc.	31.31
Per gram, cc.	20.99

An abridged presentation of all of our experimental results is given by Tables II–IV, and Figs. 2 and 3. In these tables successive determinations without intervening reevacuation of the sample are represented by the sample number followed by a letter with numerical subscripts ($8\ A_1$, $8\ A_2$, $8\ A_3$, etc.). The data under X repre-

TABLE II

HEATS OF ADSORPTION ON DEHYDRATED CHABASITE

Sample no.	7	8	9	10	13	14	15	16
Weight (anhydrous)	2.9300	1.4186	1.0324	1.0060	1.6170	1.5687	2.9612	1.4922

Sample and run	X, cc./g.	Pressure range, cm. Hg	$h_{\text{obsd.}}$, cal. per g.
		CH_4	
15 A_1	3.90	37–25	1.80
15 A_2	8.08	49–35	2.69
15 A_3	11.36	38–14	3.20
15 B_1	1.66	29–19	0.90
15 B_2	3.90	29–12	1.84
		C_2H_4	
8 A_1	5.13	77–44	3.17
8 A_2	9.03	77–39	5.60
8 B_1	6.79	76–51	4.37
8 B_2	13.83	76–38	7.79
8 B_3	19.16	76–15	9.54
		N_2O	
8 A_1	7.58	76–58	4.31
8 B_1	5.33	77–63	3.03
8 C_1	7.05	75–45	4.03
8 C_2	15.28	75–50	8.76
8 C_3	22.67	75–45	13.33
8 C_4	29.95	75–42	17.18
		H_2S	
9 A_1	6.29	76–56	4.05
9 A_2	13.60	76–46	9.00
10 A_1	15.08	77–51	8.88
10 A_2	28.61	78–44	17.76
10 A_3	34.46	77–47	20.83
10 A_4	43.51	77–14	25.76
		CO_2	
8 A_1	7.60	74–55	3.99
8 A_2	12.91	74–56	6.90
8 A_3	17.35	74–54	8.94
8 A_4	21.21	74–51	11.21
16 A_1	15.20	39–0.2	8.55
16 A_2	35.38	53–0.1	19.21
16 A_3	56.37	57–3	29.58
16 B_1	0.93	2–0.1	0.31
16 B_2	4.97	10–0.3	2.74
16 B_3	18.03	36–0.3	10.59
		CH_3Cl	
14 A_1	1.34	4–0.0	0.85
14 A_2	4.89	10–0.8	2.99
14 A_3	10.09	16–0.9	6.34
16 B_1	1.51	4–0.0	1.03
16 B_2	3.11	4–0.1	2.14
16 C_1	1.81	5–0.2	1.36
16 C_2	5.07	9–0.6	3.03
16 C_3	16.31	29–1.5	9.00
		C_2H_5Cl	
8 A_1	4.45	76–64	2.49
8 A_2	10.75	76–56	5.05
7 A_1	1.83	76–68	0.60
7 B_1	3.04	76–59	1.74
7 B_2	6.42	76–53	3.51
7 C_1	10.78	76–23	5.28
		CH_3OH	
16 A_1	1.09	3–0.3	1.55
16 A_2	1.84	3–0.4	2.29
16 B_1	0.42	1–0.2	0.55
16 B_2	1.67	4–0.6	1.98
16 B_3	2.79	4–0.7	3.16
16 B_4	3.54	3–1.1	3.69
16 B_5	4.14	3–1.5	4.08
16 C_1	2.95	10–1.5	3.27
16 C_2	5.07	8–1.7	5.35
16 C_3	7.70	9–2	8.18
16 C_4	12.10	9–2	13.28
		CS_2	
13 A_1	4.92	15–4	3.94
13 A_2	9.77	14–3	7.72
13 A_3	14.49	14–8	11.12
15 A_1	0.83	11–6	0.38
15 A_2	2.85	17–6	2.00
15 A_3	4.81	16–4	3.72
		C_2H_5OH	
16 A_1	1.89	6–1	1.37
16 A_2	3.80	6–1	2.02
16 A_3	5.68	6–1	2.23
16 B_1	0.33	0.8–0.0	0.32
16 B_2	0.77	1–0.1	0.59
16 B_3	2.15	4–0.2	1.32

