HEATS OF ADSORPTION AND THEIR BEARING ON THE PROBLEM OF ADSORPTION

H. R. KRUYT AND JOHANNA G. MODDERMAN

Van't Hoff Laboratory of the State University of Utrecht, Holland

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I. INTRODUCTION

The process of adsorption involves the generation of heat. If no external work is done during the adsorption, the liberated heat is equal to the product of the quantity adsorbed by the difference in the energy of the gas before and after adsorption (Hückel). If we reduce all values to those for one gram of adsorbent, the irreversible integral heat of adsorption is

$$q = a\ (E - \epsilon),$$

in which a represents the number of gram-molecules of gas per gram of adsorbent, E the energy per gram-molecule of gas before adsorption and ϵ the same after adsorption.

If a is increased by da, without any external work, the irreversible differential heat of adsorption per gram-mol is

$$q_d = E - \epsilon - a \frac{d\epsilon}{da}$$

for an ideal gas.

If the adsorption takes place isothermally while the total number of molecules is kept constant, e.g. by moving a piston, then work is done. This work is $p\ dV$ (dV is the volume of the gas which disappears), consequently $p \frac{RT}{p}\ da$. Per gram-mol of gas adsorbed the work consequently is RT and

$$q_{\text{isotherm}} = q_d + RT.$$

An isobar heat of adsorption is possible, whereby a and T are varied at a constant p, as well as an isostere heat of adsorption whereby a remains constant, but a new p against T equilibrium is put in. Freundlich compares this heat with heat of evaporation, because during evaporation the composition of the phases also remains unchanged and only p and T are altered. This comparison however is confusing, as Williams has already pointed out. For if we bring the system water:water-vapor to a higher temperature, but in such a way that absolutely no water evaporates or condenses (hence by reducing the total volume), the heat supplied has nothing to do with the heat of evaporation, but only with the specific heat of water and water-vapor and with a small amount of heat of compression. In the case of the isostere heat of adsorption the same is also true, for this is a specific heat. The heat of adsorption which has been determined experimentally is not exactly defined theoretically. It lies between q_d and q_{isotherm}, as it does not take place quite without external work, but it cannot be decided whether, and to what extent, this work is transferred to the calorimeter as heat. When adsorption of a vapor takes place until the adsorbent is in equilibrium with the saturated pressure, we get the same condition which results when the evacuated adsorbent is directly wetted by the liquid in question. Furthermore, this wetting gives a heat effect smaller than the heat of adsorption, because the difference between these two, the heat of condensation, is always positive. The heat of wetting is usually determined by wetting a known amount of solid with an excess of liquid. This heat of wetting is hardly reproducible.

II. EXPERIMENTAL DATA ON HEATS OF ADSORPTION

We have published in the International Critical Tables, Vol. V, pp. 139–143, all reliable data on heats of adsorption determined experimentally, in so far as they were published before the year 1927. At the end of this section we shall give a summary of the more recent experiments.

The oldest quantitative experiments on the heat of adsorption are those of Favre, dating from 1874. Using a mercury-calorimeter he determined the integral heat evolved by the adsorption of different gases on charcoal at room temperature and at a pressure of one atmosphere. He used six types of charcoal, made from various kinds of wood, but the results obtained with a single kind of charcoal differ from one another about as much as those obtained with various sorts of charcoal. Also, the quantity of gas adsorbed by the charcoal at one atmosphere varies considerably in control experiments, but the quotient of heat and quantity of gas adsorbed, i.e. the mean liberated heat per cubic centimeter, is approximately constant.

Nine years later, in 1883, Chappuis published his measurements on the heat of adsorption of various gases on charcoal (made of wood of *Evonymus europaeus*) and on meerschaum. The method applied by him has been used by most investigators since then.

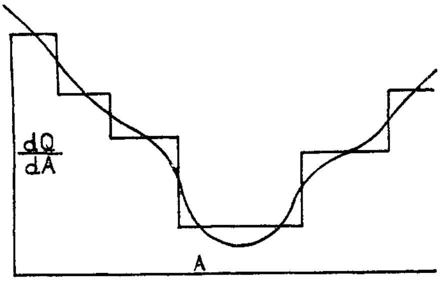

FIG. 1. DIFFERENTIAL HEAT OF ADSORPTION

To a weighed amount of evacuated charcoal in the ice-calorimeter, gas is admitted in known small portions. Before every admission and after adjustment of the equilibrium the pressure is measured, and since the volume of the apparatus is known, the quantity adsorbed per gram of charcoal can be calculated; we call this ΔA and express A in normal cubic centimeters (under normal conditions of temperature and pressure).[1] From the displacement of the thread of mercury the heat developed by the adsorption of ΔA is known; let this be ΔQ. We can now draw graphically $\frac{\Delta Q}{\Delta A}$ (the evolved heat per cubic centimeter of gas

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[1] When the adsorbed gas is expressed in gram-mols we write a, when expressed in normal cubic centimeters we write A. In the case of vapors condensing at normal temperature and pressure, 1 normal cubic centimeter (ncc.) means 1/22,400 gram-molecule.

adsorbed) against A, and we then get a stepped figure (figure 1). From this the real dependence of the heat of adsorption on A can be estimated by drawing a smooth curve, in such a way that each time the surface between that curve, the abscissa and two lines parallel to the ordinate, is equal to the surface enclosed by the steps.

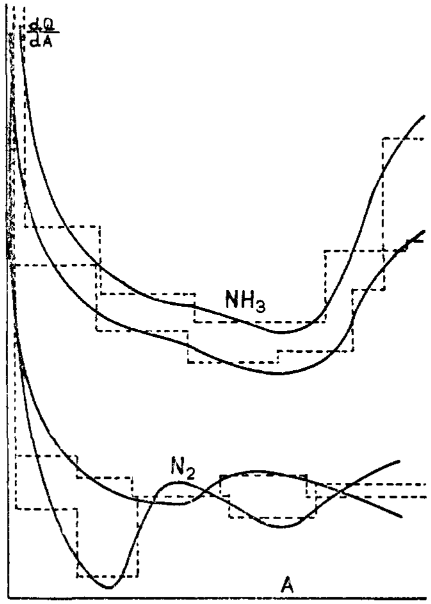

FIG. 2. CONTROL DETERMINATIONS OF N_2 AND NH_3 ON CHARCOAL AT 0°C. (TITOFF)

The scale of A and the value of $\frac{dQ}{dA}$ of the abscissa are different for the two gases.

Chappuis, in general, took too large volumes of gas (the steps were therefore too broad) to conclude much from his measurements except that $\frac{\Delta Q}{\Delta A}$ does not decrease in all cases with increasing A, as was expected, but that the curve sometimes shows a minimum, for instance with NH_3 on charcoal. This was evident in Titoff's experiments of 1910; he determined very accurately the heats of adsorption of N_2, CO_2 and NH_3 on cocoanut charcoal.

The results of his control determinations with NH_3 and N_2 are shown in figure 2. From this we get an impression of the reproducibility of these experiments, which is not great even when one works very accurately. This method of graphical representation reveals experimental errors in a very sensitive way; we deal here always with quotients of two values, of which one (ΔQ) is especially subject to a considerable percentage error.

Many investigators therefore draw their results only in the form of a Q against A curve, or express them in an exponential formula of the type $Q = m A^n$ (in which m and n are constants). The influence of experimental errors is then much smaller, but the curve no longer reveals much. Moreover, in those cases in which the $\frac{dQ}{dA}$ curve has an extremum, the Q against A curve must have an inflexion-point which cannot be expressed by the exponential formula. That in some cases the latter does not seem so unsatisfactory is due to the fact that the deviations between the real curve and that of the formula are distributed on both sides and are therefore unjustly attributed to experimental errors (figure 3). Therefore $\frac{\Delta Q}{\Delta A}$ is always given in the following tables.

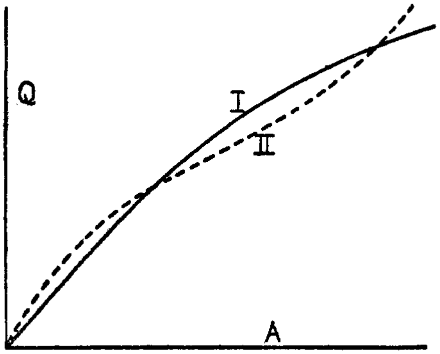

Fig. 3. I—Curve Which Can Be Represented by an Exponential Equation; II—Real Curve

For the present we must content ourselves with knowing the approximate course of the $\frac{dQ}{dA}$ against A curve, without being able to indicate exactly where there is, for instance, a minimum. This is still more evident when we compare the results of different authors investigating the same system, such as ether on charcoal. This system has been examined by Lamb and Coolidge, by Keyes and Marshall at 0°C. and by Pearce and Lloyd McKinley at 25°C. (see table 2). Considering that they worked with charcoals of different structures and of very different adsorbing capacities, the agreement between their results is certainly satisfying (figure 4). In all cases the curve first falls steeply, then runs about horizontally, falls again and rises a little at the end. Whether the horizontal part is real, in that $\frac{dQ}{dA}$ indeed remains constant during some distance, or whether the real course shows perhaps a minimum and a maximum, cannot be decided for the present.

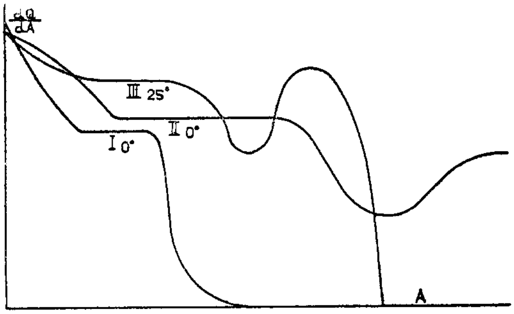

FIG. 4. ETHER ON CHARCOAL
I, Keyes: II, Lamb and Coolidge; III, Pearce and Lloyd McKinley

The latter course was found by Williams (85) for SO_2 on blood charcoal at –20°C. in an investigation which he continued until the saturation pressure of SO_2 was reached; the curve then ends at the heat of condensation (figure 5). Many vapors of organic liquids show a similar behavior (see table 2 (Pearce and Lloyd McKinley) and table 3 (Gregg)). Also for CO_2 on charcoal Gregg (31) found that the curve after a flat minimum begins to rise again (see table 3); this rise however lies at a higher pressure than is usually investigated. Going further still, the curve is due to bend again, as the heat of condensation of CO_2 (0.11 calorie per normal cubic centimeter) is much lower.

That the heat of adsorption is greatest for the gas first adsorbed is only relatively true. There are systems, where $\frac{dQ}{dA}$ rises first and does not decrease until afterwards. Cases where this was clearly found to be true are the following: O_2 on charcoal (Garner and McKie, see table 6); H_2 on nickel containing thorium oxide (Fryling, see also Beebe and Taylor); H_2O on charcoal (Keyes and Marshall); while Gregg observed with N_2 and N_2O on charcoal that the first $\frac{\Delta Q}{\Delta A}$ lies sometimes lower than the next one, but this difference is comparatively small. The charcoal used by Gregg was activated with N_2 containing 0.5 per cent O_2.

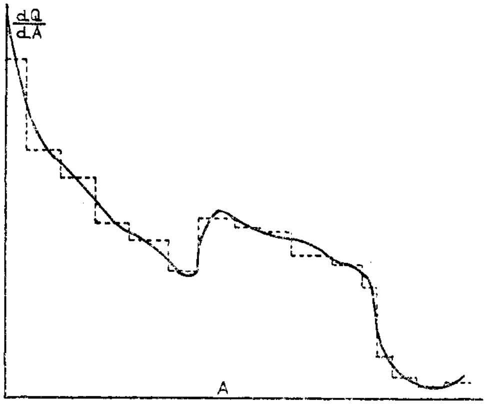

FIG. 5. SO_2 ON BLOOD CHARCOAL AT −10°C.

The investigations of Garner and McKie and of Fryling are very important owing to the small concentrations used, and owing to the great differences in the heats of adsorption found. With Garner the first value of $\frac{\Delta Q}{\Delta A}$ is one-fourteenth of the maximum. The maximum values for the heat of adsorption of O_2 on various kinds of charcoal, examined by Garner, are almost equal (also nearly equal to the value found by Keyes and Marshall), but the concentration of the maximum differs.

