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THE HEAT OF ABSORPTION OF VAPORS ON CHARCOAL.[1]

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Introduction.

In the study of the properties of active charcoal for use in gas masks it appeared of importance to determine the adsorption isotherms of a large variety of vapors upon charcoal, and the quantity of heat thereby evolved. It was soon found that the precise adjustment of adsorption pressure equilibria is very slow and exhibits irregularities apparently connected with the presence in the charcoal of minute traces of air and other impurities. The study of this aspect of the problem was, therefore, postponed, and attention was directed chiefly to the study of the amounts of heat evolved during adsorption.

In these thermal measurements complete adjustment of the adsorption equilibrium is also slow; but at least at low pressures, the greater portion of the gas is taken up in a few minutes, so that accurate calorimetric measurements can be made quite rapidly by a suitable method as, for instance, that using the ice-calorimeter, provided the gradual adsorption of the remaining vapor by the charcoal be prevented. This can be done by closing off the system after an appropriate interval, close to the charcoal. The little residual vapor thus entrapped, even if it were completely adsorbed, could not evolve a measurable quantity of heat.

Our general method of procedure was to enclose in a glass tube, a weighed quantity of charcoal freed from gaseous impurities by evacuation at a high temperature, place this tube in an ice-calorimeter, and when constant readings had been obtained, to introduce a measured quantity of the vapor in question at low pressure into the tube. We waited until most of it had been adsorbed, then shut the residual gas off from the charcoal, and finally observed the stationary reading of the ice-calorimeter. This process could be repeated with fresh samples until an equilibrium pressure had been attained beyond which it was impossible to go without condensation of the vapor at 0°. Similar measurements using an ice-calorimeter have previously been made on nitrogen, carbon dioxide and ammonia by Titoff.[3]

The apparatus, materials and experimental procedure are first described; the results obtained and a discussion of them follow.

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[1] Published by permission of Maj. Gen. W. L. Sibert, Director, C. W. S., U. S. Army.

[2] The authors wish gratefully to acknowledge their indebtedness to Margaret S. Coolidge for her skilful execution of a number of the measurements recorded in this paper.

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

Apparatus.

The apparatus used in these measurements presents certain advantages as compared with that used by Titoff; it is shown in Fig. 1. It consists essentially of the bulb A in which the gas or vapor is stored; the manometer B; the ice-calorimeter C, and the valve D.

The bulb A, together with the connecting tubes and the parts of the manometer and valve which are occupied by gas, constitute the volume used in calculating the quantity of gas adsorbed. The temperature of the greater part of the system is given by that of the water at room temperature which surrounds A; that of the small volume represented by the valve, manometer, and connections, will not differ sufficiently to cause appreciable error.[1]

B serves as a manometer, and also as a valve to isolate the system from the pump (a Gaede mercury pump) so that the latter may be stopped or used for other purposes. The small side-tube *a* can be used as a simple MacLeod gage to indicate the vacuum attained. A cathetometer is used to read the manometer, and since it can be relied on to only 0.05 mm., it is not necessary to employ refined methods of measuring the vacuum. We have not used a permanently exhausted manometer, because of the difficulty of cleaning and refilling. The one we used can be easily cleaned by emptying the mercury through *b* and pouring in cleaning solution by means of a funnel inserted through the filling plug *p*.

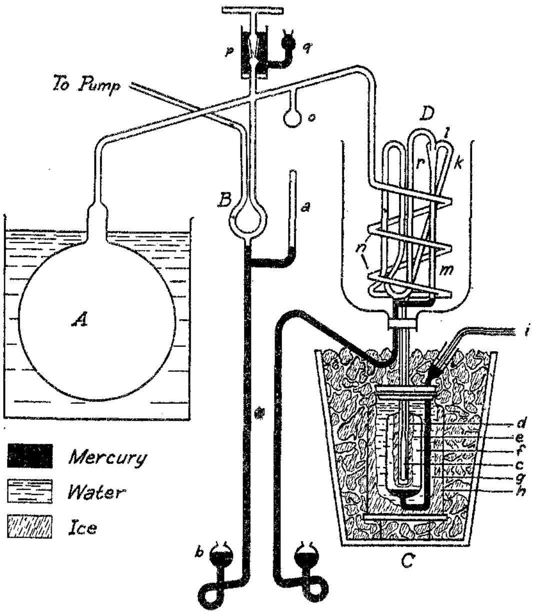

Fig. 1.—Adsorption apparatus and ice-calorimeter.

The sample of charcoal is contained in the small bulb *c*, which can be inserted in an ice-calorimeter of the usual design. The latter is protected from heat exchange by immersion in a glass jar containing distilled water

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[1] In a later form of apparatus, the large bulb was inverted and the connecting tubes all sloped to drain into B or D. This was a great improvement, as mercury is certain sooner or later to fly about in the apparatus, but with this arrangement it all runs out again. In the old apparatus there was usually a little puddle of mercury in A, whose volume had to be estimated and corrected for, and which could be removed only by taking the apparatus apart.

and lined with pure ice by previous immersion in a freezing mixture. The addition of 2 drops of alcohol to the water in the jar serves to balance the depression of the freezing point of the water in the calorimeter due to the pressure of the mercury in the leading-out tube, and we have no correction for heat exchange. This probably has no advantage over a small constant heat exchange so far as accuracy is concerned, but is much more convenient, as it is unnecessary to record the time accurately and then to calculate the correction. In the diagram, *d* is the inside tube of the calorimeter, surrounded by the sheath of ice *e*; *f* is the calorimeter jacket, *g* the protective coating of ice on the inside of the jar *h*. Heat is conducted from *c* to *d* by the water which fills the space between them up to a point just below the top of the ice sheath. The whole is packed in a tub of crushed ice, and mounted on an adjustable platform by means of which it can be run under the charcoal tube and raised into position.

The ice-calorimeter is read by a capillary tube *i* inserted through the cork sleeve; one millimeter of the scale used in calibrating corresponded to 0.589 cal. at 15°. This constant was determined by dropping in known weights of water and glass previously brought to constant room temperature. The bulb used weighed 2.986 g. and the specific heat of its glass, separately determined, was 0.189. The bulb contained 2.730 g. of water of average specific heat of 1.004, making the total heat capacity of the filled bulb 3.304 cal. Four separate experiments gave values varying between 0.587 and 0.590 cal. per mm. of the scale, with a mean value of 0.589.

Ostwald[1] gives 1.546 g. of Hg per cal.; since 75.1 mm. of this capillary contained 0.6835 g. of Hg this corresponds to 0.5885 cal. per mm.

The capillary tube used in the present experiment was somewhat smaller than the above, and its constant, found by weighing a column of mercury, was 0.587 cal. per mm. There were also small corrections for variations in its bore, amounting to between —0.1 and +0.1 mm. which were determined and applied.

The admission of the gas to the charcoal is controlled by the mercury valve D. When the level of the mercury is lowered, gas enters the charcoal tube through *k*, while the trap *l* separates any mercury carried over and returns it through *m*. N is a spiral glass tube which is immersed in ice and water after the pressure of the gas has been read, but before it is admitted to the charcoal. This insures that the entering gas will not carry in any extraneous heat.[2] The arrangement designed to make

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[1] Ostwald-Luther, "Hand-und Hülfsbuch," 3rd Ed., p. 334.

[2] The apparatus was so arranged that the principal drop in pressure between the reservoir and the charcoal occurred inside the calorimeter. An approximate computation demonstrated that neither the kinetic energy of the inflowing gas nor the Joule-Thomson effect could have produced any significant error.

as small as possible the space in connection with the charcoal after the valve has been closed, since with a large dead space the gradual adsorption of small quantities of gas would continue for some hours, and a definite reading would be difficult to obtain. Some of the gases studied condense at the pressures used when the temperature is reduced to zero. It was feared that if this were allowed to occur in the valve, the gas on re-evaporating might be cooled and enter the calorimeter below the freezing point. To prevent this, a bulb *o* is provided; by immersing this in ice and water, the gas can be condensed there and the pressure so lowered that no further condensation occurs when D is subsequently cooled. Naturally, this is not done till the pressure and temperature of the gas have been ascertained.