TABLE III

HEATS OF ADSORPTION OF CARBON DIOXIDE ON DEHYDRATED BRUCITE

Weight (anhydrous), 4.7568

Sample and run	X, cc./g.	Pressure range, cm. Hg	$h_{\text{obsd.}}$, cal. per g.
2 A_1	0.34	29–28	0.97
2 A_2	1.84	28–27	2.20
2 A_3	5.51	27–25	3.41
2 A_4	7.69	25–23	4.01
2 B_1	1.53	7–5	1.94
2 B_2	3.51	5–4	3.08
2 B_3	4.91	4–3	3.21
2 C_1	2.92	6–4	2.49
2 C_2	4.01	4–3	2.88

TABLE IV

HEATS OF ADSORPTION OF CARBON DIOXIDE ON DEHYDRATED THOMSONITE

Weights (anhydrous): Sample 1, 0.8253 g.; 2, 5.1136 g.

Sample and run	X, cc./g.	Pressure range, cm. Hg	$h_{\text{obsd.}}$, cal. per g.
1 A_1	2.21	36–33	1.27
2 B_1	4.10	43–8	2.27
2 C_1	3.56	58–28	1.54
2 D_1	3.23	56–28	1.85
2 E_1	2.25	56–36	1.03

sent the corrected volumes of gas adsorbed per gram of *completely* dehydrated adsorbent, those under $h_{\text{obsd.}}$ the heat evolutions accompanying these adsorptions.

In Fig. 2 the heats of adsorption are plotted against the amount adsorbed. Most of the curves differ but slightly, and in two cases not at all, from straight lines. This means that the heat of adsorption per cubic centimeter of adsorbed gas is nearly or quite independent of the amount adsorbed. This is the same behavior previously observed with charcoal.[6] Indeed, the empirical equation, $h = ax^n$, which was there found to express the experimental results satisfactorily is equally applicable here, as is shown by Fig. 3 where these deviations are plotted on a large scale against the amount adsorbed. It can be seen that the deviations are usually small and for the most part lie upon smooth curves to within the previously estimated accuracy of our

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(6) Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).

measurements irrespective of the sample taken and of the number of times it had been re-evacuated. The only marked exception to this is with carbon dioxide where the measurements with sample No. 8 give definitely different results than those with sample No. 16. The values of the constants in these formulas are collected in Table V and it can be seen that here, as in the case with charcoal, the value of n is usually not far from unity.