Curves with a maximum are also found for H_2 with copper catalysts by Kistiakowsky, Flosdorf and Taylor, who however published only curves, without numerical data. They found that with an active catalyst H_2 gives a curve with a maximum at a low concentration (figure 6, curve 1). If the catalyst has lost much of its activity by being heated for a long time at 250–300°C., the $\frac{dQ}{dA}$ curve has a much flatter form (curve 2); when the catalyst is poisoned by O_2, we get curve 3. For CO with the same catalysts a curve was found which first descends and then shows a minimum at the same quantity of adsorbed gas which gives a maximum in the H_2 curve.

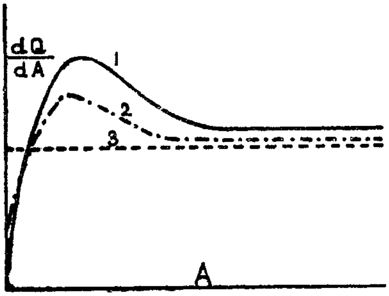

FIG. 6. H_2 ON COPPER CATALYSTS
1—catalyst very active; 2—catalyst less active; 3—catalyst poisoned

If we compare the values for one gas on various kinds of charcoal, we see that in most cases only the initial values of $\frac{\Delta Q}{\Delta A}$ are strongly divergent. As a matter of fact, with each adsorbent the influence of its previous treatment is important for the first cubic centimeters of gas, but becomes less and less as more gas is adsorbed. If we calculate $\frac{\Delta Q}{\Delta A}$ over a large range of A (for instance, from $p = 0$ to $p = 760$ mm. Hg) the original condition of the adsorbent can be only faintly traced (see table 1.)

When on the contrary we take the values for the first volumes of gas admitted, there is a great difference. For charcoal, outgassed at 600°C., Magnus and Kälberer have found 0.558 calorie (see table 4) for the initial $\frac{\Delta Q}{\Delta A}$; for the same charcoal, outgassed at 100°C., the value is 0.378 calorie. Foresti (24) has determined the influence of the temperature of outgassing on the heat of adsorption of H_2 on nickel. The quotient of Q and A (between 0 and 760 mm. Hg.) decreases considerably at a lower temperature of evacuation.

Lamb and Coolidge have worked with two sorts of cocoanut charcoal of a different activity. The activation was done by treating the charcoal with steam during some hours at a high temperature. As a measure of the activity the "service time" was measured, i.e. the time during which the charcoal can retain all the poisonous gas, for instance chloropicrin, out of a mixture of air and poisonous gas of constant concentration and rate of flow. The relation between this service time (which is of great interest for charcoal for gasmasks, and about which many investigations have been made) and the further properties of a charcoal is not simple. On the other hand, the investigation of Lamb and Coolidge shows that the heat of adsorption is almost independent of a change in the activity.

TABLE 1

Adsorption of carbon dioxide on charcoal

INVESTIGATOR	TEMPERATURE OF OUTGASSING	$\frac{\Delta Q}{\Delta A}$ 0 to 76 cm.	KIND OF CHARCOAL
Keyes and Marshall	900°C.	0.313	French gasmask
Magnus and Kälberer	600°C.	0.313	Wood charcoal
Favre	?	±0.311	Various kinds
Gregg (31)	400°C.	0.311	Birchwood
Titoff	400°C.	0.311	Cocoanut charcoal
Magnus and Kälberer	100°C.	0.308	Wood charcoal
Chappuis	?	0.304	*Evonymus europaeus*

The influence of the temperature on the heat of adsorption has been examined by Gregg (31) (see table 3), who measured SO_2 and N_2O on charcoal at many temperatures. Also by comparing the results of Dewar, who worked at —183°C., with those of Titoff and Whitehouse, and by comparing the measurements of Lamb and Coolidge at 0°C. with those of Pearce and Lloyd McKinley (see table 2), who worked at 25°C., some knowledge may be obtained concerning the influence of the temperature on the heat of adsorption.

In these cases it appeared that the heat effect was greater at a higher temperature. Recent investigations however lead to another result. Magnus and Giebenhain (table 4) find for CO_2 on charcoal and on SiO_2 a smaller integral heat of adsorption at 25°C. than at 0°C. Kälberer and Schuster (table 7), who measured the heat of adsorption of CO_2 on SiO_2 at 0°C. and at 75°C., find that for high concentrations $\frac{dQ}{dA}$ is greater at 0°C., but they suppose that at a small A the opposite will be true.

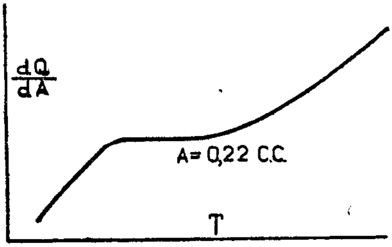

FIG. 7. CHANGE OF THE HEAT OF ADSORPTION OF O_2 ON CHARCOAL WITH T AT CONSTANT A

For O_2 on charcoal Garner and McKie give a graph for the relation between $\frac{dQ}{dA}$ at constant concentration and temperature (figure 7). There is a range of temperature between 100°C. and 200°C. where the heat of adsorption remains constant; afterwards it rises again. Whether this is a special case, or whether it is a general phenomenon, is unknown. It is true that we often find in the literature the opinion that the temperature coefficient of the heat of adsorption should be very small, although this has never been proved.

The investigation by Keyes and Marshall of H_2O on charcoal is remarkable not only because of the shape of the curve found, but also because the heat of adsorption (from 0.38 to 0.47 calorie) is smaller here than the heat of condensation, which amounts to 0.487 calorie per normal cubic centimeter. Usually the heat of adsorption is much greater, especially with vapors of organic substances on charcoal. For benzene the heat of evaporation is 0.348 calorie at 0°C., the heat of sublimation 0.476 calorie, and the heat of adsorption on charcoal more than 0.6 calorie per normal cubic centimeter. Consequently the heat of wetting of charcoal with benzene and other organic liquids must be positive, and that of charcoal with water negative. Gaudechon, working with benzene on sugar charcoal (dried at 100°C.) found a heat of wetting of 4.2 calories per gram of charcoal. Gurvic obtained on bone black 11.1 calories per gram. The charcoal used by Lamb and Coolidge, which had been evacuated at 350°C., adsorbs more than 100 normal cubic centimeters of benzene per gram on saturation at 0°C.; this should give therefore a heat of wetting of at least 25 calories.

For carbon disulfide the relation is analogous: Gaudechon finds 4.0 calories per gram of sugar charcoal; Gurvic finds 13.9 calories per gram of bone black, and at least 150 × (0.505 calories —0.305 calories) = 30 calories per gram is calculated. (We assume that 150 normal cubic centimeters is adsorbed at 0°C. and that the heat of condensation of CS_2 is 0.305 calories per normal cubic centimeter.)[2]

Hence it is clear that unless the same charcoal, evacuated at the same temperature, is used, such comparisons are not justified. For H_2O this is still more important; here Gaudechon finds 3.9 calories per gram of animal charcoal, Gurvic and also Harkins and Ewing find 18.5 calories per gram of bone charcoal and Katz finds 20.9 calories per gram of animal charcoal. With the exception of Gaudechon, all used charcoal with a large ash content (investigations with ash-free charcoal have not been made); Keyes made his charcoal free of ash save for 0.36 per cent. The influence of this, especially for H_2O adsorption, will be discussed later on.

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[2] In recent investigations Bartell and Ying Fu publish a heat of wetting of 32.7 calories for benzene on charcoal and of 31.2 calories for carbon disulfide on charcoal.

All of the experiments with water on charcoal have given a positive heat effect; on sand, however, such is not the case. Jungk, Schwalbe, Bellati and others observed a lowering of temperature when well-dried river sand at 0°C. was wetted by water. The effect was always small and has never been determined quantitatively.

In an investigation by Parks, various sorts of SiO_2 of very different specific surfaces were wetted by H_2O. Parks was able to determine the diameter of the particles microscopically and to calculate the surface from this. He found that the heat liberated per square centimeter of surface was constant.

This explains at the same time, why the values obtained with various sorts of charcoal vary so widely—namely, because the inner surfaces of charcoals are so different.

The values, expressed in joules, of the heats of adsorption of the following substances are given in the International Critical Tables, Vol. V, pp. 139–143: charcoal as adsorbent—air, NH_3, A, C_6H_6, CO_2, CS_2, CO, CCl_4, Cl_2, $CHCl_3$, CCl_3NO_2, C_2H_5OH, C_2H_5Br, C_2H_5Cl, $(C_2H_5)_2O$, $HCOOC_2H_5$, C_2H_5I, H_2, HBr, HCl, HI, CH_4, CH_3OH, CH_3Cl, N_2, N_2O_3, O_2, SO_2, H_2O; SiO_2 as adsorbent—SO_2, H_2O; meerschaum as adsorbent—NH_3, CH_3OH, SO_2; Ni as adsorbent—CO_2, C_2H_6, C_2H_4, H_2; Cu as adsorbent—H_2; Pt as adsorbent—H_2, O_2. In tables 2 to 8 the values of the heats of adsorption are expressed in calories. Unless otherwise indicated, *A* is given in normal cubic centimeters. In the case of vapors condensing at normal temperature and pressure, 1 normal cubic centimeter (1 ncc.) means 1/22,400 gram-molecule. In the following alphabetical summary of the substances whose heats of adsorption are given in tables 2 to 8, the figures refer to the tables; the letters to the sections of the tables:

Charcoal as adsorbent

$(CH_3)_2CO$	C_2H_2	C_6H_6	CO_2	CS_2	CCl_4	$CHCl_3$	C_2H_6
2A	3A	2I	3D, 4A	2C	2E	2D	3C

C_2H_5Cl	C_2H_4	$(C_2H_5)_2O$	CH_3OH	C_3H_7Cl	N_2O	O_2	SO_2
2F	3B	2B	2H	2G	3E, 3F	5, 6A, 6B	3G, 3H

Other adsorbents

ADSORBENT	GAS					
	NH_3	A	CO_2	C_2H_4	H_2	N_2
SiO_2		7A	4B, 7D	7C		7B
Ni	8B				8B	
Cu	8A					
Fe	8C					

TABLE 2

Heats of adsorption of organic vapors on cocoanut charcoal outgassed at 550°C.

PEARCE AND LLOYD MC KINLEY

p mm. from to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
A. Acetone at 25°C.			
0.0 - —	6.44	4.59	0.713
— - —	15.90	11.21	0.700
— - —	29.45	19.36	0.601
— - 1.1	47.93	30.89	0.624
1.1 - 2.45	64.76	42.90	0.714
2.45- 40.85	99.87	62.52	0.559
40.85-130.24	109.28	67.87	0.569
B. Ethyl ether at 25°C.			
0.0 - —	8.39	6.36	0.758
— - —	24.26	17.85	0.724
— - —	39.81	28.81	0.705
— - —	55.36	38.29	0.610
— - 41.85	66.99	46.71	0.724
41.85-367.2	78.00	50.30	[0.326]
C. Carbon disulfide at 25°C.			
0.0 - —	7.50	4.82	0.643
— - —	20.56	12.35	0.577
— - —	31.78	18.17	0.519
— - —	42.27	23.11	0.471
— - —	62.70	33.64	0.515
— - 6.3	84.29	44.41	0.499
6.3 - 17.4	106.08	55.06	0.489
17.4 -211.4	130.45	65.88	0.444
D. Chloroform at 25°C.			
0.0 - —	9.40	6.76	0.719
— - —	20.83	14.45	0.673
— - —	34.84	23.24	0.627
— - —	56.41	35.84	0.584
— - 4.65	74.80	46.59	0.585
4.65-123.8	94.45	56.71	0.515
E. Carbon tetrachloride at 25°C.			
0.0 - —	9.44	7.88	0.835
— - —	21.58	16.45	0.706
— - —	32.95	23.86	0.652
— - —	42.35	29.88	0.640
— - 59.8	53.23	36.66	0.623
59.8 - 94.96	57.67	39.03	0.534

p mm. from to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
F. Ethyl chloride at 25°C.			
0.0 - —	7.00	3.82	0.546
— - —	23.37	12.47	0.528
— - —	40.39	20.52	0.491
— - 14.55	63.78	31.82	0.470
14.55- 43.0	81.80	40.64	0.489
43.0 -223.4	99.49	50.76	0.572
G. Propylchloride at 25°C.			
0.0 - —	8.39	6.48	0.772
— - —	24.65	17.36	0.669
— - 1.90	37.99	26.10	0.655
1.90- 5.90	54.54	36.51	0.629
5.90- 55.09	66.10	43.16	0.575
55.09-349.5	77.98	48.83	0.477
H. Methylalcohol at 25°C.			
0.0 - —	8.96	6.72	0.750
— - —	23.42	15.41	0.601
— - —	33.13	20.39	0.513
— - —	48.41	28.73	0.546
— - 4.85	74.65	43.44	0.561
4.85- 7.25	98.80	56.01	0.520
7.25- 14.30	126.41	73.47	0.632
14.30- 41.35	158.03	88.09	0.462
I. Benzene at 25°C.			
0.0 - —	14.00	10.67	0.762
— - —	27.30	19.63	0.674
— - —	46.52	32.30	0.659
— - —	66.39	45.09	0.644
— - —	79.22	52.99	0.616
— - 60.65	87.29	58.00	0.621

TABLE 3

Heats of adsorption of gases on charcoal from birchwood activated during three hours at 600°C. and outgassed at 400°C.