The substance under examination is admitted to the system through the filling plug *p*. This is not lubricated, but is ground at an angle large enough to prevent sticking. It is normally covered with mercury, and is perfectly tight when so sealed. When it is in a certain position, a scratch on the upper half of the socket meets one on the lower half of the plug, forming a very narrow channel. In filling, liquid is poured on top of the mercury forming the seal, which is then lowered until the top of the grinding is covered with the liquid. The plug is then turned, and the liquid flows in through the scratch until the desired pressure has been attained, when the plug is again turned and the mercury seal replaced. It is generally necessary to boil away the superfluous liquid, as otherwise its capillary properties enable it to creep under the mercury seal and through the grinding, causing the pressure in the apparatus to increase slowly. When the plug is dry, the pressure remains constant indefinitely. This plug is more satisfactory than any other device we have thought or read of, as it does not depend on lubricants, which are rapidly attacked by some of the substances examined, nor on sweeping out the air in an intermediate chamber, which is uncertain, wasteful of material, and involves filling the pumps with liquids which may dissolve in the oil of the backing pump and be removed with difficulty.

Materials.

All the liquids used were carefully purified by appropriate chemical treatment, and were fractionated in a glass still with an efficient still-head until the main portion came over within a few hundredths of a degree. All liquids were used immediately after preparation.

The charcoal used in all but a few of the measurements was from one lot of a steam-activated cocoanut charcoal of excellent quality, as shown by the following service time tests made according to the standard C W. S. accelerated chloropicrin tube-test method.

When allowed to stand overnight in the tubes the tested samples showed 6 minutes recuperative run to the break.

	Weight. G.	Temperature. ° C.	Pressure drop. Mm. H_2O.	Time. Min.
	8.59	29	33	48.6
	8.51	29	31	49.6
Average,	8.55	29	32	49.1

A few measurements were made with a less active charcoal (E-622). This charcoal was also a cocoanut charcoal of the same mesh as the above and had been activated in a similar way. It ran only 14.4 minutes when tested according to the same procedure. It is referred to in what follows as "inactive" charcoal.

Method of Experimentation.

Preliminary Treatment of the Charcoal.—The tube in which the charcoal is to be contained is first sealed to one part of a ground glass connection and weighed. It is then filled with charcoal, attached to the Gaede pump by the ground joint, and evacuated for an hour and a half at 350°, and at a pressure of 0.01 mm.,[1] the heating being accomplished by a small electric tube furnace. While still hot and evacuated, the bulb is sealed off, and when cool is weighed together with the original part of the ground joint, so that exactly the same portions of glass figure in each weighing, and the difference is the charcoal taken, freed from adsorbed gases and moisture. The charcoal tube is now sealed to the apparatus in the proper place, and again heated and exhausted for an hour, after which the valves are closed, the charcoal tube cooled in ice, and the calorimeter placed in position. It requires half an hour for the latter to come to equilibrium.

Introduction of the Gas.—While the charcoal is cooling, gas is introduced through the filling plug, its temperature and pressure read, and, if necessary, it is partially condensed in *o*. When the calorimeter readings have become constant, ice and water are placed around the valve, which is then opened, allowing the gas to flow into the charcoal. After a few minutes, the valve is closed again, the pressure of the gas remaining in the system noted, and the calorimeter watched until its readings become constant. The pressure in the charcoal tube may be compared with that in the main volume at *r*, which, with the volume of dead space, gives the quantity of gas removed from the main volume but not adsorbed by the charcoal. This is generally negligible. This pressure in the bulb at the end of an experiment is not in general the true equilibrium pressure, which may require hours and sometimes days to be established, but in a carefully prepared and unpoisoned charcoal differs but little from it. Another portion of gas is now admitted to the charcoal and the heat measured; this is repeated until the final pressure in the tube reaches or

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[1] Since the heat of adsorption was found to be nearly independent of the amount already adsorbed it would seem that a small amount of residual gas could hardly be of much importance.

exceeds 20 mm. These consecutive "experiments" constitute a "run" according to our nomenclature. The charcoal may be heated and evacuated and another run made, either with the same or with a different substance. All the runs made with one sample of charcoal constitute a "series."

Calculation of Results.

Results are expressed in 15° calories and cubic centimeters of gas at normal temperature and pressure, per gram of gas-free adsorbing charcoal. In calculating the gas volumes, a correction representing the effect of molecular attraction is first added to the observed pressure. This is obtained from the values of the constant *a* of Van der Waals' equation (Landolt-Börnstein), and as a rule amounts to about 0.3%. (The effect of the volume of the molecules is negligible at these pressures). The resulting ideal pressure is then used to reduce the volume to 0° and 760 mm., according to the laws of an ideal gas. The complete calculation of an experiment is as follows:

Weight of charcoal sealed in tube, exhausted	19.287 g.
Minus weight of glass	15.909 g.
Plus weight of displaced air, 6 cc.	0.007 g.
True weight of charcoal	3.385
Volume of system	1187 cc.
Temperature	22.0°
Pressure before adsorption	77.3 mm.
Correction for attraction (Van der Waals')	0.2 mm.
Pressure after adsorption	1.9 mm.
Pressure drop	75.6 mm.
Gas removed, $1187 \times \frac{273.0}{295.0} \times \frac{75.6}{760}$	109.3 cc. at NTP
Pressure in charcoal tube at end	1.5 mm.
Volume of same	12.0 cc.
Gas removed but not adsorbed	0.1 cc.
Gas adsorbed	109.3 cc. at NTP
Ditto per gram charcoal "*x*"	32.30 cc. at NTP
Reading of calorimeter, initial	0.0 mm.
Ditto, final	126.7 mm.
Heat evolved, 126.7 × 0.587	74.4 cal.
Heat evolved per gram charcoal, "*h*"	21.98 cal.

The results of each experiment are added to those of all preceding experiments of the same run, thus giving the total gas in the charcoal, *x*, and the total heat evolved during its adsorption, *h*.

The Results.

All the results which we recorded are reported in the following tables. They are also shown in the accompanying Figs. 2, 3 and 4. Three of the results, however, which are bracketed in the tables as obviously wild, are omitted from the plots because it would not be clear to which curve they belong.

TABLE I.—HEAT OF ADSORPTION MEASUREMENTS ON ACTIVE CHARCOAL.

Carbon Tetrachloride.

$h = 0.893\ x^{0.930}$.

Charcoal and run.	Adsorbed gas. x n cc.	Heat evolved, h. Observed. cal.	Heat evolved, h. Computed. cal.	Difference. Δ cal.	Pressure. mm.
L_3	23.56	16.87	16.86	+0.01	..
B_1	30.35	21.47	21.35	+0.12	..
D_1	33.50	23.46	23.40	+0.06	..
C_3	34.91	24.30	24.31	—0.01	..
A_1	39.50	26.61	27.27	—0.66	..
B_1	60.94	41.71	40.82	+0.89	4
	76.4	.....	.....	.....	7
A_1	78.32	51.53	51.55	—0.02	10
R_1	78.80	51.40	51.83	—0.43	..
	91	.....	.....	.....	21
	108	.....	.....	.....	46

C_3 Used for ether. Exhausted 90 minutes.
A_1 Fresh. Exhausted overnight.
B_1 Same.
D_1 Fresh. Exhausted 2 hours.
L_2 Used for methyl alcohol.

Ether.