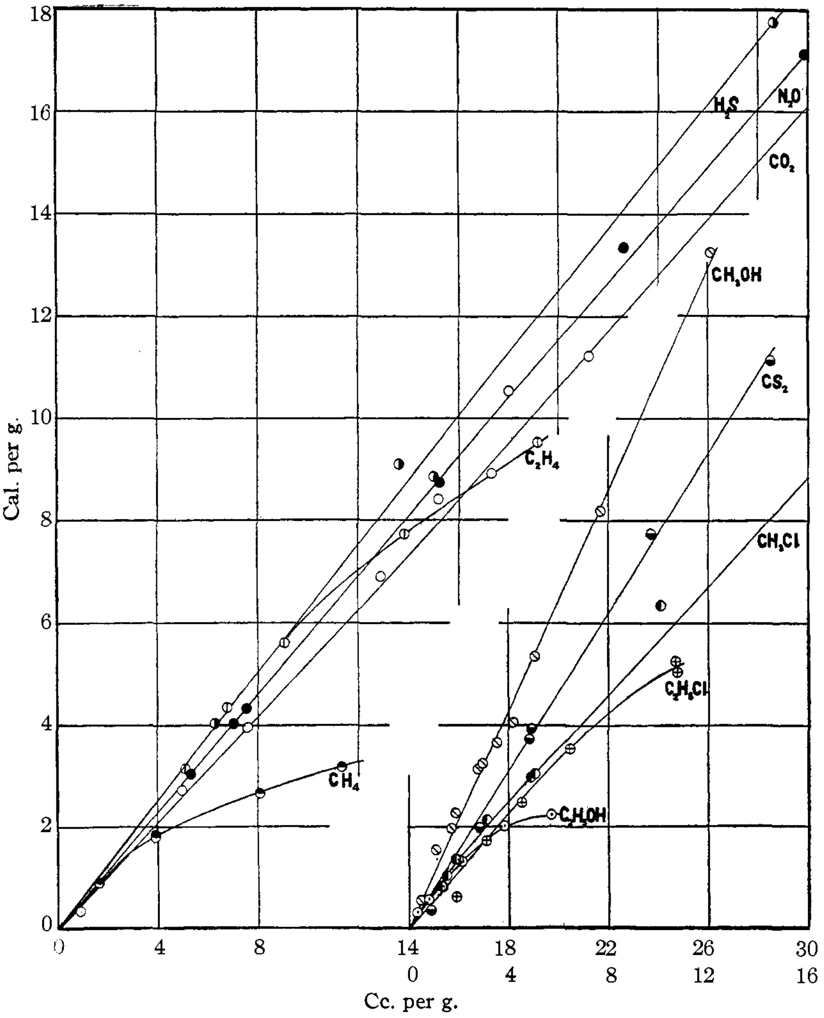

Fig. 2.—○, CO_2; ⦶, C_2H_4; ⊘, CH_3OH; ⊕, C_2H_5Cl; ⊙, $C_2H_5O_4$; ◑, H_2O; ◐, CH_3Cl; ◒, CS_2; ●, N_2O; ◓, CH_4.

Molar Heat of Adsorption.—The empirical formulas permit a convenient calculation of the molar heats of adsorption of the respective gases at the same molar concentration in the adsorbent. Values thus computed for 11 cc. of gas per gram (0.0005 mole per gram), which is in general within the range of the empirical equations, are given in the fourth column of Table V. It is interesting that these values are not very different from those previously found for adsorption upon charcoal (Col. 5).

The curves in Fig. 4 present our results for the heat of adsorption of carbon dioxide on dehydrated chabasite, thomsonite and brucite along with corresponding results of others with charcoal and silica gel. The constants of the empirical formulas which express these results and the molar heats of adsorption calculated from them are collected in Table VI.

It is clear that the crystallogenetic adsorbents show a considerably greater heat of adsorption for carbon dioxide than do charcoal and silica gel.

It is of interest that while most of the curves in Fig. 4 are straight lines (and the exponent n in the empirical equation nearly unity), that of dehydrated brucite has a marked curvature showing that the molar heat of adsorption increases decidedly for small amounts adsorbed. The heat of reaction of magnesia and carbon dioxide to form massive magnesium carbonate is 26.7 kg. cal. and is represented by the dotted line shown in Fig. 4. It can be seen from the position of this line that the molar heat of adsorption for small amounts adsorbed is as great or greater than this heat of reaction. A similar behavior has been reported in other cases.[7]

Effect of Dehydration on Heat of Adsorption.—In order to ascertain the relation between the extent of dehydration of these adsorbents and the heats of adsorption to which they give rise, we have measured the heat evolved when methyl alcohol is adsorbed on chabasite and on brucite after successive portions of water have

[7] Keyes and Marshall, THIS JOURNAL, **49**, 156 (1927); Ward and Rideal, *J. Chem. Soc.*, 3117 (1927); Marshall and Bramston-Cook, THIS JOURNAL, **51**, 2019 (1929); Buck and Garner, *Nature*, **124**, 409 (1929); Cameron, *Trans. Faraday Soc.*, **26**, 239 (1930).