GREGG (31)

p mm. from – to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
A. C_2H_2 at 0°C.			
0 – 3.44	6.99	2.87	0.411
3.44 – 10.8	14.07	5.61	0.387
10.8 – 25.8	22.14	8.36	0.340
25.8 – 64.4	32.90	12.05	0.343
64.4 – 198.6	47.67	17.8	0.388
198.6 – 822.2	64.90	23.4	0.329
B. C_2H_4 at 0°C.			
0 – 1.18	4.27	1.54	0.360
1.18 – 6.64	13.04	4.49	0.336
6.64 – 32.6	25.90	8.26	0.293
32.6 – 119	38.66	11.86	0.282
119 – 897	55.75	16.5	0.273
C. C_2H_6 at 0°C.			
0 – 1.91	7.49	3.20	0.427
1.91 – 6.10	16.45	6.78	0.399
6.10 – 29.3	35.26	14.13	0.391
29.3 – 74.8	46.05	18.1	0.370
74.8 – 434.5	62.27	23.9	0.359
D. CO_2 at 0°C.			
0 – 6.98	4.63	1.63	0.351
6.98 – 97.5	26.08	8.34	0.299
97.5 – 661	57.31	17.6	0.296
661 – 813	60.57	18.7	0.335
813 – 964	63.13	19.9	0.363
E. N_2O at 0°C.			
0 – 5.2	5.41	1.90	0.351
5.2 – 118	33.4	11.4	0.339
118 – 168	38.9	13.0	0.292
168 – 483	57.0	18.0	0.282
483 – 728	64.0	20.2	0.313
F. N_2O at 40.35°C.			
0 – 46.6	7.97	3.05	0.382
46.6 – 153	17.1	6.38	0.366
153 – 293	24.5	9.04	0.358
293 – 718	38.5	13.93	0.349
G. SO_2 at 0°C. The charcoal had been activated at 800°C. (during 4 hours) and outgassed at 400°C.			
0 – 0.43	10.8	5.69	0.528
0.43 – 1.33	27.2	13.6	0.480
1.33 – 8.61	56.9	26.6	0.440
8.61 – 25.0	72.7	33.3	0.421
25.0 – 93.1	86.0	39.9	0.499
93.1 – 258	93.4	43.6	0.495
258 – 838	102.2	47.0	0.392
H. SO_2 at 40.35°C. The charcoal had been activated at 600°C. (during 3 hours), had been used for adsorption of CO, and then had been outgassed at 150°C.			
0 – 2.88	8.69	6.88	0.791
2.88 – 8.53	16.0	12.16	0.724
8.53 – 21.8	32.2	20.2	0.499
21.8 – 44.7	43.5	26.4	0.547
44.7 – 93.1	54.6	32.0	0.502
93.1 – 405	71.5	39.7	0.456

TABLE 4

Heats of adsorption of carbon dioxide

A. On wood charcoal

Charcoal outgassed at 600°C.

MAGNUS AND KÄLBERER

p mm. from	to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
CO_2 at 0°C.				
0	0.0765	0.31	0.172	0.558
0.0765	0.484	0.99	0.465	0.431
0.484	0.938	1.54	0.681	0.386
0.938	2.38	2.81	1.143	0.366
2.38	18.3	10.4	3.680	0.336
18.3	150	32.7	10.57	0.308
150	521	50.6	15.92	0.299

Charcoal outgassed at 280°C.

MAGNUS AND GIEBENHAIN

p mm. from	to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
CO_2 at 0°C.				
0	0.232	0.273	0.101	0.368
0.232	0.413	0.467	0.171	0.362
0.413	0.742	0.809	0.293	0.358
0.742	1.641	1.62	0.576	0.349
1.641	2.329	2.22	0.786	0.348
2.329	6.800	5.03	1.736	0.338
CO_2 at 25°C.				
0	0.517	0.184	0.063	0.340
0.517	0.867	0.300	0.104	0.351
0.867	1.905	0.626	0.216	0.344
1.905	4.015	1.28	0.431	0.330
4.015	6.300	1.92	0.645	0.332
6.300	13.300	3.56	1.181	0.327

B. On silica gel outgassed at 350°C.

MAGNUS AND GIEBENHAIN

CO_2 at 0°C.

p mm. from	to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
0	0.630	0.100	0.0330	0.330
0.630	1.300	0.204	0.0673	0.330
1.300	8.70	1.24	0.403	0.322
8.70	36.40	4.39	1.392	0.314
36.40	92.50	9.08	2.836	0.308

CO_2 at 25°C.

p mm. from	to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
0	1.350	0.0716	0.0222	0.310
1.350	4.746	0.252	0.0783	0.310
4.746	19.15	0.942	0.285	0.300
19.15	55.90	2.58	0.783	0.304
55.90	122.10	5.00	1.488	0.291

TABLE 5

Heats of adsorption of oxygen at 0°C. on wood charcoal outgassed at 1000°

MARSHALL AND BRAMSTON COOK

p mm. from – to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
0	0.0305	0.119	3.902
0	0.0907	0.324	3.400
0	0.1902	0.647	3.246
0	0.3405	1.095	2.981
0 – 0.05	0.4973	1.575	3.061
0.05– 0.40	0.7930	2.409	2.820
0.40– 6.85	1.221	3.009	1.402
6.85– 20.25	1.783	3.609	1.068
20.25– 43.50	2.493	3.840	0.325
43.50–128.2	4.823	4.472	0.271
128.2 –259.0	7.757	5.072	0.204
259.0 –374.0	10.147	5.521	0.188
374.0 –513.9	12.513	5.963	0.187

TABLE 6

Heats of adsorption of oxygen

A. On adsorbent charcoal "Norit," purified and activated at 950°C.

MC KIE

Temperature	A ncc. from – to	$\frac{\Delta Q}{\Delta A}$ calories
20°C.	0 – 0.25	3.12
57°C.	0 – 0.16	4.04
97°C.	0 – 0.18	4.82
150°C.	0 – 0.17	5.09
200°C.	0 – 0.17	5.18

B. Adsorbent: same as in A

GARNER AND MC KIE

18°C.	0.0022 0.013 ncc.	0.223
	0.09	2.68
	0.18	2.77
	0.22	3.12
	0.27	3.17
	0.34	3.17

TABLE 7

Heats of adsorption of various gases on silica gel

KÄLBERER AND SCHUSTER

p mm. from to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
A. Argon at 0°C.			
0 -103.9	0.25	0.0322	0.129
103.9-206.9	0.47	0.0670	0.158
206.9-500.5	1.09	0.178	0.179

B. N_2 at 0°C.

With N_2 on SiO_2 at 0°C. curves are found, which rise with increasing A. With various samples of SiO_2, which are different in structure, the values found diverge very much. With one sample $\frac{\Delta Q}{\Delta A}$ rises from 0.047 to 0.152 calories when A increases from 0 to 1.16 cc.; with another sample $\frac{\Delta Q}{\Delta A}$ rises from 0.064 to 0.134 calories.

C. C_2H_4 at 0°C.

With C_2H_4 at 0°C. the values of $\frac{\Delta Q}{\Delta A}$ differ much for various samples of the gel, but $\frac{\Delta Q}{\Delta A}$ always falls with increasing A, e.g.:

With sample I from 0.296 to 0.270 calories.
With sample II from 0.321 to 0.301 calories.
With sample III from 0.336 to 0.306 calories.

D. CO_2 at 0°C. and at 75°C.

With CO_2 at 0°C. curves of different types are found, according to the previous history of the gel. Whether the gel had already previously adsorbed CO_2, or even N_2, appeared to be especially important. In the case of a gel which had not yet been used for adsorption, $\frac{\Delta Q}{\Delta A}$ increased with increasing A from 0.280 to 0.354 calories. Also in other cases $\frac{\Delta Q}{\Delta A}$ varies between these values, but the shape of the curve at small concentrations is often quite different.

With CO_2 at 75°C. the following curve was found:

p mm. from to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
0 - 40.5	0.47	0.245	0.521
40.5-117.5	1.15	0.494	0.366
117.5-230	2.33	0.790	0.251
230 -359	3.59	1.106	0.251

TABLE 8

Heats of adsorption of NH_3 at 0°C. on catalysts

DEW AND TAYLOR

p mm. from – to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
A. Adsorbent: Cu, from Kahlbaum's "brown label" CuO, reduced for 22 days at 140°C.			
0 –155	0.20	0.0824	0.412
155 –760	0.50	0.172	0.297
B. Adsorbent: Ni, from the nitrate, heated at 300°C. and reduced for 50 days at 300°C. The value of Q/A for H_2 on this catalyst at 0°C. is 0.668 calorie.			
0 – 62.5	0.22	0.112	0.508
62.5–212	0.34	0.165	0.423
212 –465	0.45	0.205	0.352
465 –759	0.57	0.235	0.266
C. Adsorbent: Fe, from the nitrate, heated and reduced for 30 days at 460°C.			
0 – 16	0.153	0.107	0.696
16 –102.5	0.275	0.158	0.426
102.5–368	0.376	0.203	0.437
368 –756	0.466	0.235	0.357

III. CALCULATION AND CALCULATED VALUES OF THE ISOTHERMAL HEAT OF ADSORPTION

Let there be given a volume, closed by a piston, in which one gram of adsorbent, e.g. charcoal, is in equilibrium with a gas at pressure p and temperature T°. Let the amount of adsorbed gas be a gram-mols, of non-adsorbed gas a' gram-mols. Let the thermodynamic potential of the charcoal with the adsorption layer be Z; then Z depends on T, p and a. Let the thermodynamic potential of the unadsorbed gas be Z'. Then $Z' = a' \zeta (T. p)$, where ζ represents the thermodynamic potential of 1 gram-mol of gas and therefore depends on T and p. At equilibrium at constant p and T the thermodynamic potential is a minimum, therefore

$$\delta(Z + Z')_{p.T.} = 0.$$

Since

$$\delta a' = -\delta a, \quad \frac{\delta Z}{\delta a} = \frac{\delta Z'}{\delta a'}.$$

$$\frac{\delta Z'}{\delta a'} = \zeta\ (T.\ p)$$

consequently

$$\frac{\delta Z}{\delta a} = \zeta\ (T.\ p) \tag{1}$$

By pushing in the piston, a is increased by Δa, and the amount of heat ΔQ is liberated; the entropy of gas and charcoal decreases. If H' represents the entropy of the gas, and H that of the charcoal with the adsorption layer, the change of entropy is

$$-\Delta(H + H') = \frac{\Delta Q}{T}$$

The pressure is increased by $\frac{\delta p}{\delta a}\ \Delta a$ and the change of a' is

$$\Delta a' = -\Delta a.$$

Then:

$$\frac{1}{T}\frac{\Delta Q}{\Delta a} = \frac{-\Delta H - \Delta H'}{\Delta a} = -\frac{\delta H}{\delta a} - \frac{\delta H}{\delta p}\frac{\delta p}{\delta a} - \frac{\delta H'}{\delta a'}\frac{\delta a'}{\delta a} - \frac{\delta H'}{\delta p}\frac{\delta p}{\delta a} =$$

$$-\frac{\delta H}{\delta a} + \frac{\delta H'}{\delta a'} - \frac{\delta H}{\delta p}\frac{\delta p}{\delta a} - \frac{\delta H'}{\delta p}\frac{\delta p}{\delta a} \tag{2}$$