$h = 0.917\ x^{0.9215}$

Charcoal and run.	Adsorbed gas. x n cc.	Heat evolved, h. Observed. cal.	Heat evolved, h. Computed. cal.	Difference. Δ cal.	Pressure. mm.
I_1	18.10	13.39	13.21	+0.18	..
C_1	35.00	24.15	24.29	—0.14	..
I_1	37.68	26.06	25.98	+0.08	..
C_2	43.18	29.45	29.48	—0.03	3
I_1	58.07	39.06	38.70	+0.36	..
C_2	75.68	49.31	49.40	—0.09	..
C_1	78.76	51.40	51.29	+0.11	..
	81.7	.....	.....	.....	10
I_1	86.77	53.78	56.07	(—2.29)	10
I_1	99.34	60.61	63.48	(—2.87)	63

C_1 Exhausted 90 minutes.
C_2 Same.
I_1 Fresh. Heated overnight at low pressure, and in vacuum one hour.

Chloroform.

$h = 0.8295\ x^{0.935}$.

Charcoal and run.	Adsorbed gas. x n cc.	Heat evolved, h. Observed. cal.	Heat evolved, h. Computed. cal.	Difference. Δ cal.	Pressure. mm.
J_1	22.30	14.91	15.11	—0.20	..
H_1	30.89	20.28	20.40	—0.12	..
G_1	32.69	21.88	21.59	+0.29	..
J_1	45.49	29.41	29.40	+0.01	..
H_1	60.49	38.09	38.40	—0.31	..
G_1	68.66	43.20	43.21	—0.01	..
H_1	78.36	48.84	48.90	—0.06	7
	104	.....	.....	.....	15
G_1	107.10	65.67	68.50	+0.17	..

G_1
H_1 All fresh samples,
J_1

TABLE I (*continued*).

Ethyl Formate.

$h = 0.944\ x^{0.9075}$.

Charcoal and run.	Adsorbed gas. x n cc.	Heat evolved, h.		Difference. Δ cal.	Pressure mm.
		Observed. cal.	Computed. cal.		
P_2	20.72	15.07	14.79	+0.26	..
P_1	32.30	21.97	22.11	—0.14	..
P_2	53.77	35.10	35.12	—0.02	..
P_1	62.88	40.27	40.47	—0.20	..
P_2	80.02	50.39	50.37	+0.02	3
P_1	96.73	59.70	59.83	—0.13	10
P_1	120.15	73.00	72.87	+0.13	35

P_1 Fresh.

P_2 Same.

Carbon Disulfide.

$h = 0.7525\ x^{0.9205}$.

Z_2	23.91	13.93	13.99	—0.06	..
Z_3	38.07	21.82	21.45	+0.37	..
Z_2	48.40	26.71	26.76	—0.05	..
E_1	66.58	35.60	35.81	—0.21	6
Z_2	70.02	37.63	37.59	+0.04	..
Z_3	74.92	40.19	40.00	+0.19	..
Z_2	97.94	51.41	51.19	+0.22	3
Z_3	111.98	58.13	57.92	+0.21	7
Z_2	127.67	65.40	65.36	—0.04	12
E_1	128.28	65.25	65.61	—0.36	24
Z_3	137.78	69.90	70.11	—0.21	15
Z_2	143.37	69.19	72.73	(—2.55)	21
Z_3	153.19	76.87	77.27	—0.40	40

Z_2 Used for CS_2. Exhausted overnight.

Z_3 Same.

E_1 Fresh. Heated at low pressure over night, and in vacuum 2 hours.

Methyl Alcohol.

$h = 0.742\ x^{0.938}$.

S_1	21.67	13.39	13.30	+0.09	..
S_1	47.42	27.64	27.71	—0.07	..
S_1	75.27	42.76	42.24	+0.02	..
S_1	103.27	57.44	57.48	—0.04	13
S_1	127.40	70.08	69.98	+0.10	18

S_1 Fresh. After 2nd expt. the charcoal tube was removed from calorimeter, and allowed to stand in the air overnight. Next morning the run was continued.

Ethyl Chloride.

$h = 0.7385\ x^{0.915}$.

U_2	29.10	16.05	16.14	—0.09	..
U_3	42.66	23.02	22.90	+0.12	..
U_2	67.01	34.78	34.62	+0.16	..
U_2	102.81	51.21	51.21	.....	15
U_2	124.80	61.03	61.17	—0.14	52

U_2 Used for benzene.

U_3 Same sample.

TABLE I (*continued*).

Ethyl Bromide.

$h = 0.900\ x^{0.900}$.

Charcoal and run.	Adsorbed gas. x n cc.	Heat evolved. h. Observed. cal.	Heat evolved. h. Computed. cal.	Difference. Δ cal.	Pressure. mm.
W_1	48.90	29.85	29.83	+0.02	..
Y_2	54.10	32.65	32.67	—0.02	..
W_1	91.73	52.55	52.54	+0.01	10
W_1	120.48	67.15	67.13	+0.02	37

Y_2 Previously used with ethyl alcohol.
W_1 Fresh.

Ethyl Iodide.

$h = 0.737\ x^{0.956}$.

U_4	34.42	21.71	21.72	—0.01	..
U_4	67.52	41.40	41.36	+0.04	2
U_4	99.17	59.97	59.77	+0.20	5
U_4	124.72	74.11	74.39	—0.28	39

U_4 Previously used with ethyl chloride.

Benzene.

$h = 0.774\ x^{0.959}$.

U_1	28.37	19.16	19.17	0.01	..
U_1	54.70	35.90	35.93	—0.03	2
U_1	81.03	52.54	52.39	+0.15	3
U_1	102.04	65.30	65.34	—0.04	13

U_1 Fresh.

Ethyl Alcohol.

$h = 0.871\ x^{0.928}$.

X_1	4.59	3.62	3.60	+0.02	..
X_1	8.40	6.27	6.28	—0.01	..
X_1	14.23	10.19	10.24	—0.05	..
Y_1	14.65	10.41	10.52	—0.11	..
X_1	27.83	19.11	19.08	+0.03	..
Y_1	31.40	21.38	21.34	+0.04	..
Y_1	46.91	31.01	30.96	+0.05	..

$\left.\begin{matrix}X_1\\Y_1\end{matrix}\right\}$ Both fresh.

TABLE II.—HEAT OF ADSORPTION MEASUREMENTS ON INACTIVE CHARCOAL.

Carbon Tetrachloride.

$h = 0.841\ x^{0.930}$.

Charcoal and run.	Adsorbed gas. x n cc.	Heat evolved. h. Observed. cal.	Heat evolved. h. Computed. cal.	Difference. Δ cal.	Pressure mm.
V_2	24.33	16.39	16.36	+0.03	..
T_3	26.12	17.45	17.48	—0.03	..
V_2	36.27	22. 5	23.73	(1.18)	21

TABLE II (*continued*).

Charcoal and run.	Adsorbed gas. x n cc.	Heat evolved, h. Observed. cal.	Heat evolved, h. Computed. cal.	Difference. Δ cal.	Pressure. mm.
		Methyl Alcohol. $h = 0.754\ x^{0.938}$.			
T_1	32.65	19.95	19.84	+0.11	..
T_1	60.95	35.61	35.63	—0.03	2
T_1	88.35	50.41	50.46	—0.05	4
T_1	117.09	65.65	65.73	—0.08	14
		Benzene. $h = 0.824\ x^{0.955}$.			
V_1	18.48	13.35	13.33	+0.02	..
T_2	23.71	16.74	16.94	—0.20	..
V_1	36.28	25.44	25.44	±0.00	4
V_1	47.93	33.16	33.16	±0.00	9

In the first column of the tables there are letters indicating the charcoal samples used, together with the subscript indicating the number of the run. A_1, for instance, indicates that this measurement was made with charcoal A and is one of the experiments in the first run made with this sample. U_3 would mean the third run with charcoal sample U. The second column contains the quantities of gas (x) in normal cc. adsorbed per g. of gas-free adsorbent. In the third column are given the observed values of h, the heat evolved, in 15° calories per g. of gas-free charcoal. In the fourth column are given the values of h computed from an empirical exponential formula, placed at the top of the column. In the fifth column are given the differences between the observed and calculated values ($\Delta = h_{\text{obs.}} - h_{\text{calc.}}$). The sixth column contains the equilibrium pressures observed at the time when the final calorimetric readings were made. The previous history of each charcoal sample is given below the results for each liquid.