TABLE V

NET HEATS OF ADSORPTION

Substance	a, cals.	n	$h$molar Chabasite, kg. cal.	$h$molar Charcoal,[e] kg. cal.	ϕ	hm − ϕ chabasite, kg. cal.	hm − ϕ charcoal, kg. cal.	Mol. vol. liq. at 0°, cc.	hm − ϕ per cc. liq. 0°
CH_4	0.875	0.537	6.43	...	0	6.43	...	..	..
C_2H_4	.807	.857	12.89	...	1.50	11.39	...	81.2	0.140
CO_2	.593	.968	12.41	7.7[a]	2.46	9.95	5.2	47.6	.209
N_2O	.573	1.000	12.83	7.76[b]	2.59	10.24	5.1	48.3	.212
H_2S	.689	0.963	14.23	...	4.24	9.99	...	36.8	.271
CH_3Cl	.676	.948	13.47	7.18[c]	4.95	8.52	2.23	52.9	.161
C_2H_5Cl	.671	.870	11.06	13.49[d]	6.00	5.06	7.49	69.8	(.073)
CH_3OH	1.230	.928	23.32	14.3[d]	9.10	14.22	5.2	39.5	.359
CS_2	0.770	1.000	17.25	13.9[d]	6.80	10.45	7.1	58.8	.178
C_2H_5OH	.747	0.753	9.27	16.4[d]	10.12	...	6.3	57.1	(..)

[a] Titoff, Ref. 4. [b] Gregg, *J. Chem. Soc.*, 1494 (1927). [c] Wood charcoal. Chappuis, *Wied. Ann.*, 19, 21 (1883). [d] Lamb and Coolidge, Ref. 2. [e] Coconut charcoal.

TABLE VI

HEATS OF ADSORPTION OF CARBON DIOXIDE ON VARIOUS ADSORBENTS AT 0°

	a in $h = ax^n$	n in $h = ax^n$	Molar heat of adsorption, kg. cal.
Chabasite dehydrated	0.593	0.968	12.89
Thomsonite dehydrated	.552	.973	12.32
Brucite dehydrated	1.603	.443	9.44
Charcoal[a]	0.184	.957	7.70
Silica gel[b]	.248	.96	7.01

[a] Titoff, Ref. 4. [b] Magnus and Kalberer, *Z. anorg. Chem.*, **164**, 357 (1927).

been removed from them. The procedure was the same as in the preceding measurements except that at the completion of a run the phosphorus pentoxide tube was attached and the alcohol was pumped off at room temperature, *after* which additional quantities of water were removed by gradual and gentle heating and pumping.

It proved to be impossible at low degrees of dehydration to remove all of the alcohol in this way without removing some of the water at the same time. The stated values for the degree of dehydration must therefore in these cases be considered as only approximate. At higher degrees of dehydration no such effect was detected. The experimental results are collected in Fig. 5.

It can be seen from these figures that the heats of adsorption on the slightly dehydrated material are decidedly less than on the more completely dehydrated material; however, the difference is proportionately smaller as the water content becomes less. The relationship is brought out even more clearly by Fig. 6, where the heats of adsorption of 0.000178 mole per gram, expressed as percentages of the maximum heat of adsorption, are plotted against the percentage of complete dehydration. It is evident that the points, with a single exception, for both adsorbents lie on a single curve which is nearly a straight line.

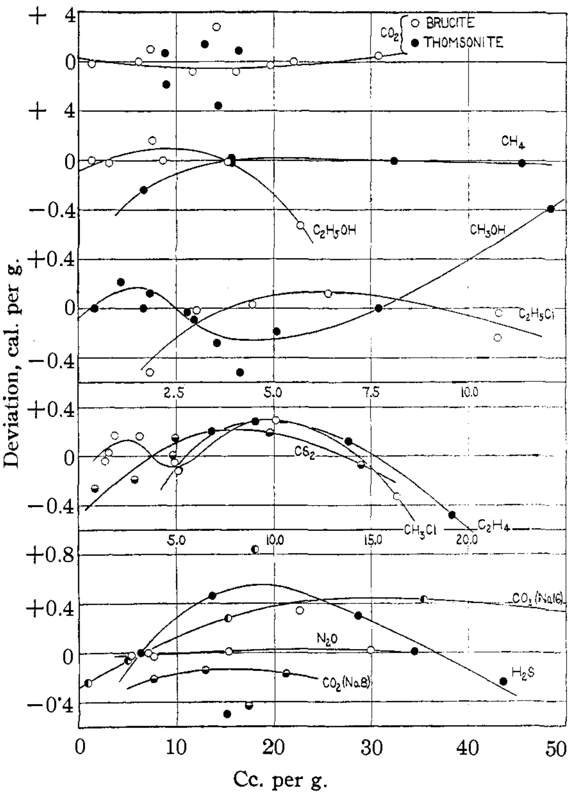

Fig. 3.—Deviations from empirical equation.