If η represents the entropy of 1 gram-mol of gas, we may write

$$H' = a'\ \eta\ (T.\ p)$$

therefore,

$$\frac{\delta H'}{\delta a'} = \eta\ (T.\ p).$$

Since $\eta = -\frac{\delta\zeta}{\delta T}$, we may write:

$$\frac{\delta H'}{\delta a'} = -\frac{\delta\zeta}{\delta T} \text{ and } \frac{\delta H'}{\delta p} = -a' \frac{\delta^2\zeta}{\delta T\,\delta p}.$$

Also:

$$H = -\frac{\delta Z}{\delta T}, \text{ therefore } \frac{\delta H}{\delta a} = -\frac{\delta^2 Z}{\delta a\,\delta T} \text{ and } \frac{\delta H}{\delta p} = -\frac{\delta^2 Z}{\delta p\,\delta T}.$$

Substituting this in equation (2):

$$\frac{1}{T}\frac{\Delta Q}{\Delta a} = \frac{\delta^2 Z}{\delta a\,\delta T} - \frac{\delta\zeta}{\delta T} + \frac{\delta^2 Z}{\delta p\,\delta T}\frac{\delta p}{\delta a} + a'\frac{\delta^2\zeta}{\delta p\,\delta T}\frac{\delta p}{\delta a} \tag{3}$$

For two states of equilibrium with the same a but different values of p and T, the total change is:

$$\frac{\delta^2 Z}{\delta a\,\delta T}\delta T + \frac{\delta^2 Z}{\delta p\,\delta a}\delta p = \frac{\delta\zeta}{\delta T}\delta T + \frac{\delta\zeta}{\delta p}\delta p,$$

or

$$\frac{\delta^2 Z}{\delta a\,\delta T} - \frac{\delta\zeta}{\delta T} = \frac{\delta\zeta}{\delta p}\frac{\delta p}{\delta T} - \frac{\delta^2 Z}{\delta p\,\delta a}\frac{\delta p}{\delta T}.$$

Substituting this in equation (3):

$$\frac{1}{T}\frac{\Delta Q}{\Delta a} = \frac{\delta\zeta}{\delta p}\frac{\delta p}{\delta T} + a'\frac{\delta^2\zeta}{\delta T\,\delta p}\frac{\delta p}{\delta a} + \frac{\delta^2 Z}{\delta p\,\delta T}\frac{\delta p}{\delta a} - \frac{\delta^2 Z}{\delta p\,\delta a}\frac{\delta p}{\delta T} \tag{4}$$

In the case of an ideal gas:

$$\zeta = RT\ln p - C_p T\ln T + \alpha T + \beta,$$

when C_p is the specific heat at constant p, and α and β are constants. From this it follows that:

$$\frac{\delta\zeta}{\delta p} = \frac{RT}{p} \text{ and } \frac{\delta^2\zeta}{\delta p\,\delta T} = \frac{R}{p}.$$

Substituting this in equation (4) and, for the sake of clearness, using $\left(\frac{\delta p}{\delta T}\right)_a$ instead of $\frac{\delta p}{\delta \mathrm{T}}$ etc., the equation becomes

$$\frac{\Delta Q}{\Delta a} = RT^2\left(\frac{\delta \ln p}{\delta T}\right)_a + a'\,RT\left(\frac{\delta \ln p}{\delta a}\right)_T - T\frac{\delta}{\delta p}\left(\frac{\delta Z}{\delta a}\right)\left(\frac{\delta p}{\delta T}\right)_a + T\frac{\delta}{\delta p}\left(\frac{\delta Z}{\delta T}\right)\left(\frac{\delta p}{\delta a}\right)_T \qquad (5)$$

Both of the last terms on the right hand side are negligible, since the direct influence of the pressure on a solid is very small. This holds here also, because the dependence of a on p is explicitly taken into account. We can imagine the direct influence of the pressure (at constant a) most clearly by assuming an indifferent gas, which is not at all adsorbed. Then a and p can be varied independently, and the influence of p on the condition of the solid is not measurable. The meaning of both terms can be seen clearly as follows:

$$\frac{\delta}{\delta p}\frac{\delta Z}{\delta a} = \frac{\delta}{\delta a}\frac{\delta Z}{\delta p} = \frac{\delta}{\delta a}V,$$

if V represents the volume of the charcoal with the adsorption layer. The increase of this volume at greater a is very insignificant, as well as $\frac{\delta}{\delta p}\frac{\delta Z}{\delta T} = \frac{\delta}{\delta T}V$, the increase of this volume per 1° rise in temperature at constant a.

The second term on the right hand $a'RT\left(\frac{\delta \ln p}{\delta a}\right)_T$ represents the heat due to compression of the unadsorbed gas. However a' is not constant, but the sum $a + a' = B$ remains constant.

$$a'\,RT\left(\frac{\delta \ln p}{\delta a}\right)_T = BRT\left(\frac{\delta \ln p}{\delta a}\right)_T - RT\left(\frac{\delta \ln p}{\delta \ln a}\right)_T.$$

The heat, due to compression from p_1 (corresponding with a_1) up to p_2 (corresponding with a_2) is

$$\int dW = BRT\int_{a_1}^{a_2}\frac{\delta \ln p}{\delta a}\,da - RT\int_{a_1}^{a_2}\frac{\delta \ln p}{\delta \ln a}\,da$$

If, according to Freundlich, the isotherms are represented by a formula $a = \alpha p^{\frac{1}{n}}$, in which α and $\frac{1}{n}$ are constants, then $\frac{\delta \ln p}{\delta \ln a} = n$ and is therefore constant; and the heat of compression is

$$BRT \ln \frac{p_2}{p_1} - RT\, n(a_2 - a_1)$$

In order to estimate the importance of this term, we shall calculate it with data taken from Titoff's study of NH_3 on charcoal at 0°C. When the adsorbed gas is expressed in gram-mols, we write a, when expressed in normal cubic centimeters, we write A.

Let $A_1 = 5.407$ normal cubic centimeters, $A_2 = 30.157$ normal cubic centimeters, $p_1 = 2.9$ mm., and $p_2 = 28.8$ mm. In this case $\frac{1}{n} = 0.75$, therefore $n = 1.3$. If 1 normal cubic centimeter remains unadsorbed, $B = A_2 + A' = 31.157$ normal cubic centimeters. From this we find that $\int dW = 0.95$ calorie.

The total heat effect, found by Titoff, was 12.16 calories; consequently 7.8 per cent of this should not be heat of adsorption, but should be attributed to compression. For a gas with a small heat of adsorption this error is still greater, for instance for N_2 at 0°C. (Titoff) $A_1 = 0.258$ normal cubic centimeter, $A_2 = 2.21$ cc. and 0.8 cc. remains unadsorbed. $p_1 = 10.7$ mm., $p_2 = 91.6$ mm., $\frac{1}{n}$ is 0.98, and therefore $n = 1.02$. Then $B = 3.01$ cc. From this $\int dW$ is calculated to be equal to 0.109 calorie. The total heat effect, observed by Titoff, was 0.507 calorie; therefore 21.5 per cent of this quantity should be heat of compression.

However, this derivation of the isothermal heat of adsorption does not quite correspond with the experiments. In reality the increase of pressure does not take place by moving a piston, but by admitting gas at a higher pressure. Hence in the first place $A + A'$ is not constant, and secondly we do not know exactly what really happens on the admission of gas. Possibly we get at first compression of the gas already present in the apparatus, and afterwards expansion of the remaining unadsorbed quantity; this depends on the ratio between the rate of admission of the gas and the rate of adsorption. For this the heat effect cannot be calculated; probably the error caused by the heat of compression will be much smaller than has been calculated above. The estimation was only for the purpose of demonstrating that the heat of compression is not necessarily negligible with respect to the heat of adsorption.

Therefore

$$\frac{dQ}{dA} = RT^2 \left(\frac{\delta \ln p}{\delta T}\right)_A \tag{6}$$

the equation which also applies to the heat of evaporation. This whole derivation is of course applicable also to the heat of evaporation, if we replace the charcoal by liquid. Both terms with $\left(\frac{\delta p}{\delta A}\right)_T$ become 0, and $\frac{\delta}{\delta p}\frac{\delta Z}{\delta A}$ is then the change in volume of the liquid. This term also appears in the formula of Clausius-Clapeyron for the heat of evaporation; if r is the heat of evaporation

$$\frac{r}{v_1 - v_2} = T\frac{dT}{dp},$$

when v_1 and v_2 represent the specific volumes of vapor and liquid; here v_2, being small compared with v_1, is also usually neglected.

Over a restricted range of temperature and pressure, equation (6) becomes

$$\frac{dQ}{dA} = \frac{R\,T_1\,T_2}{T_1 - T_2} \ln \frac{p_1}{p_2}$$

Here p_1 and p_2 are the equilibrium pressures at the same A at T_1 and T_2.

The tables in and at the end of this chapter are always calculated in such a way that for a value of A, for which p_1 and T_1 are given, the corresponding p_2 is sought at T_2 by means of graphical interpolation in the isotherm. Consequently only one graphical interpolation is necessary for each calculation, and the arbitrariness attached to an interpolation, especially in a curve in which the given points are situated far from each other, becomes as small as possible.

Complete agreement between values found and those calculated cannot be expected. If gas is adsorbed without any heat, due to external work being given to the calorimeter, the value calculated ought to exceed the value found with RT. Usually this is not the case.

There are still other causes, which may explain the difference between the values found and those calculated.

1. If gas is adsorbed by a charcoal, which has been evacuated at a high temperature during a long time, the adsorption of the very first quantity is often an irreversible process. This is always the case when the gas cannot be recovered completely at the same temperature but remains bound to the adsorbent; then the derivation given above is no longer correct.

2. If the charcoal is not completely outgassed, but still contains small quantities of air, and a strongly adsorbable gas is admitted, the latter will displace the air from the charcoal. Owing to the liberation of this quantity of air, the total final pressure is higher than the partial pressure of the adsorptive; it appears therefore that a quantity smaller than the real one has been adsorbed, this quantity being determined by the difference between the admitted and the unadsorbed gas. For this reason the heat per normal cubic centimeter of gas seems higher than it really is.

However, the heat of desorption of the air driven out must be subtracted from the heat of adsorption of the gas. Therefore the error will be important only when the gas has a heat of adsorption much higher than that of air.

If we calculate the heat of adsorption from isotherms determined on charcoal which is not completely outgassed, and suppose that the same quantity of air is driven off at T_1 and T_2, and that the apparatus has the same volume, it is necessary to subtract small amounts, which are in the proportion of $T_1:T_2$, from p_1 and p_2. The ratio $p_1:p_2$ being much higher than $T_1:T_2$, the denominator of the fraction is diminished relatively more, hence the fraction becomes larger; in other words, the real heat of adsorption is greater than the heat calculated, or the calculation gives a value which is too low.

When working at pressures where the gas laws are not applicable, the experimental as well as the calculated values are found to be too low. The density of a gas is greater than has been calculated from the pressure; at definite p there is consequently less gas adsorbed than expected. Since the heat per cc. of gas is greater than we think, the experimental value is too low. The calculated value is also too low, the isotherm at high pressures being lower than the value found. The real A will therefore correspond to a greater p than that found. Because of the shape of the isotherm, the deviation from the gas laws is less important at p_2 which is smaller and lies at a lower T. Therefore the resulting values for $\frac{p_1}{p_2}$ and $\frac{dQ}{dA}$ are too low. The error depends on the so-called "dead volume" of the apparatus, but will be unimportant in most of the cases with respect to RT. Many investigators in fact take these deviations into account. From the examples it is evident that, taking everything into consideration, the agreement is satisfactory. As RT per normal cubic centimeter amounts to 0.026 calorie at 10°C., we may therefore expect this difference, and the use of the third decimal place is not justified when comparing values found with those calculated. However, the third decimal may be important in relation to the general shape of a curve.