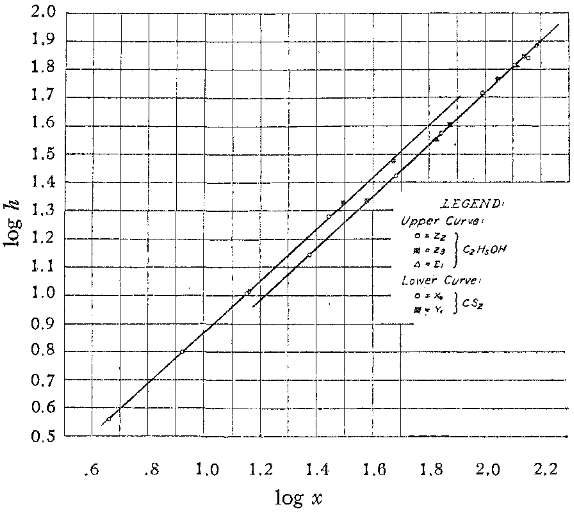

Fig. 2.—Agreement between the results of separate runs.

If the observed values of x and h are plotted, they are found to lie on a system of lines slightly concave towards the x-axis. If the logarithms of the values are plotted, they are found to lie very precisely upon straight lines, and this has been adopted as the most convenient way of representing our results graphically. (See Figs. 2, 3 and 4.) From the position and slope of these lines we obtain at once the constants of equations of the form

$$\log h = a + b \log x, \quad \text{or} \quad h = mx^n$$

where $m = 10^a$ and $n = b$. The equations obtained in this way have been used to compute numerically the values of h given in the fourth column of the above tables.

Reproducibility and Reliability of Results.—The results presented above (Tables I and II and the curves) have been obtained with various weights of both active and inactive charcoal, some fresh, others previously used, and with various portions of gas, with reference to the weight of the charcoal. The agreement for each charcoal is very satisfactory. The average error of a single experiment seems to be about 0.7%, but that of the higher results is much less, due to compensation of errors in adding. The agreement between runs is about as good as that between experiments. This is shown particularly well by Fig. 2, where typical values obtained in 3 separate runs with ethyl alcohol and 2 separate runs with carbon disulfide are given. It is seen that the points lie very accurately on the same straight lines.

This close agreement shows that the total quantity of heat evolved during the adsorption by empty charcoal of a quantity of gas is definite and reproducible. It is not affected by the manner in which the gas is added (whether slowly or rapidly, all at once or in several portions) nor by the previous experiences of the charcoal, at least in our laboratory, provided that all the gas is first removed by heating to 350° and evacuating. In other words, it makes no difference whether the charcoal comes fresh from the can or has been previously used for other experiments, either with the same or a different gas; or, in the latter case, whether the gas has been immediately pumped out, or allowed to remain some time, or the charcoal even left open to the air. One interesting exception will be described later.

The reading of the calorimeter usually becomes constant after 15 minutes to a half an hour as stated above, and no slow creep of the calorimeter is noticeable; indeed, at least one of the runs (S_1) was begun and finished on different days. Had any appreciable heat been given off during the night the subsequent points, since each "experiment" was additive, would have been too low. No such effect was found. These facts demonstrate that if any slow sinking-in of gas occurred, no heat is thereby liberated. This is in agreement with the fact mentioned later, which our results have demonstrated in a striking fashion, that the heat of adsorption is almost independent over a wide range of the amount of vapor already adsorbed. Any transfer, then, of adsorbed gas from the outer to the inner portions of the charcoal grain would liberate but a small and presumably inappreciable quantity of heat.

The measurements of the equilibrium adsorption pressure at the completion of an experiment do not have the same accuracy as the thermal measurements. Except in the case of carbon disulfide, however, these pressures must be very nearly correct, for no further noticeable change occurred after many hours. In the case of carbon disulfide there was a progressive decrease in pressure, so that in duplicate runs made at different speeds the one made more rapidly, that is, with longer waits between the separate additions of the gas and hence with more opportunity for adsorption, gave higher pressures corresponding to the same amount of adsorption. In spite of this the heats evolved in the adsorption of the same amount of gas by the 2 charcoals differed by hardly more than the experimental error.

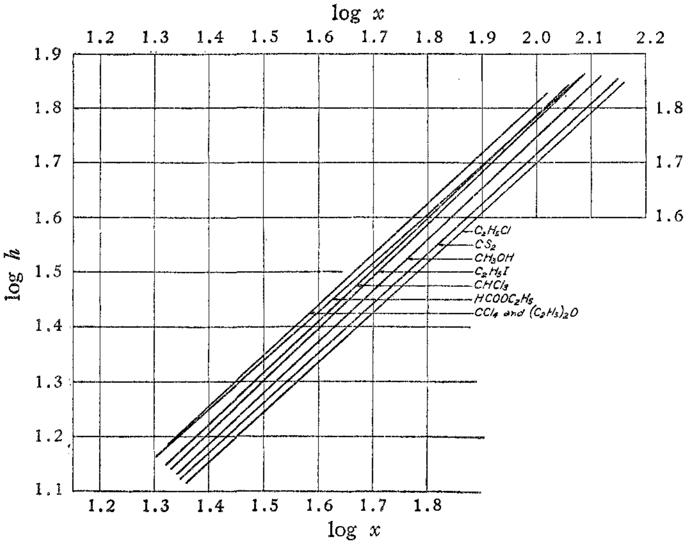

Fig. 3.—Variation of heats of adsorption with the amount adsorbed.

A very interesting effect occurs when carbon tetrachloride and other of the above-mentioned vapors containing halogen, except ethyl chloride, are used. Once having been used with these gases, a sample of charcoal cannot be brought back to its original condition, but appears to be changed in such a manner that in all subsequent experiments with it, less heat is evolved than would be by a new sample of the same weight. This is shown by the results tabulated in Table III.

TABLE III.—EXPERIMENTS WITH POISONED CHARCOAL.

Carbon Tetrachloride.

$h = 0.700\ x^{0.974}$.

Charcoal and run.	Adsorbed gas. x n cc.	Heat evolved. h. Observed. cal.	Heat evolved. h. Computed. cal.	Difference. Δ cal.	Pressure. mm.
D_6	34.40	21.90	21.96	—0.06	..
A_3	34.80	22.25	22.22	+0.03	..
A_4	47.60	30.18	30.13	+0.05	..
A_3	63.03	39.81	39.57	+0.24	..
A_3	90.58	56.12	56.36	—0.24	20

A_3 Used first for CCl_4 and then for ether.

A_4 Same sample.

D_6 Used 5 times with CCl_4.

Ether.

$h = 0.838\ x^{0.926}$.

K_2	28.65	18.60	18.70	—0.10	..
A_2	42.10	26.60	26.73	—0.13	..
K_2	55.94	34.90	34.75	+0.15	..
A_2	78.50	48.01	47.65	+0.36	12
K_2	81.44	49.54	49.32	+0.22	10
K_2	96.60	57.48	57.60	—0.12	80

A_2 Used with CCl_4.

K_2 Used with CCl_4. Pumped in a vacuum overnight.

Chloroform.

$h = 0.716\ x^{0.960}$.

G_2	30.20	18.47	18.84	—0.37	..
F_2	31.68	19.72	19.74	—0.02	..
F_2	65.01	39.42	39.38	+0.04	..

F_2 Used previously with chloroform.

G_2 Ditto. Stood 2 days under water, and exhausted one hour at 350°.

Ethyl Bromide.