These effects would appear to indicate that the heat of adsorption per mole is decidedly greater at high degrees of dehydration than at low. On the other hand, since water is certainly desorbed from the slightly dehydrated adsorbents along with alcohol on pumping at room temperatures, it is probable that some desorption of water occurs under these conditions when the alcohol is adsorbed in the calorimeter and this would diminish the true heat of adsorption of the alcohol by the (negative) heat of desorption of the water. The observed heat of adsorption would therefore be too small by the amount of this disturbing factor. It is unlikely, however, that this can have affected the points for the more completely dehydrated samples or that it would give curves that are so nearly linear.

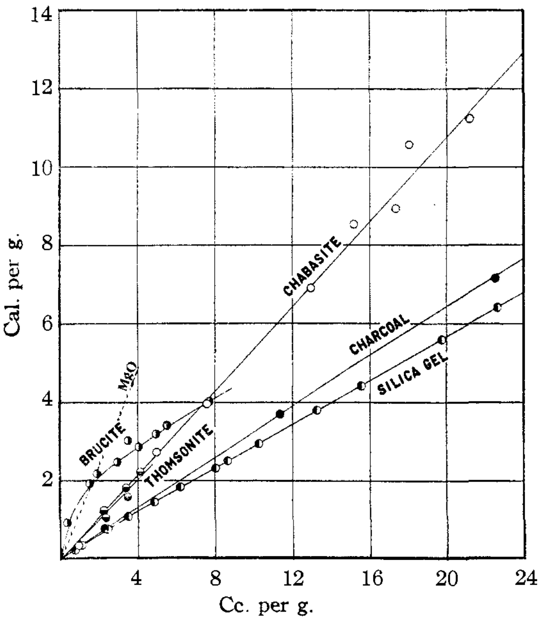

Fig. 4.—Heats of adsorption of carbon dioxide on various adsorbents.

Net Heats of Adsorption.—The *net* heats of adsorption have been obtained by subtracting from the molar heats of adsorption (h_m) the molar latent heats of vaporization of 0° (ϕ). The resulting values listed in the seventh column of Table V are, except for the value for methane which was obtained by using the empirical equation far beyond its range and those for ethyl chloride and ethyl alcohol which are aberrant for other reasons to be explained later, not very divergent among themselves and are in general considerably larger than the corresponding values upon charcoal at the same concentration (Column 8).

It has been shown[6] in the case of eleven volatile organic liquids, first, that while the net *molar* heats of adsorption vary considerably among themselves (from 6.22 to 10.65 kg. cal.) the net heats of adsorption per cubic centimeter of the *liquid* are nearly identical (0.0877 kg. cal. ±7.4%) and second, that the pressures which would be required to produce, by compression, heats equal to these net heats of adsorption are even more nearly identical (28,100 atmospheres ±4%).

To test the first relationship by the present data we have computed the net heats of adsorption per cubic centimeter of the liquids by dividing the net heats of adsorption per mole by the molar volumes of the liquids at zero degrees. The resulting values, given in Column 10, while they are all of about the same magnitude (average deviation from the mean ±25%) are by no means as concordant as in the case of the above-mentioned organic liquids adsorbed on charcoal and are indeed less concordant than the net molar heats. This is, however, not surprising, for this relationship would only be expected to hold closely when the molar volumes are measured under the high virtual pressures prevailing in the adsorption layer or when they are proportional to the molar volumes at zero degrees measured at atmospheric pressure. In the case of the organic liquids with similar critical temperatures and compressibilities this proportionality probably exists, but in the case of the substances here studied with quite different critical temperatures and compressibilities it presum-