Example I. CO_2 on charcoal (Titoff). $\frac{dQ}{dA}$ is calculated from isotherms at 0°C. and 30°C. $\frac{\Delta Q}{\Delta A}$ is measured at 0°C.

A ncc.	p at 0°C. calculated mm.	p at 30°C. mm.	$\frac{dQ}{dA}$ calculated calories	$\frac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
1.82	1.2	5.3	0.363	0.345	0 to 2.3
4.02	3.6	14.7	0.344	0.324	2.3 " 11.3
10.3	14.2	50.7	0.311		
19.72	41.8	138.5	0.293	0.305	11.3 " 22.6
28.87	89.6	283.3	0.281	0.300	22.6 " 33.4
34.07	122.5	398.9	0.288	0.294	33.4 " 43.9
38.14	155	498.1	0.285		
41.4	189.4	621.8	0.290		
44.9	234	758.6	0.287	0.292	43.9 " 50.8

Example II. Methyl alcohol on charcoal. $\frac{dQ}{dA}$ is calculated from isotherms at 0°C. and 33.3°C. by Coolidge (12). $\frac{\Delta Q}{\Delta A}$ is measured at 0°C. by Lamb and Coolidge.

A ncc.	p at 0°C. calculated mm.	p at 33.3°C. mm.	$\frac{dQ}{dA}$ calculated calories	$\frac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
29.7	0.057	0.9	0.615	0.619	0 to 21.7
65.4	0.33	4.1	0.563	0.553 0.542	21.7 " 47.4 47.4 " 75.3
126.5	1.18	12.9	0.533	0.524	75.3 " 127.4

Example III. Ethyl formate on charcoal. $\frac{dQ}{dA}$ from isotherms of Coolidge (12) at 0°C. and 44.8°C. $\frac{\Delta Q}{\Delta A}$ is measured at 0°C. by Lamb and Coolidge.

A ncc.	p at 0°C. calculated mm.	p at 44.8°C. mm.	$\frac{dQ}{dA}$ calculated calories	$\frac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
59.2	0.060	2.08	0.607	0.598	32.3 to 62.9
76.2	0.25	6.00	0.551	0.580	62.9 " 96.7
95.5	1.10	26.7	0.549	0.568	96.7 " 120
122.8	23.5	477.6	0.519		

Even in those cases where different investigators use a different kind of charcoal the results agree fairly well. The agreement between the values for N_2 on charcoal, measured by Titoff, and those calculated from his isotherms is even worse than that between $\frac{dQ}{dA}$ and $\frac{\Delta Q}{\Delta A}$ for different charcoals, as shown in example IV.

Example IV. N_2 on charcoal. $\frac{dQ}{dA}$ is calculated from isotherms on cocoanut charcoal at 0°C. and 9.3°C. determined by Miss Homfray. $\frac{\Delta Q}{\Delta A}$ is determined by Gregg (31) at 0°C. on birchwood charcoal.

A ncc.	p at 0°C. calculated mm.	p at 9.3°C. mm.	$\frac{dQ}{dA}$ calculated calories	$\frac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
1.5	68	89	0.198	0.195	0 to 3
3.5	171	216	0.171	0.209	3 " 5.5
4.6	236	316	0.214		
5.6	294	386	0.200	0.205	5.5 " 7.7
8.1	473	624	0.203	0.210	7.7 " 13.5

Example V. H_2O on charcoal. $\frac{dQ}{dA}$ is calculated from isotherms at 0°C. and 20°C. on sugar charcoal, determined by Coolidge (14). $\frac{\Delta Q}{\Delta A}$ is measured by Keyes at 0°C. on charcoal of French gasmasks.

A ncc.	p at 0°C. calculated mm.	p at 20°C. mm.	$\frac{dQ}{dA}$ calculated calories	$\frac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
0.41	0.23	0.76	0.423	0.381	0 to 20.6
1.49	0.78	2.85	0.459		
4.21	1.48	5.5	0.465		
16.3	1.85	7.2	0.481	0.474	20.6 " 60.7
191	2.77	11.6	0.507	0.472	60.7 " 102.1
198	3.20	13.2	0.502	0.467	102.1 " 143.8
208	4.00	16.8	0.508		

When comparing calculated values with those found on various types of charcoal, we must recall the curves for ether in figure 4.

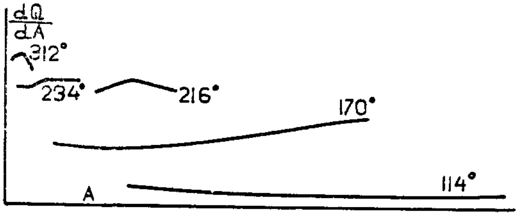

FIG. 8. ARGON ON CHARCOAL

Also from the above example of H_2O on charcoal it is evident that the general shape of the curve calculated is the same as that of the curve found. This however does not mean that at the same A the same $\frac{dQ}{dA}$ appears in both cases. In fact, this cannot be expected; for the quantities taken up by various charcoals at saturation with a vapor differ very much. Since the inner surfaces and inner volumes of the charcoals are different, at the same A the relative saturation is quite different. If the capacity, C, of the charcoal is the quantity taken up at the saturated pressure of the adsorptive at a certain temperature, we should compare values of $\frac{dQ}{dA}$ at the same $\frac{A}{C}$, or at the same p, but not at the same A. Up to the present this is hardly possible, because the investigators who determine the heat of adsorption usually do not measure the pressure at all, or at most very inaccurately.

From the calculated values conclusions can now be drawn as to the influence of the temperature. In some cases this is very simple. With argon on charcoal (figure 8) or with H_2 the $\frac{dQ}{dA}$ against A curves are nearly straight, and lie higher at increasing temperatures (see tables 9A and 10D). At constant A, $\frac{dQ}{dA}$ increases much more rapidly than the absolute temperature, at least below 250° K. At $A = \pm 50$ normal cubic centimeters, $\frac{dQ}{dA}$ for argon is 0.025 calorie per normal cubic centimeter at 114°K, 0.083 calorie at 170°K and 0.161 calorie at 215°K. (The temperature mentioned is always the average of that of both isotherms, from which the values are calculated.) $\frac{dQ}{dA}$ is here approximately proportional to the third power of the absolute temperature, and to the second power at higher temperatures.

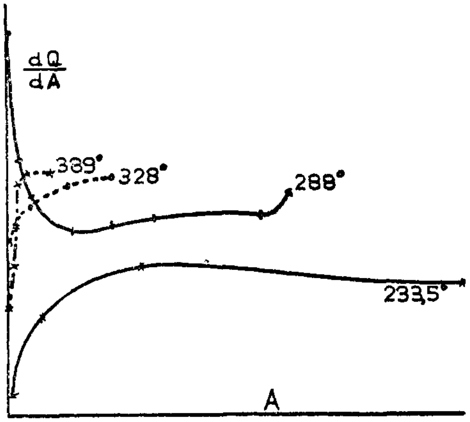

FIG. 9. N_2 ON COCOANUT CHARCOAL AT FOUR TEMPERATURES (CALCULATED FROM TITOFF'S ISOTHERMS)

With gases which are adsorbed more strongly the relations are more complicated. Such is the case with N_2 on charcoal (figure 9). A calculation from Titoff's isotherms gives for the heat of adsorption, at 233°K as well as at 328°K and 378°K, curves, which after an initial rise, at larger values of A approach a constant value which is higher for higher temperatures (see tables 9C and 10A). The form of these curves when A is very small is unknown. It is possible that $\frac{dQ}{dA}$ lies much higher at $A = 0$ but falls steeply to a minimum and then rises again. Only then does the course discussed above set in. This at least is the shape of the curve which Polanyi and Welke calculated for SO_2 on charcoal. They determined the isotherms for very small values of A at 0°C. and at 5.3°C. on charcoal which had been evacuated during 30 days at 750°C. The curve for the heat of adsorption calculated from this has a sharp minimum at $A = 0.33$ cc. (see figure 10), and the value of $\frac{dQ}{dA}$ in the minimum is lower than the heat of condensation of SO_2 (which is shown in the figure by a horizontal line). If the investigation had not been extended to very low concentrations, one would get the impression that this curve was of exactly the same type as that for N_2 on charcoal.

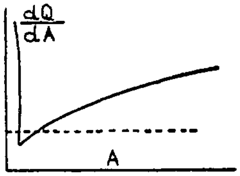

FIG. 10. SO_2 ON CHARCOAL AT 2.5°C. AND VERY SMALL CONCENTRATIONS (Dotted line = heat of condensation of SO_2)

From the figure for N_2 it appears that at greater values of A the curves lie higher at a higher temperature, but that at small values this is not at all the case. That the temperature coefficient for the heat of adsorption may have a different sign when determined at different concentrations, is still more evident from the curves for ether on charcoal, calculated from the very accurate measurements of Goldmann and Polanyi (figure 11 and tables 11A and 12C). The shapes of the curves at 266°K and 283° K are about the same (flat minimum, sharp maximum, then steep decline to about the heat of condensation of ether), but at a higher temperature the curve is shifted to the left and somewhat upward. As the curves intersect twice, the sign of the temperature coefficient changes twice. Other vapors, such as *n*-pentane (see figure 14), and ethyl chloride (table 11) etc., show an analogous behavior. For NH_3, calculated from Titoff's isotherms (table 10) only the shifting to the left is noticeable, as at greater values of A no pressures are measured; from the isotherms of Richardson the difference in height is also evident (see figure 11 and table 13).

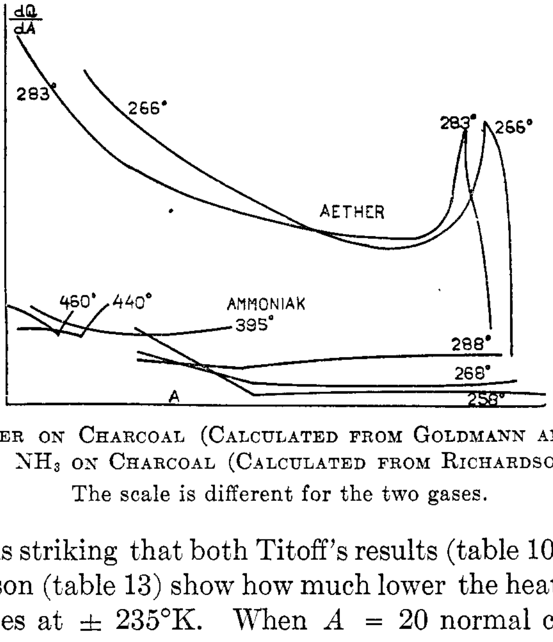

FIG. 11. ETHER ON CHARCOAL (CALCULATED FROM GOLDMANN AND POLANYI). NH_3 ON CHARCOAL (CALCULATED FROM RICHARDSON)
The scale is different for the two gases.

For CO_2 it is striking that both Titoff's results (table 10) and those of Richardson (table 13) show how much lower the heat of adsorption becomes at ± 235°K. When $A = 20$ normal cubic centimeters (Titoff), $\frac{dQ}{dA} = 0.299$ calorie at 328°K, 0.293 calorie at 288°K, and 0.140 calorie at 235°K. No influence of the critical temperature (304°K) is noticeable.

With the calculation from isotherms on SiO_2 etc. nothing essentially new appears. The greatest range of temperatures has been examined here with SO_2 on SiO_2 by McGavack and Patrick (table

17). The curves calculated for the heat of adsorption remind one of those of N_2 on charcoal. Here also we find at 206°K as well as at 363°K a curve which rises at the beginning, while on the contrary all the curves in the neighborhood of 280°K at once fall steeply.