$h = 0.543\ x^{1.02}$.

Y_3	29.80	17.32	17.32	.....	..
U_5	31.45	18.30	18.30	.....	..

Y_3 Used once with ethyl alcohol, and once with ethyl bromide.

U_5 Used successively with benzene, twice with ethyl chloride, and with ethyl iodide. As the 2 results with the chloride were identical, it was considered that the poisoning was not due to that, but to the iodide.

It can be seen that the values obtained are perfectly consistent with themselves, whether made with carbon tetrachloride or ether, or chloroform. They run about 10% lower than with new charcoal, though the effect is a little less for the higher values. The capacity of the charcoal to adsorb gas is not noticeably affected. Subsequent experiments with carbon tetrachloride show no further effect on the charcoal, which continues to reproduce the results of the second run made.

The exact numerical relation can be seen from Table IV, where the characteristic constants for the fresh and "poisoned" charcoal are collected.

TABLE IV.—COMPARISON OF FRESH AND POISONED CHARCOAL.

	m.		*n.*	
	Fresh.	Poisoned.	Fresh.	Poisoned.
CCl_4	0.893	0.700	0.930	0.974
$(C_2H_5)_2O$	0.917	0.838	0.9215	0.926
$CHCl_3$	0.8285	0.716	0.935	0.960
C_2H_5Br	0.900	0.543	0.900	1.02

It can be seen that except for ethyl bromide where only 2 measurements are available the *n*'s are substantially the same, while the *m*'s for poisoned charcoal are decidedly smaller.

These facts are shown even more clearly in Fig. 4, where the broken lines represent the behavior of the poisoned, and the unbroken lines that of the fresh charcoal. The 2 curves are almost exactly parallel, but the poisoned charcoal shows a constant lower heat evolution.

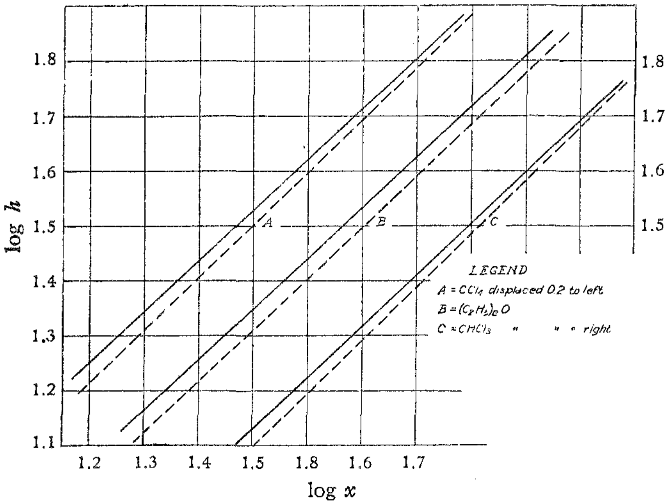

Fig. 4.—Poisoning effect of halogen-containing vapors. Solid lines represent fresh. broken lines "poisoned" charcoal.

The explanation of this behavior is not simple. That it is not due to incomplete removal of the carbon tetrachloride, is proved by the fact that in the second and subsequent runs just as much new gas is taken up (to a given pressure) as in the first; only the heat evolved is less. We, therefore, believe that the chloride reacts with some constituent of the charcoal, and that the reaction is completed during the first run or the subsequent exhaustion, after which no further change occurs. It seems unlikely that the change occurs *during* the first run, since the higher points determined ought to show the effect of it by running low. We thought it might happen during the exhaustion preliminary to the second run, and tried varying the time and temperature of the exhaustion, but without influencing results. We did find, however, that if when a run is complete, the charcoal is removed from the calorimeter and allowed to stand at room temperature for an hour without removing any gas from it, and if the run is now resumed, the heat values will run somewhat low. If the charcoal is allowed to stand overnight, it will be found that the change has completely occurred, and the heats obtained from future experiments in the same run will correspond to those of second and later runs. This suggests that the change, whatever it may be, does not occur at all during the intervals of observation at the freezing point, occurs slowly at room temperature, and at any higher temperature occurs so rapidly that the change is completed even during the shortest period of exhaustion which we tried. Since prolonged exhaustion at high temperature does not cure this effect, it appears that there is no way of restoring a sample of charcoal which has once adsorbed carbon tetrachloride, except presumably by reactivation at a very high temperature, with air or another oxidizing agent.

Discussion of Results.—Since the above table and curves show clearly that the observed heats of adsorption on unpoisoned charcoal can be represented with satisfactory accuracy over the whole range as a simple exponential function of the amount of gas adsorbed, it is most convenient to discuss the results from the point of view of these equations, and the characteristic constants (m and n) which they contain. These constants have been collected in the first 2 columns of Table V.

TABLE V.—SUMMARY OF CALORIMETRIC RESULTS FOR ACTIVE CHARCOAL.

	n.	$(1-n.)$	m.	h_m. cal.
C_2H_5Cl............	0.915	0.085	0.7385	12.0
CS_2...............	0.9205	0.079	0.7525	12.5
CH_3OH...........	0.938	0.062	0.742	13.1
C_2H_5Br...........	0.900	0.100	0.900	13.9
C_2H_5I.............	0.956	0.044	0.737	14.0
$CHCl_3$.............	0.935	0.065	0.8285	14.5
$HCOOC_2H_5$........	0.9075	0.092	0.944	14.5
C_6H_6..............	0.959	0.041	0.774	14.7
C_2H_5OH..........	0.928	0.072	0.871	15.0
CCl_4..............	0.930	0.070	0.893	15.3
$(C_2H_5)_2O$..........	0.9215	0.079	0.917	15.5

In the first place it is noteworthy that the exponents (n), are but slightly less than unity. This means that over the range studied the heat attending the adsorption of each successive equal increment decreases but slightly; in other words, that the system exhibits only slight fatigue. This becomes particularly evident if we express our equation in differential form,

$$\frac{dh}{dx} = \frac{mn}{x^{(1-n)}}.$$

Evidently when $(1 - n) = 0$, dh/dx becomes a constant, that is, the heat evolved becomes independent of the amount already adsorbed. It can be seen that $(1 - n)$ is very small for these vapors.

How small these values are becomes particularly striking if we compare them with the corresponding constant for ammonia. The heats of adsorption of this gas on meerschaum have been measured over a fairly wide range at 0° by Chappuis,[1] and we have collected his results expressed in similar units to our own in Table VI. We have also computed an empirical equation of similar form to our own, and have included the values of (h) computed from this equation, in the table. It can be seen that there is an excellent correspondence between the observed and computed results.

TABLE VI.—HEAT OF ADSORPTION OF AMMONIA ON MEERSCHAUM.
According to Chappuis.

$$h = 2.23\,x^{0.695}.$$

Adsorbed gas. x, n cc.	Heat evolved, h. Observed. cal.	Calculated. cal.	Difference. Δ cal.	Pressure. mm.
24.2	20.5	20.5	0	0
48.3	33.2	33.2	0	0.5
72.3	44.5	44.0	—0.5	3.71
95.3	53.47	53.4	+0.1	21.5
117.0	61.07	61.5	—0.4	57.56

The value of $1 - n$ for ammonia, 0.305, is 3 or 4 times as great as is the case for the vapors we have studied. The heat of adsorption of ammonia evidently changes rapidly with the amount of adsorption.

There is a decided parallelism between the exponents, n, and the boiling points of the above liquids. This is brought out in Fig. 5, where values of these constants for all the liquids studied are graphically represented. This parallelism means that the higher the boiling point of a liquid, the less marked the "fatigue." This relationship is confirmed by the large value of $1 - n$ for ammonia above mentioned.

The factors m (Table V), give an approximate measure of the heat effect for each gas, as the exponent n is so nearly unity and relatively so constant. It varies more widely than n; namely from 0.737 for ethyl iodide to 0.944 for ethyl formate. There is a noticeable tendency for m to be large when n is small. This is particularly apparent when the value for ammonia is considered.