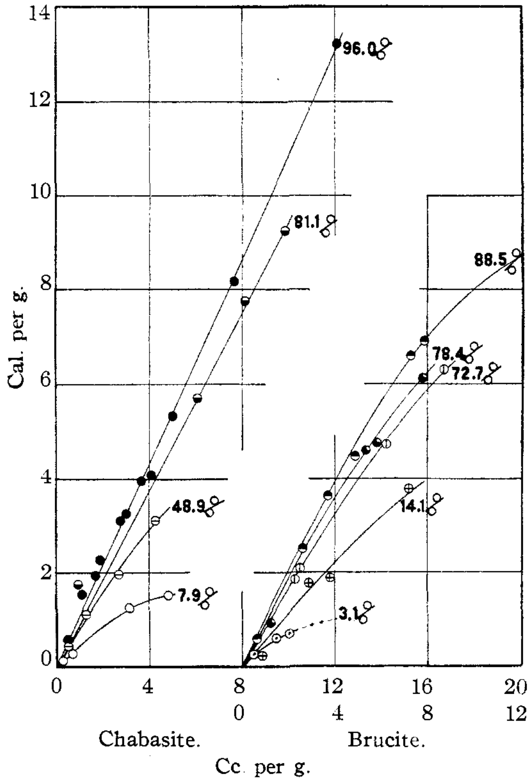

Fig. 5.—Methanol on partially dehydrated adsorbent.

ably does not and hence no such close concordance is to be expected.

We have not been able to test the second relationship since the data necessary to compute the heats of compression are lacking. It is clear, however, that in order to produce by real or virtual compression of the adsorbed layer, the considerably greater net heats of adsorption observed in these crystallogenetic adsorbents, the adsorptive pressure must be correspondingly greater than was found for charcoal.

The marked difference in the behavior of ethyl chloride and ethyl alcohol as compared with the other substances which we have studied should also be remarked. These substances are adsorbed but slightly, their heats of adsorption vary considerably with the amount adsorbed and their net heats of adsorption are small; indeed, that of ethyl alcohol is apparently negative. The explanation of this behavior is doubtless to be found in the decidedly greater dimensions of the molecules of these substances computed from known atomic radii and atomic distances, as compared with those of the other substances that we have studied. As has been pointed out previously,[8] molecules larger than a certain size are apparently unable to enter the fine pores of these crystallogenetic adsorbents, and the slight adsorption observed in these instances is presumably chiefly confined to the outer surfaces and to the inter- rather than intra-crystalline porosity. It is not surprising that this slight and mostly unoriented adsorption should evolve less heat than the more extensive and oriented adsorption within the dehydrated crystals.

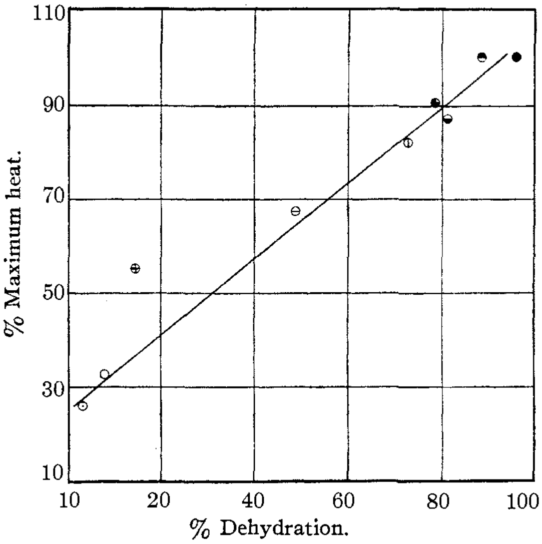

Fig. 6.

Summary

1. The heats of adsorption of a number of gases and vapors on dehydrated chabasite, thomsonite and brucite have been measured at 0°.

2. The molar heats of adsorption of such of these substances as are copiously adsorbed by these materials are in general somewhat larger than those previously observed on charcoal and silica gel but, like them, vary only slightly with the amount adsorbed and can be represented by the same empirical equation.

3. The net heats of adsorption are also considerably greater than those previously observed with charcoal and this indicates that the adsorbate on these adsorbents is subjected on the average to a more intense adsorptive and compressive force than on charcoal.

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[8] Lamb, U. S. Patent 1,813,174 [Applied for Sept. 25 (1925)]; McBain, "Colloid Symposium Monograph," 1926, Vol. IV, p. 1; *Kolloid Z.*, **40**, 1 (1926); Schmidt, *Z. physik. Chem.*, **133**, 280 (1928).