From the above it is evident that the curve of figure 7 for the relation between the temperature and the heat of adsorption of O_2 on charcoal at constant A is not at all an exception. For each value of A the dependence of $\frac{dQ}{dA}$ on T will have a somewhat different course. For many values of A there is a range where the heat of adsorption changes but little with changing T. However, when approaching the temperature at which A is equal to the saturation quantity of the charcoal, $\frac{dQ}{dA}$ begins to rise steeply with increasing T (see figure 11). At small values of A the temperature coefficient of $\frac{dQ}{dA}$ can be very great; in those cases no agreement can be expected between experimental and calculated values of $\frac{dQ}{dA}$, when the temperature is not exactly the same. Yet such comparisons are often unjustly made.

If we plot $\frac{dQ}{dA}$ against p instead of against A, we find parallel lines for $\frac{dQ}{dA}$ at different temperatures in those cases where the isosteres run parallel. For $\frac{dp}{dT}$ is constant there; at constant p the heats of adsorption must then be proportional to T^2 (or at constant $\frac{p}{RT}$ to T). At small pressures and at pressures near saturation such a regular course is, however, out of the question.

In the following alphabetical summary of the substances, data concerning which are given in tables 9 to 19, the figures refer to the tables; the letters to the sections of the tables in which the data appear:

Charcoal as adsorbent

NH_3	A	C_6H_6	CO_2	CS_2	CO	CCl_4	$CHCl_3$	C_2H_5Cl	C_2H_4
10C, 13B	9A	12B	9E, 10B, 13A	11B, 12E	9F	12H	12G	11D	9D

$(C_2H_5)_2O$	$HCOOC_2H_5$	H_2	CH_4	CH_3COOCH_3	CH_3OH	N_2	C_5H_{12}	H_2O	
11A, 12C	12I	10D	9B	12F	12D	9C, 10A	11C	12A	

Other adsorbents

ADSORBENT	GAS									
	C_2H_2	C_4H_{10}	CO_2	C_2H_6	C_2H_4	H_2	CH_3Cl	NO_2	N_2O	SO_2
SiO_2		14	15A					16	15B	17
SnO_2	19A			19C	19B	19D				
Titania gel		18A					18B			

TABLE 9

Adsorption of gases on cocoanut charcoal

A. Argon on cocoanut charcoal

HOMFRAY

A ncc.	p^* at	p at	$\frac{dQ}{dA}$ in calories at
	83°K	145°K	114°K
15.8	4.6	19.6	0.025
65.6	17.0	42.8	0.016
76.9	37.9	820	0.013
	145°K	194.7°K	170°K
1.4	4.0	19.0	0.078
5.1	6.0	24.0	0.070
9.7	12.4	54.2	0.074
15.4	19.0	98.4	0.083
18.6	25.6	129.0	0.081
24.0	35.0	218.0	0.092
28.8	44.2	295.0	0.096
39.4	69.2	564.0	0.106
47.0	86.4	758.0	0.109
	195°K	236°K	216°K
11.9	70.6	309.6	0.147
14.3	88.4	417.0	0.154
17.1	111.2	568.4	0.161
21.9	176.8	815.0	0.152
	194.7°K	273°K	234°K
1.6	8.0	97.5	0.150
3.8	19.0	230	0.150
5.1	24.0	319	0.156
9.7	54.2	727	0.156
	273°K	351°K	312°K
0.9	51	291.6	0.190
1.9	118	722.4	0.197
2.9	175	868.0	0.174
	351°K	373°K	362°K
1.0	77	123	0.247
2.0	155	247	0.246
3.1	254	403	0.243
5.2	454	708	0.234
	373°K	455°K	414°K
0.3	38	313	0.387
1.3	153	626	0.258

B. CH_4 on cocoanut charcoal

HOMFRAY

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	240°K	255°K	247.5°K
11.8	36	71.4	0.247
18.5	76	153.4	0.254
24.6	132	250.2	0.231
30.8	215	412.6	0.236
33.7	270	503.2	0.225
	255°K	273°K	264°K
6.9	33.6	67	0.236
17.8	144.4	274	0.219
23.5	228.8	451	0.232
26.4	288.0	578	0.239
29.1	362.0	702	0.227
	273°K	293°K	283°K
6.9	67	132	0.240
11.4	134	260	0.235
14.1	191	362	0.226
17.8	274	527	0.232
30.7	358	685	0.230
33.5	451	854	0.228
	293°K	319°K	306°K
2.4	38	92	0.282
3.8	66	140	0.239
6.3	117	278	0.275
13.0	318	676	0.262
	319°K	351°K	335°K
2.4	92	184	0.215
3.8	140	321	0.257
6.3	278	556	0.215
7.8	347	707	0.221

* The pressure is always given in mm. of Hg.

TABLE 9—*Continued*

C. N_2 on cocoanut charcoal

HOMFRAY

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	194.7°K	244.5°K	220°K
3.9	11	75	0.166
6.5	20	136	0.166
9.4	27.2	236	0.187
12.9	37.6	373	0.198
17.1	65.4	573	0.188
	244.5°K	273°K	259°K
3.9	75	197	0.200
6.5	136	351	0.197
9.4	236	590	0.190
	273°K	282.3°K	278°K
1.5	68	89	0.198
3.5	171	216	0.171
4.6	236	316	0.214
5.6	294	386	0.200
8.1	473	624	0.203

D. C_2H_4 on cocoanut charcoal

HOMFRAY

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	273°K	293°K	283°K
36.7	70	177	0.329
39.8	93	228	0.318
46.4	168	426	0.330
	293°K	319°K	306°K
19.2	31	88	0.332
23.6	50	137	0.321
35.5	160	444	0.325
38.3	201	570	0.332
	319°K	351°K	335°K
19.2	88	260	0.336
23.6	137	407.5	0.338
28.0	209	639	0.346
	351°K	373°K	362°K
9.7	81	157	0.349
12.7	130	237	0.317
18.8	250	465	0.327
	373°K	405°K	389°K
11.8	210	477	0.343
14.4	297	678	0.345
17.3	403	887	0.330
	405°K	455°K	430°K
2.7	70	220	0.374
5.3	150	475	0.376
8.2	288	841	0.350

TABLE 9—*Concluded*

E. CO_2 on cocoanut charcoal

HOMFRAY

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	273°K	293°K	283°K
20.8	59.2	128	0.273
25.9	85.4	186	0.276
31.5	120	258	0.271
37.8	174	374	0.271
43.8	235	500	0.267
	293°K	319°K	306°K
6.5	29	71	0.285
12.7	63	158	0.293
20.8	128	311	0.283
25.9	186	446	0.278
31.5	258	626	0.282
	319°K	333°K	326°K
15.0	197	304	0.292
20.1	294	475	0.322
24.7	411	726	0.382
	319°K	351°K	335°K
6.4	70	180	0.293
9.4	121	268	0.246
12.5	151	383	0.288
15.3	200	503	0.286
	351°K	373°K	362°K
3.2	72	127	0.299
4.6	117	193	0.264
6.2	176	283	0.250
9.1	255	441	0.289
12.1	365	648	0.303
14.7	479	810	0.277
	373°K	405°K	389°K
5.7	251	492	0.281
8.3	391	768	0.282
	373°K	455°K	414°K
1.3	50	251	0.296
2.5	98	488	0.294
3.6	149	736	0.293

F. CO on cocoanut charcoal

HOMFRAY

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	194.7°K	239.4°K	217°K
6.2	6	60	0.213
17.1	30	257.5	0.199
20.7	40	365	0.204
27.4	72	635	0.201
	239.4°K	244.5°K	242°K
13.8	184	229	0.222
19.2	316	382	0.193
22.1	420	500	0.177
25.0	525	635	0.193
27.6	645	786	0.201
	244.5°K	273°K	258.8°K
2.5	18	73	0.290
5.5	57	180	0.239
8.4	104	304	0.222
12.7	200	540	0.206
14.9	255	713	0.213
17.1	327	882	0.206
	273°K	293°K	283°K
2.5	73	135	0.218
5.5	180	328	0.213
8.4	304	550	0.210
	293°K	319.2°K	306.1°K
3.1	110	214	0.210
4.5	260	509	0.212
6.8	415	835	0.221

TABLE 10

Adsorption on cocoanut charcoal

A. N_2 on cocoanut charcoal

TITOFF

A ncc.	*p* at	*p* at	$\frac{dQ}{dA}$ in calories at
	194°K	273°K	233.5°K
0.145	1.5	5.6	0.078
0.894	4.6	35.4	0.121
3.468	12.5	150	0.148
12.042	66.4	694	0.139
	273°K	303°K	288°K
0.082	2.8	8.6	0.274
0.227	8.8	20.3	0.204
0.766	30.4	64.5	0.184
1.718	73.2	144.6	0.166
2.764	118.6	239.6	0.172
3.875	170.0	347.6	0.175
6.646	315.6	650.0	0.176
7.490	350.4	752.3	0.187
	303°K	353°K	328°K
0.082	8.6	20.0	0.160
0.227	20.3	51.2	0.175
0.766	64.5	167.2	0.180
1.718	144.6	399.2	0.192
2.764	239.6	669.0	0.195
	353°K	424.5°K	389°K
0.0371	9.7	18.9	0.124
0.0754	19.0	41.8	0.146
0.1416	33.6	83.4	0.169
0.3168	69.4	194.4	0.191
0.5052	108	316.1	0.199
1.172	264	770.7	0.199

B. CO_2 on cocoanut charcoal

TITOFF

A ncc.	*p* at	*p* at	$\frac{dQ}{dA}$ in calories at
	196.5°K	273°K	235°K
15.26	0.3	25.8	0.139
41.50	1.8	190.0	0.145
50.24	5.2	315.9	0.128
61.37	11.0	589.1	0.121
65.85	14.2	755.1	0.124
	273°K	303°K	288°K
1.82	1.2	5.3	0.363
4.02	3.6	14.7	0.344
10.29	14.2	50.7	0.311
19.72	41.8	138.5	0.293
28.87	89.6	283.3	0.281
38.14	155.0	498.1	0.285
44.93	234.0	758.6	0.287
	303°K	353°K	328°K
0.507	1.3	7.8	0.339
1.82	5.3	31.0	0.335
4.02	14.7	78.0	0.316
10.29	50.7	256	0.307
19.72	138.5	672	0.299
	353°K	424.5°K	389°K
0.146	2.0	16.1	0.387
0.378	6.0	36.6	0.336
0.720	12.0	68.1	0.322
1.605	28.0	154.5	0.317
3.154	57.0	319.4	0.320
4.25	82.6	447.5	0.314
5.78	119.2	525.2	0.275
7.46	167.0	747.7	0.278

TABLE 10—*Concluded*

C. NH_3 on cocoanut charcoal

TITOFF

A ncc.	*p* at	*p* at	$\frac{dQ}{dA}$ in calories at
	249.5°K	273°K	261°K
5.5	0.3	2.6	0.563
17.2	2.9	12.4	0.379
45.0	16.3	49.4	0.289
119.3	112.2	332	0.283
	273°K	303°K	288°K
8.64	4.4	20.5	0.376
19.8	15.4	62.0	0.340
40.4	43.2	151.3	0.305
60.0	75.6	269.1	0.310
77.0	124	408.2	0.291
103.5	225	785.4	0.305
	303°K	353°K	328°K
2.62	1.2	14.0	0.465
3.78	4.0	27.8	0.367
6.72	13.5	76.2	0.328
8.64	20.5	115.0	0.327
16.85	50.8	279.6	0.323
24.03	80.0	431.2	0.319
38.59	143.8	762.9	0.316
	353°K	424.5°K	389°K
1.02	1.6	16.6	0.434
2.10	8.8	64.8	0.371
3.98	30.0	176.2	0.329
5.47	53.4	286.0	0.311
7.20	86.0	432.7	0.300
8.86	120.0	576.8	0.291
10.46	151.4	721.8	0.290

D. H_2 on cocoanut charcoal

TITOFF

A ncc.	*p* at	*p* at	$\frac{dQ}{dA}$ in calories at
	194°K	273°K	233.5°K
0.0586	7.9	25.0	0.068
0.1480	19.0	66.5	0.074
0.5310	67.5	247.5	0.077
1.1214	141.9	530	0.078
	273°K	353°K	313°K
0.0446	19.5	73.9	0.142
0.1096	47.2	183.1	0.145
0.2538	113	454.0	0.148
0.4011	182	727.3	0.148