To obtain an exact measure of the heat effect of a given gas, we may compute the value for h of some particular value of x. Selecting $x = 44.6$, which is about the middle of our range, and which corresponds to

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[1] Chappuis, *Ann. Physik.*, **19**, 21 (1883).

one mol of gas per 500 g. of charcoal, and multiplying by 500, we obtain the values in the fifth column of Table V, which are the molecular heats of adsorption on 500 g. of this charcoal expressed in 15° kilogram calories.

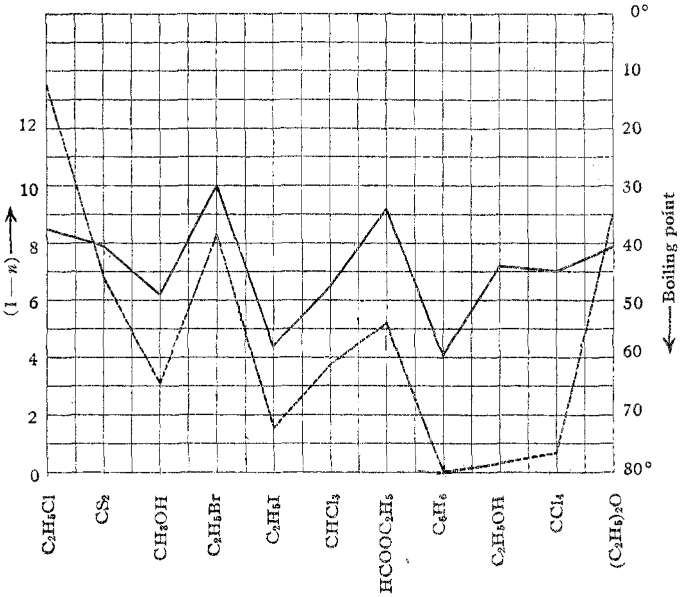

Fig. 5.—Relation between (1 — n) and the boiling point.
Solid line = (1 — n); broken line = boiling point.

The relatively small variation in the molecular heats of adsorption is noteworthy and would indicate some sort of compensating effect between the various factors on which the heat of adsorption depends.

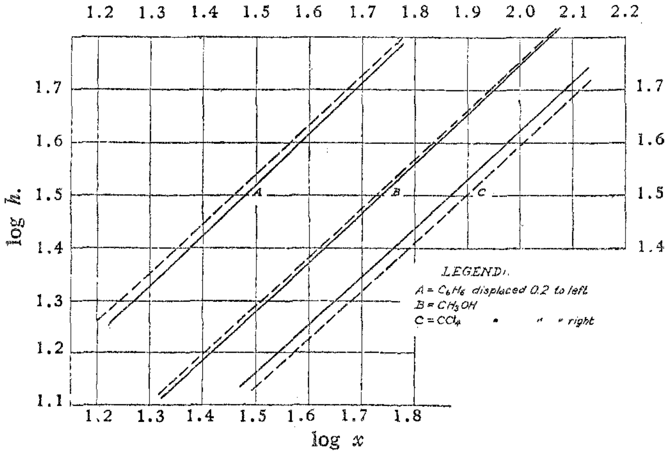

Fig. 6.—Comparison of active and inactive charcoal.

The behavior of the inactive as compared with the active charcoal can be seen from examination of curves in Fig. 6 and the results collected in Table VII.

TABLE VII.—COMPARISON OF ACTIVE AND INACTIVE CHARCOAL.

	m.		n.	
	Active.	Inactive.	Active.	Inactive.
CCl_4	0.893	0.841	0.930	0.930
CH_3OH	0.742	0.754	0.938	0.938
C_6H_6	0.774	0.824	0.959	0.955

It can be seen that so far as *n* is concerned there is scarcely any difference between the 2 charcoals; *m* is slightly smaller for carbon tetrachloride and somewhat larger for methyl alcohol and benzene. It will be noted that with benzene and carbon tetrachloride the pressure is much higher for the same amount of adsorption on the inactive charcoal, indicating a considerably lesser adsorptive power. With methyl alcohol there is little difference in this respect between the 2 charcoals.

All told, the heat values for the inactive charcoal agree quite closely with those of the active charcoal, particularly as regards the "fatigue" term.

The Net Heat of Adsorption.

The process of the adsorption of a gas can be pictured as taking place in 2 steps; first, the compression of the gas to such a point that liquefaction ensues, and second a further compression of this liquid by the adhesive forces of the adsorbent. The observed heat of adsorption will then be made up of 2 quantities, the latent heat of vaporization of the liquid, and what may be called the *net heat of adsorption.*

This is evidently nearly the same as the heat of wetting—and is precisely identical with it at the saturation pressure of the liquid. Since the latent heats of vaporization of these liquids are either known directly or can be calculated with accuracy from their known vapor pressure curves, the net heats of adsorption can readily be calculated from the observed heats of adsorption. The results thus obtained are given in Table VIII; the numbers in Col. 2 representing the molecular heats of adsorption when one cc. of the liquid is adsorbed per 10 g. of charcoal; those in Col. 3 the molecular heats of vaporization, and those in Col. 4 the net heats of adsorption under the same conditions.

It is evident from these figures that in general the net heats of adsorption are approximately of the same magnitude as the latent heats of vaporization. They vary from a third as much in the case of methyl alcohol to a third more in the case of ethyl ether.

With these facts before us we can now understand the regularity abovementioned connecting 1 — *n* and the boiling points. Since the latent heats will, of course, exhibit no "fatigue," the greater the latent heats, other things being equal, the less the fatigue. Since the net heats of adsorption do not as a matter of fact show any regular variation with the boiling points, and since high boiling liquids have high latent heats, these should in general show less fatigue and will, therefore, give smaller values of 1 — *n*, as was found to be the case.

TABLE VIII.—RELATION BETWEEN HEATS OF ADSORPTION AND HEATS OF COMPRESSION.

Column 1. Gas.	2. *h.* K. cal.	3. *Q.* K. cal.	4. *h-Q.* K. cal.	5. (*h-Q.*) 1 cc. K. cal.	6. $\left(\frac{dQ}{dP}\right)$ 1 cc. cal.	7. $\frac{\text{Col. 5}}{\text{Col. 6}}$ × 1000 at.	8. $\left(\frac{dQ}{dP}\right)$ 1 cc. cal.	9. $\frac{\text{Col. 5}}{\text{Col. 8}}$ × 1000 at.
C_2H_5Cl......	12.33	6.22[a]	6.11	0.0864	0.0101	8.5	0.00314	27.5
CS_2.........	12.63	6.83	5.80	0.0991	0.0073	13.5	0.00326	30.2
CH_3OH.....	12.95	9.33	3.62	0.0908	0.0076	12.0	0.00312	28.9
C_2H_5Br.....	14.33	6.85[a]	7.48	0.1020	0.0086	11.9	0.00349	29.2
C_2H_5I.......	14.25	7.81[a]	6.44	0.0815	0.0074	11.0	0.00312	26.1
$CHCl_3$......	14.93	8.00	6.93	0.0875	0.0071	12.3	.....	....
$HCOOC_2H_5$..	15.42	8.38	7.04	0.0901	0.0087	10.3	.....	....
C_6H_6........	15.17	7.81	7.36	0.0850	0.0074	11.5	.....	....
C_2H_5OH.....	14.98	10.65	4.33	0.0768	0.0066	11.6	0.00269	28.2
CCl_4........	16.09	8.00	8.09	0.0856	0.0076	11.3	.....	....
$(C_2H_5)_2O$....	16.09	6.90	9.19	0.0803	0.0097	8.3	0.00298	26.9
	Average			0.0877		11.1		28.1
	Mean deviation			+7.4%		±10%		±4%

[a] Computed from vapor pressure data.