TABLE 11

Adsorption on charcoal

A. Ethyl ether on charcoal			
GOLDMANN AND POLANYI			
A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	257.7°K	273°K	265.4°K
37.3	0.0175	0.0848	0.643
46.3	0.0502	0.215	0.592
68.0	0.375	1.3	0.506
89.5	1.980	6.3	0.471
107.8	7.53	24.1	0.474
113.0	12.21	42.5	0.508
117.2	23.7	100.5	0.588
119.8	43.7	174.6	0.564
122.4	78.0	184.8	0.351
	273°K	293°K	283°K
23.8	0.0125	0.0844	0.676
46.0	0.212	0.980	0.542
66.8	1.295	5.01	0.479
107.2	23.0	91.6	0.490
111.0	33.5	152.8	0.538
113.0	42.6	216.2	0.575
114.7	58.5	235.5	0.493
118.1	128.2	373.4	0.378

B. CS_2 on charcoal			
GOLDMANN AND POLANYI			
A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	257.7°K	273°K	265.4°K
42.4	0.065	0.228	0.511
63.8	0.245	0.761	0.462
95.2	0.849	2.46	0.504
117.2	1.64	4.56	0.416
150.3	3.77	10.5	0.417
183.9	9.7	28.0	0.427
195.7	18.9	54.0	0.427
	273°K	293°K	283°K
21.7	0.0294	0.154	0.573
42.2	0.226	0.931	0.490
63.2	0.74	2.78	0.458
93.4	2.3	8.20	0.440
114.0	4.3	14.5	0.421
143.8	9.1	29.0	0.401
171.6	17.2	57.0	0.415
189.5	35.0	114.8	0.411
202.0	94.0	271.3	0.367

TABLE 11—*Concluded*

C. n-Pentane on charcoal

GOLDMANN AND POLANYI

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	209.3°K	257.7°K	233.5°K
100.2	0.024	3.6	0.494
112.1	0.067	8.6	0.478
122.6	0.233	50.0	0.529
124.3	0.288	72.3	0.544
	257.7°K	273°K	265.4°K
46.8	0.034	0.1405	0.582
67.6	0.25	0.89	0.521
81.7	0.83	2.5	0.452
90.2	1.6	5.0	0.467
105.0	5.0	14.6	0.439
112.8	9.1	29.2	0.478
116.0	13.2	45.4	0.507
118.8	20.0	80.7	0.572
121.7	39.3	161.0	0.578
	273°K	278.2°K	275.6°K
81.7	2.5	3.9	0.571
90.2	5.0	7.4	0.503
105.0	14.6	21	0.467
116.0	45.4	68	0.519
118.8	80.7	126	0.572
	273°K	293.5°K	283.2°K
37.6	0.0533	0.284	0.579
50.6	0.203	0.99	0.548
67.6	0.89	3.86	0.508
90.2	5.0	21.2	0.500
105.0	14.6	55.6	0.463
112.8	29.2	138	0.538
116.0	45.4	254	0.596
118.8	80.7	390	0.545

D. Ethyl chloride on charcoal

GOLDMANN AND POLANYI

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	257.7°K	273°K	265.4°K
16.1	0.0177	0.065	0.530
22.9	0.0479	0.175	0.528
40.5	0.289	0.896	0.461
66.6	1.410	3.99	0.424
119.9	12.02	30.5	0.379
131.1	17.81	47.0	0.395
150.1	35.6	91.3	0.384
161.5	58.4	168	0.430
168.1	105.7	304	0.430
170.1	131.1	316	0.342
	273°K	293°K	283°K
9.26	0.014	0.0678	0.559
20.8	0.135	0.552	0.499
49.2	1.61	5.60	0.442
91.1	11.2	35.8	0.412
114.6	26.7	82.7	0.400
127.0	41.2	124.8	0.423
141.9	68.2	204.2	0.388
152.9	101.7	311.1	0.396
158.8	138.0	448.0	0.417

TABLE 12

Adsorption on charcoal

A. H_2O on sugar charcoal

COOLIDGE

The following isosteres are taken from Coolidge (14) p. 715, table III.

A ncc.	p 243°K	p 273°K	p 293°K	p 334°K	p 373°K	p 429°K
0.41	0.0175	0.23	0.76	5.8	20.5	76
1.49	0.066	0.78	2.85	19.5	74	257
4.21	0.125	1.48	5.5	45	173	710
16.3	0.16	1.85	7.2	68	330	1500
191	0.22	2.77	11.6	120	760	
198	—	3.20	13.2	142		
208	0.28	4.00	16.8			

From this is calculated:

A ncc.	$\frac{dQ}{dA}$ at 258°K calories	283°K	313.5°K	353.5°K	401°K
0.41	0.505	0.423	0.428	0.357	0.332
1.49	0.484	0.459	0.409	0.377	0.315
4.21	0.484	0.465	0.443	0.381	0.357
16.3	0.479	0.481	0.475	0.447	0.383
191	0.496	0.507	0.494	0.522	
198	—	0.502	0.502		
208	0.521	0.508			

The measurements of organic vapors on cocoanut charcoal by Coolidge cover a wide range of temperatures, but are less accurate than those of Goldmann and Polanyi (table 11).

Heats of adsorption are calculated partly from isosteres which Coolidge interpolated from his isotherms and published (J. Am. Chem. Soc. **46**, 596 (1924)), partly from the original isotherms which Coolidge kindly sent us and for which we wish to express our gratitude.

The unpublished values are used in those cases, where a more accurate value for the heat of adsorption could be expected by taking temperatures closer to each other and diminishing the number of interpolations.

Values taken from Coolidge's isosteres are marked*.

The third decimal of the values of $\frac{dQ}{dA}$ and the pressures may be omitted.

TABLE 12—*Continued*

B. Benzene on cocoanut charcoal

COOLIDGE

*Between 273°K and 333°K		*Between 333°K and 423°K	
A ncc.	$\frac{dQ}{dA}$ at 303°K calories	A ncc.	$\frac{dQ}{dA}$ at 378°K calories
25	0.65	5	0.74
50	0.61	25	0.64
75	0.58	50	0.59
100	0.56	75	0.56

Between 420.5°K and 489°K		Between 489°K and 576°K	
A ncc.	$\frac{dQ}{dA}$ at 454°K calories	A ncc.	$\frac{dQ}{dA}$ at 532.5°K calories
6.3	0.73	0.8	0.85
10.8	0.72	1.9	0.79
		2.6	0.76
		7.1	0.69

TABLE 12—*Continued*

C. Ethyl ether on cocoanut charcoal

COOLIDGE

Between 273°K and 306°K

A ncc.	$\frac{dQ}{dA}$ at 289.5°K calories
57	0.60
78	0.56
86	0.60
91	0.53
106	0.47

Between 332°K and 372°K

A ncc.	$\frac{dQ}{dA}$ at 352°K calories
21	0.63
32	0.57
58	0.51

Between 420°K and 489°K

A ncc.	$\frac{dQ}{dA}$ at 454.5°K calories
8	0.79
14	0.63
21	0.60
31	0.57

Between 306°K and 332°K

A ncc.	$\frac{dQ}{dA}$ at 319°K calories
32	0.64
58	0.49
90	0.54

Between 372°K and 420°K

A ncc.	$\frac{dQ}{dA}$ at 396°K calories
14	0.69
21	0.64
32	0.59
57	0.53

Between 489°K and 576°K

A ncc.	$\frac{dQ}{dA}$ at 532.5°K calories
1.1	1.14
2.2	1.03
3.1	0.96
5.9	0.76
7.7	0.69
14	0.79
20	0.67
22.4	0.59

D. Methyl alcohol on cocoanut charcoal

COOLIDGE

Between 273°K and 306.3°K

A ncc.	$\frac{dQ}{dA}$ at 289.6°K calories
30	0.62
65	0.56
126	0.53
173	0.50
194	0.47
220	0.52
237	0.52
241	0.50
251	0.46

*Between 323°K and 373°K

A ncc.	$\frac{dQ}{dA}$ at 348°K calories
10	0.71
20	0.58
30	0.55
100	0.50
150	0.49

*Between 373°K and 423°K

A ncc.	$\frac{dQ}{dA}$ at 398°K calories
5	0.88
10	0.71
20	0.56
30	0.52
100	0.48

TABLE 12—*Continued*

E. Carbondisulfide on cocoanut charcoal

COOLIDGE

*Between 273°K and 333°K

A ncc.	$\frac{dQ}{dA}$ at 303°K calories
25	0.53
75	0.48
150	0.46

*Between 333°K and 423°K

A ncc.	$\frac{dQ}{dA}$ at 378°K calories
5	0.56
25	0.51
75	0.47
100	0.45

Between ± 422°K and 489°K

A ncc.	$\frac{dQ}{dA}$ at 455.5°K calories
2.1	0.61
3.2	0.58
4.1	0.55
10	0.48
15	0.42

Between 489°K and 576.8°K

A ncc.	$\frac{dQ}{dA}$ at 533°K calories
3.1	0.58
8.1	0.44
20	0.55

F. Methyl acetate on cocoanut charcoal

COOLIDGE

*Between 273°K and 373°K

A ncc.	$\frac{dQ}{dA}$ at 323°K calories
50	0.58
75	0.56
100	0.55

G. Chloroform on cocoanut charcoal

COOLIDGE

Between 273°K and 317.8°K

A ncc.	$\frac{dQ}{dA}$ at 295.4°K calories
71	0.55
94	0.55
103	0.45
118	0.56
123	0.46

Between 317.8°K and 372°K

A ncc.	$\frac{dQ}{dA}$ at 344.9°K calories
47	0.55
67	0.54
70	0.55
95	0.55

H. Carbon tetrachloride on cocoanut charcoal

COOLIDGE

Between 273°K and 317.6°K

A ncc.	$\frac{dQ}{dA}$ at 295.3°K calories
75	0.58
88	0.58

Between 317.6°K and 371.6°K

A ncc.	$\frac{dQ}{dA}$ at 344.6°K calories
44	0.52
66	0.57
73	0.59
81	0.56

TABLE 12—*Concluded*

I. Ethyl formate on cocoanut charcoal

COOLIDGE

Between 273°K and 317.7°K		Between 317.7°K and 371.8°K	
A ncc.	$\frac{dQ}{dA}$ at 295.3°K calories	A ncc.	$\frac{dQ}{dA}$ at 344.7°K calories
59	0.61	26	0.61
76	0.55	43	0.58
95	0.55	59	0.52
123	0.52	76	0.55
		96	0.53

The determinations of Richardson cover a very large stretch of p and T. However they are not very accurate, since Richardson outgassed his charcoal at too low a temperature (400°C.); therefore he found differences of many per cents in pressure, whether working at rising or decreasing T. Hence the third decimal of $\frac{dQ}{dA}$ and the pressures may be omitted.