Another interesting regularity appears when the net heats of adsorption *per cc.* of liquid are compared. These values, obtained by dividing the net molecular heat of adsorption by the molecular volume of the liquid at 0°, are given in Col. 5 of Table VIII. It can be seen that they are all very nearly identical, the average deviation from the mean (0.0877) being but 7.4%.

Additional evidence on this point can be obtained from the measurements of the heat of adsorption of ammonia and carbon dioxide on charcoal at zero degrees made by Titoff.[1] Plotting his somewhat irregular results for the heat evolved per cc. as a function of the volume adsorbed and taking data for the densities and latent heats at this temperature from the Landolt-Börnstein Tabellen, the values given in the second column of Table VIII*a*, for the heat of adsorption per cc. of liquid on 10 g. of charcoal are obtained.

TABLE VIII*a*.

	h. per cc. kg. cal.	*Q.* kg. cal.	(*h*—*Q.*) 1 cc. kg. cal.
CO_2............	0.138	0.052	0.086
NH_3............	0.293	0.187	0.105

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

It can be seen that the values of the net heats of adsorption per cc. (Col. 4, Table VIII*a*), agree very closely with the average value which we obtained (0.0877).

This is a very illuminating fact. It indicates that the heat of adsorption is indeed due to the attractive forces of the charcoal upon the liquid, and that for a given volume of liquid, that is for a given volume of filled capillary space, the heat liberated is identical or nearly so for all the liquids studied.

If this net heat of adsorption does result from the forces of attraction acting on the liquid, it should be possible to compute from the known heats of compression how great this attractive force must be. The heats of compression of the liquids studied, in small calories per atmosphere per cc. of liquid at atmospheric pressure, have been calculated from the thermal dilatation at 0° by the well-known relation

$$dQ = \left(\frac{dv}{dT}\right)\frac{T}{42.7}.$$

The thermal dilatations here used were obtained by differentiating the series formulas given in the Landoldt-Börnstein Tabellen, or in the more recent "Tables Annuelles." The results are given in Table VIII, Col. 6. With one or two exceptions they parallel quite closely the net heats of adsorption.

The quotients of the net heats of adsorption divided by the heats of compression should evidently represent the attractive forces acting on the respective liquids. These quotients are given in Col. 7, Table VIII. It can be seen that they are very nearly constant and of the order of 11,000 atmospheres. This high pressure, however, indicates at once that we are not justified in using heats of compression at one atmosphere pressure in making the computation. Instead we should use the mean heats of compression obtained by integration over the whole pressure range covered. Fortunately the heats of compression of 7 of the liquids we have studied have been computed by Bridgman[1] at pressures up to 12,000 atmospheres, based on his measurements of their compressibilities. Unfortunately, his pressure measurements were made only at 20°, 40°, 60° and 80°; but by plotting his values for the total heat of compression at 12,000 atmospheres against the temperature, smooth curves are obtained which permit a fairly accurate extrapolation to 0°. These extrapolated values of the heats of compression up to 12,000 atmospheres, expressed in small calories per atmosphere per cc. are given in Col. 8. Dividing now the net heats of adsorption by these more rigorous values, the attractive forces listed in Col. 9 are obtained. It can be seen that they show an even greater constancy and this indicates that the compressive

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[1] *Proc. Am. Acad.*, 49, 1 (1913).

force exerted by the charcoal on all of these 7 very different liquids is identical within the experimental error.

This computed absolute value of the attractive force is still somewhat too small, for in general the mean heat of compression per atmosphere will be somewhat smaller at 28,000 atmospheres than at 12,000 atmospheres. As nearly as can be estimated from Bridgman's curves a further correction from 12,000 to 28,000 would lead to an average heat of compression of about 0.0024, and, therefore, to an attractive force of approximately 37,000 atmospheres. The relative values of the attractive force will be but slightly altered by this further refinement.

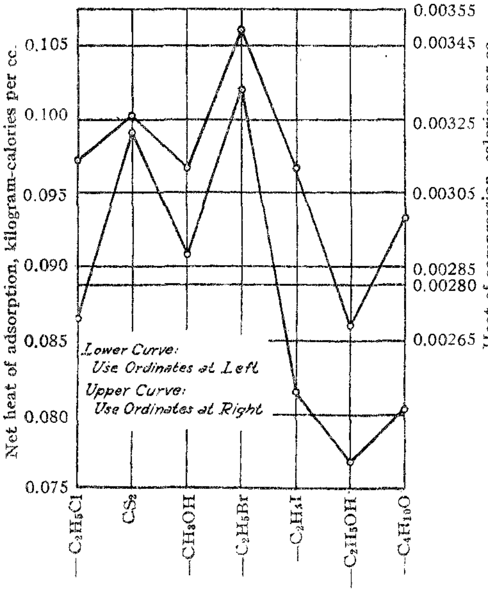

Fig. 7.—Parallelism between wet heat of adsorption and heat of compression.

The parallelism of heats of adsorption and of compression are even better seen by Fig. 7, where these quantities are represented diagramatically on the same scale. This evidence leaves but little doubt that the net heat of adsorption is merely a heat of compression.

Adsorbability and Molecular Volumes.—Another very interesting regularity is disclosed when one compares the adsorbability of the liquids with their molecular volumes in the liquid state. For this purpose the adsorption pressures of all the liquids that have been studied have been plotted in Fig. 8, where the pressure is represented as a function of the volume of gas adsorbed. Evidently, the volume of gas adsorbed at a particular pressure, say, 20 mm., would be a measure of the relative adsorbability of the gases. We have represented these values plotted against molecular volumes, in Fig. 9, from which it can be seen that there is marked inverse proportionality between them. In other words, for this class of liquids, the greater the molecular volume of a liquid the less will be adsorbed at any given gaseous pressure.

The same regularity appears if we compare the adsorbabilities of ammonia and carbon dioxide as measured by Titoff[1] with their molecular volumes. At 20 mm. pressure and zero degrees his charcoal adsorbed about 14 cc. of carbon dioxide and 24 cc. of ammonia, while the molec-

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

ular volumes of these gases are respectively 48 and 26.8 cc. in the liquid state at this temperature.

Compared with the adsorbed volumes of the gases which we studied these volumes of carbon dioxide and ammonia are much smaller than would be expected, and indicate that this relation does not hold over so wide a range. However, Titoff's charcoal was certainly less active than ours, and the lesser volumes adsorbed may well have been due to this fact.

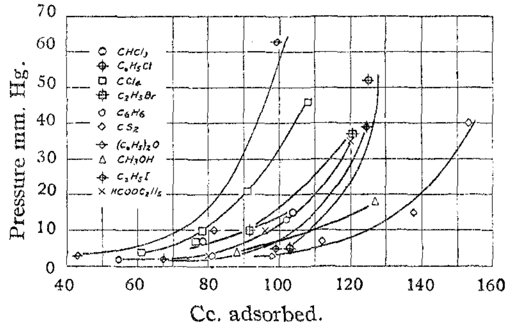

Fig. 8.—Adsorption pressures at 0°.

All the pressure measurements made are included in this figure except those for the very rapid run with carbon disulfide and one irregular result for methyl alcohol, which is shown to be very much too large by similar measurements made on a less active charcoal. It should also be noted that the curve for ethyl ether has been drawn too far to the left. It should have passed near to the observed point at the coördinates 10 and 80.

Adsorbability and Net Heat of Adsorption.—A final and at first sight still more surprising regularity appears when we compare the adsorbabilities of these liquids with the net heats of adsorption. Here again a reverse relationship is disclosed; the more adsorbable gas as measured by cc. of gas or number of mols adsorbed at a given pressure has the *lesser* heat of adsorption. This regularity is also shown graphically in Fig. 9. This relation appears at first almost paradoxical, but on further consideration it can be seen to follow neces-

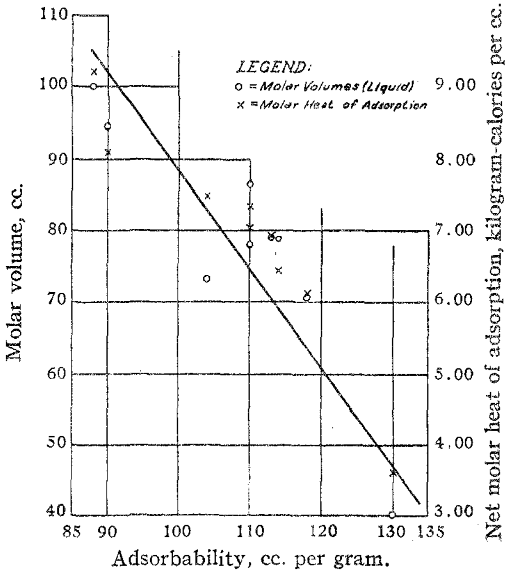

Fig. 9.

sarily from the previous relationships that have been disclosed, and indeed serves as a striking confirmation of them. Thus, since one cc. of all these liquids evolves practically the same net heat of adsorption, the net heats of adsorption per mol are directly proportional to the molecular volumes of the liquids. But since the molal adsorbabilities are inversely proportional to the molecular volumes, it follows that the adsorbabilities are inversely proportional to the net molal heats of adsorption. Thus, for instance, since one volume of ether when adsorbed contains only half as many mols as does one volume of carbon disulfide, and develops the same net heat of adsorption, then the heat of adsorption of ether, mol for mol, will be twice as great as that of carbon disulfide. On the other hand, since ether has the larger molecular volume its adsorbability will be *less* that of carbon disulfide.

Nature of the Liquid Film.—The above-mentioned observation that the heats of adsorption vary so slightly with the amount adsorbed over the whole range, and the fact that the net heats of adsorption follow so closely the heats of compression characteristic of the various liquids *en masse*, both indicate that the adsorbed liquids are present in films many molecules deep. A similar conclusion is reached from a consideration of the actual weight and volume of liquid adsorbed as compared with the probable area of the capillary surface. Thus, the largest amount of gas whose heat of adsorption was measured was in the case of carbon disulfide, of which 153 cc. was adsorbed on one g. of charcoal. This corresponds to 0.4 cc. of liquid carbon disulfide at atmospheric pressure and to about 0.25 cc. under a pressure of 37,000 atmospheres. Even with this amount of gas adsorbed the saturation pressure of liquid carbon disulfide was not reached. Hulett[1] has found that this active charcoal with a "block" density of about 1.07 has a capillary volume of about 0.42 cc. Evidently the carbon disulfide filled most of the capillary space. Hulett[2] has estimated that the capillary area of this active charcoal is no greater than 200 square meters per gram. Taking it as 100 square meters and assuming that the thickness of a molecular layer is 1×10^{-8} cm., then the above amount of carbon disulfide if spread over the whole surface would have given a layer 40 molecules deep. The smallest volume on which observations were made was in the case of ethyl alcohol, where the heat of adsorption of 3.62 cc. was measured. This corresponds to a volume of 0.01 cc. of liquid alcohol or to a layer about one molecule thick.

Finally, in support of this point of view there is the evidence presented by Quincke[3] that the molecular sphere of action of silver has a radius of 6×10^{-6} cm. and would, therefore, extend far beyond the thickest films above mentioned.

[1] THIS JOURNAL, 42, 391 (1920).

[2] *Loc. cit.*

[3] *Pogg. Ann.*, 137, 402 (1869).

The only fact that apparently conflicts with the above interpretation is the greatly reduced vapor pressure exhibited by the liquid adsorbed upon the charcoal surfaces. If this liquid is under as great a pressure as we have computed, one might at first glance expect its vapor pressure to be considerably increased. But this pressure is not an unbalanced one; it is not applied solely to the liquid phase, but exerts its effect upon the escaping gaseous molecules as well. As a result it can have no tendency to increase the vapor pressure of the liquid phase, and indeed its net effect must be to lessen the vapor pressure of the liquid film, at least until this film extends beyond the limit of its sphere of action.

Summary.

1. Measurements of the heat of adsorption of the vapors of some 11 organic liquids upon charcoal at 0° have been made over a considerable range. The resulting values have been shown to be reproducible and independent of the rate of the adsorption of the vapor and of the previous history of the charcoal.

2. The heats of adsorption of all of these vapors can be represented very precisely as functions of the amount adsorbed by the expression $h = mx^n$, where h represents the heat of adsorption per normal cc. of vapor, x the number of cc. of vapor adsorbed, and m and n constants characteristic of each vapor.

3. The constant n in the above equation has been found to be very nearly unity. The heat of adsorption, therefore, decreases but slightly with increasing amount of adsorption. In other words, there is but slight evidence of "fatigue" in the adsorptive forces.

4. It has been shown that this decrease (represented by $1 - n$) is antibat to the boiling points of the liquids; that is, the liquids with relatively high boiling points exhibit a small value of $1 - n$ and hence a slight fatigue. This is due to the fact that such liquids have high latent heats of vaporization.

5. m also varies relatively little from vapor to vapor. In general m and n tend to vary in opposite directions. In agreement with this the actual molal heats of adsorption of the various liquids measured are not very different, varying between 12.0 cals. for ethyl chloride and 15.5 cals. for carbon tetrachloride.

6. The heats of adsorption of these vapors are very nearly the same on inactive as on active charcoal of the same kind.

7. Vapors containing halogens appear to react with the charcoal when warmed, so as to decrease the heat evolved by any subsequent adsorption of gas, without, however, affecting greatly the fatigue effect.

8. The net heats of adsorption, that is the heats evolved above those corresponding to the latent heats of vaporization, are approximately of the same magnitude as the latent heats of vaporization.

9. The net heats of adsorption per cc. of liquid are very nearly identical for all the liquids studied.

10. The net heats of adsorption are closely proportional to the heats of compression under high pressure. This indicates that the liquids are all attracted by the charcoal with substantially the same force—and that the net heat of adsorption is merely a heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres where 1 cc. of liquid is adsorbed on 10 g. of charcoal.

11. The molar adsorbability, that is the number of cc. of gas adsorbed at a fixed gaseous pressure (20 mm.), is inversely proportional to the molecular volume of the liquid.

12. The molar adsorbability is inversely proportional to the net molar heat of adsorption. This, at first sight, surprising behavior is shown to follow necessarily from the previously mentioned regularities.

13. It is shown that all the above evidence indicates that the liquid films we have studied are all at least one and usually very many molecules thick, and this is confirmed by a consideration of the actual volume occupied by the liquid and the approximately known capillary volume and surface of the charcoal.

WASHINGTON, D. C.

NEW DETERMINATION OF THE ABSOLUTE VALUE OF THE RADIUM : URANIUM RATIO.[1]

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1. Historical.

The value of the radium : uranium ratio, first determined by Rutherford and Boltwood[2] in uraninite from North Carolina, was originally reported as 7.4×10^{-7}. The following year it was found[3] that a serious error had been made in the value of the radium standard solution, caused by partial precipitation of the radium. Accordingly, the value of the ratio was changed to 3.8×10^{-7}. A little later, Boltwood[4] redetermined the uranium content of the standard uraninite, which lowered the value still further to 3.4×10^{-7}. This remained the accepted value for several years.

After the International radium standard was adopted in 1910, Rutherford[5] made a comparison with his previously used radium standard,

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[2] Rutherford and Boltwood, *Am. J. Sci.*, [4] **20**, 55–6 (1905).

[3] Rutherford and Boltwood, *ibid.*, **22**, 1 (1906).

[4] Boltwood, *ibid.*, [4] **25**, 296 (1908).

[5] Rutherford, *Phil. Mag.*, [6] **28**, 320–7 (1914).