TABLE 13

Adsorption on cocoanut charcoal

A. CO_2 on cocoanut charcoal

RICHARDSON

Between 209°K and 219°K

A ncc.	$\frac{dQ}{dA}$ at 214°K calories
44	0.17
64	0.11
87	0.08
99	0.17
104	0.17

Between 230°K and 243°K

A ncc.	$\frac{dQ}{dA}$ at 236.5°K calories
22	0.26
43	0.23
63	0.18
82	0.26
88	0.29

Between 243°K and 253°K

A ncc.	$\frac{dQ}{dA}$ at 248°K calories
12	0.25
22	0.33
43	0.28
61	0.28
80	0.27

Between 263°K and 273°K

A ncc.	$\frac{dQ}{dA}$ at 268°K calories
11	0.22
21	0.27
41	0.28
56	0.33
71	0.25

Between 273°K and 283°K

A ncc.	$\frac{dQ}{dA}$ at 278°K calories
11	0.28
21	0.32
40	0.29
62	0.26
68	0.25
71	0.29

Between 388°K and 403°K

A ncc.	$\frac{dQ}{dA}$ at 395.5°K calories
6	0.34
10	0.36
16	0.58

Between 403°K and 418°K

A ncc.	$\frac{dQ}{dA}$ at 410.5°K calories
4	0.34
7	0.32
10.6	0.36
11.1	0.59
12.5	0.67

B. NH_3 on cocoanut charcoal

RICHARDSON

Between 253°K and 263°K

A ncc.	$\frac{dQ}{dA}$ at 258°K calories
26	0.36
46	0.15
69	0.15
91	0.13
113	0.13
134	0.21

Between 263°K and 273°K

A ncc.	$\frac{dQ}{dA}$ at 268°K calories
26	0.28
46	0.18
68	0.18
90	0.19
111	0.21
128	0.28
141	0.28

Between 283°K and 293°K

A ncc.	$\frac{dQ}{dA}$ at 288°K calories
26	0.27
45	0.22
66	0.27
87	0.28
105	0.33
128	0.29

Between 313°K and 328°K

A ncc.	$\frac{dQ}{dA}$ at 320.5°K calories
13	0.35
25	0.35
43	0.30
63	0.33
96	0.34

Between 328°K and 343°K

A ncc.	$\frac{dQ}{dA}$ at 335.5°K calories
12	0.34
23	0.37
53	0.36
76	0.35
91	0.34

Between 373°K and 388°K

A ncc.	$\frac{dQ}{dA}$ at 380.5°K calories
11	0.35
20	0.32
32	0.31
42	0.29
50	0.30

TABLE 13—*Concluded*

B. NH_3 on cocoanut charcoal—*concluded*

RICHARDSON

Between 388°K and 403°K		Between 433°K and 448°K	
A ncc.	$\frac{dQ}{dA}$ at 395.5°K calories	*A* ncc.	$\frac{dQ}{dA}$ at 440.5°K calories
9	0.43	7	0.37
16	0.37	12	0.37
25	0.34	18	0.34
31	0.32	22	0.45
36	0.33		
43	0.36		

Between 448°K and 473°K	
A ncc.	$\frac{dQ}{dA}$ at 460.5°K calories
5	0.44
8	0.42
11	0.39
14	0.35
15	0.40

TABLE 14

Adsorption on silica gel

Butane on silica gel (containing ±3.5 per cent H_2O)

PATRICK AND LONG

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	273°K	303°K	288°K
3.8	7.41	28	0.325
10.6	32.89	110	0.295
20.7	86.85	272	0.279
35.2	167.13	512	0.273
	303°K	313°K	308°K
3.1	19.45	34.5	0.481
6.3	51.03	81.0	0.388
8.0	77.20	114.5	0.331
14.6	169.4	250.0	0.327
15.4	187.2	268.5	0.303
21.8	287.3	410	0.299
32.1	456.2	637	0.280
	313°K	373°K	343°K
1.9	18	145.39	0.360
3.4	40	294.66	0.344
6.2	80.5	566.89	0.336
7.5	103.5	696.46	0.329

TABLE 15

Adsorption on silica gel

A. CO_2 on silica gel containing ±1.3 per cent H_2O			
PATRICK, PRESTON AND OWENS			
A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	273°K	293°K	283°K
1.45	68.82*	163.5	0.31
2.8	149.88	319	0.27
3.4	182.11	390	0.27
4.6	259.78	545	0.26
	293°K	303°K	298°K
0.62	61.28	77.5	0.18
1.57	162.81	229	0.27
2.7	297.32	420	0.27
3.9	456.64	622.5	0.24
	303°K	313°K	308°K
0.62	77.5	97.29	0.19
1.4	201.5	257.12	0.20
2.1	326	408.82	0.19
2.7	423.5	549.99	0.22
3.2	505	625.44	0.18

B. N_2O on silica gel containing ±1.4 per cent H_2O			
PATRICK, PRESTON AND OWENS			
A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	273°K	293°K	283°K
1.9	107	189.31	0.20
3.1	182.5	344.05	0.22
3.7	225	453.46	0.25
4.0	238	496.46	0.26
	293°K	303°K	298°K
0.77	68.90	111.6	0.38
1.9	189.31	277.8	0.30
3.1	344.05	463.2	0.23
	303°K	313°K	308°K
0.71	109.8	207.19	0.53
0.99	148.8	308.55	0.61
1.6	235.8	457.07	0.56
2.0	286.8	550.68	0.55

* Since control determinations diverge very much, only two decimals are given.

TABLE 16

Adsorption on silica gel

N_2O_4 on silica gel containing ±6 per cent H_2O

RAMES RAY

The amount adsorbed, A′, is given in milligrams per gram of gel. Since the molecular weight of N_2O_4 varies with T, the calculation in ncc. is impossible.

A'	p at	p at	$\frac{dQ}{dA'}$ in calories at
milligrams	288°K	330°K	309°K
41.4	1.0	11	0.481
64.2	2.5	30	0.498
95.9	5.0	88	0.575
121.7	7.5	150	0.600
157.8	13.7	270	0.597
178.0	18.8	351	0.587
196.5	25.0	450	0.579
204.6	28.6	490	0.569
	330°K	353°K	341.5°K
41.4	11	44.0	0.783
64.2	30	101.6	0.689
95.9	88	234.4	0.553
121.7	150	338.0	0.459
	353°K	373°K	363°K
18.4	10.0	30	0.641
35.6	32.6	88	0.579
48.9	60.0	150	0.534
68.5	115.0	270	0.498
80.7	151.0	351	0.492
93.8	205.8	450	0.456
99.2	230.0	490	0.441

TABLE 17

Adsorption on silica gel

SO_2 on silica gel

MC GAVACK AND PATRICK

A nec.	p at	p at	$\frac{dQ}{dA}$ in calories at
	193°K	219°K	206°K
50.3	0.13	1.3	0.332
98.8	0.58	7.4	0.363
148	1.65	19	0.352
182	3.05	32.2	0.339
207	4.60	44.0	0.325
230	8.30	56.0	0.275
	238.6°K	273°K	255.8°K
53.3	4.22	42.2	0.387
81.5	13.85	112	0.351
108.2	29.02	219.6	0.340
137.2	50.07	364.6	0.334
162.6	73.45	514.0	0.327
192.7	116.62	720	0.306
	273°K	303°K	288°K
11.8	0.8	9.50	0.614
25.7	8.4	40.56	0.390
36.5	18.4	82.32	0.372
47.8	32.0	141.46	0.369
61.3	58.6	241.77	0.351
77.5	100	408.02	0.349
99.3	182	702.40	0.335
	330°K	353°K	341.5°K
4.5	12	47.0	0.612
16.7	70.4	192.19	0.451
18.7	83.2	224.73	0.446
27.7	191.4	407.88	0.339
34.2	286	575.32	0.313
37.4	344	671.95	0.300
	353°K	373°K	363°K
6.6	71.6	105.88	0.228
12.0	134.6	229.93	0.312
17.8	208	397.00	0.377
22.0	268.2	544.20	0.413
24.6	342	671.50	0.393

TABLE 18

Adsorption on titania gel

A. Butane on titania gel

KLOSKY AND WOO

Between 273°K and 308°K

A ncc.	$\frac{dQ}{dA}$ at 290.5°K in calories
12.7	0.33
15.2	0.33

B. Methyl chloride on titania gel

KLOSKY AND WOO

Between 298°K and 318°K

A ncc.	$\frac{dQ}{dA}$ at 308°K in calories
17.6	0.29
21.0	0.29
21.9	0.31

TABLE 19

Adsorption on SnO_2

A. C_2H_2 on SnO_2*

PEARCE AND GOERGEN

Between 273°K and 351.5°K

A ncc.	$\frac{dQ}{dA}$ at 312°K in calories
0.073	0.17
0.108	0.16
0.141	0.17
0.174	0.15
0.254	0.15

B. C_2H_4 on SnO_2

PEARCE AND GOERGEN

Between 273°K and 351.5°K

A ncc.	$\frac{dQ}{dA}$ at 312°K in calories
0.071	0.19
0.131	0.19

TABLE 19—*Concluded*

Between 351.5°K and 373°K

A ncc.	$\frac{dQ}{dA}$ at 362°K in calories
0.020	0.19
0.038	0.20
0.057	0.16
0.084	0.20
0.112	0.25

C. C_2H_6 on SnO_2

PEARCE AND GOERGEN

Between 273°K and 351.5°K

A ncc.	$\frac{dQ}{dA}$ at 312°K in calories
0.86	0.18
1.49	0.18

Between 351.5°K and 373°K

A ncc.	$\frac{dQ}{dA}$ at 362°K in calories
0.019	0.43
0.036	0.45
0.054	0.39
0.070	0.38
0.090	0.32
0.107	0.30
0.136	0.27

D. H_2 on SnO_2

PEARCE AND GOERGEN

Between 273°K and 351.5°K

A ncc.	$\frac{dQ}{dA}$ at 312°K in calories
0.006	0.075
0.009	0.075
0.018	0.099

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* The heat of adsorption varies very much with the previous history and the water content of the SnO_2.

IV. STATE OF THE ADSORBED PHASE

From the standpoint of phase-equilibria the adsorption-layer is not a separate phase, but forms with the adsorbent one phase of variable composition. The system has two components, and two degrees of freedom and consequently can have only two phases. If however we mean by a "phase" a complex of identical units of volume (in which the unit must be thought very small), the adsorption-layer is not merely a separate phase, but may contain two and even more phases. The conditions for the equilibrium between three- and two-dimensional phases, such as they appear in monomolecular adsorption-layers, have been traced by Ehrenfest. He found that the pressures in the two-dimensional phases must be mutually equal, but that thermodynamically no relation can be found between the two- and the three-dimensional pressures. When adsorption of a vapor on charcoal takes place, the adsorption-layer will be in gaseous condition, in case a very small quantity has been adsorbed, i.e. the molecules are free to move within the surface. At a somewhat greater concentration we get coexistence between liquid and gas in the interface. From this the question arose as to the pressure in the adsorption-layer; the estimates vary between 30,000 atmospheres and a negative pressure. The following arguments are advanced in favor of a high pressure:

1. Lamb and Coolidge calculated the net heat of adsorption (= heat of adsorption minus heat of condensation) per unit of volume of liquid adsorbed and found that for various substances this quantity is almost the same. If, in accordance with their opinion, the net heat of adsorption arises exclusively from compression, the pressure in the adsorption layer can be found by dividing the net heat of adsorption by the heat of compression per atmosphere of the liquid. In this way 28,000 to 37,000 atmospheres was found for the pressure in various liquid layers.

2. The volumes of liquid adsorbed by the charcoal at saturation do not differ much, and the greatest volume nearly always belongs to the liquid with the greatest compressibility.

3. According to determinations made by Harkins and Ewing, Williams (89), Cude and Hulett, the specific volume of charcoal

seems to vary with the liquid used in the pycnometer. The greater the compressibility of the liquid, the smaller the specific volume found for the charcoal. The explanation lies at hand: the more compressible the liquid, the greater the difference between its real volume at high pressure and that calculated; the smaller, therefore, is the specific volume of the charcoal.

4. The net heat of adsorption of water on charcoal at 0°C. is negative, according to Keyes' determinations. As the temperature increases from 0°C. the density of water becomes greater and the heat of compression is therefore negative. Here also the net heat of adsorption can be explained by compression at a high pressure.

TABLE 20

Heats of wetting of charcoal

LIQUID	HEAT OF WETTING		
	Of bone black calories	Of sugar charcoal dried at 100°C. calories	Of sugar charcoal dried at 1200°C. calories
Water	18.5	3.9	—
Acetone	19.3	3.6	28.6
Methyl alcohol	17.6	11.5	—
Ethyl alcohol	16.5	6.9	23.3
Ethyl ether	—	1.2	—
Chloroform	14.0	2.3	—
Carbon tetrachloride	8.4	1.5	—
Carbon disulfide	13.9	4.0	31.2
Benzene	11.1	4.2	32.7

According to this representation, the emphasis lies upon the inner volume of the charcoal, not upon the surface. One might suppose that the quantity adsorbed at saturation could exactly fill a monomolecular layer. Then the surface, covered by this quantity, should always be equal for various liquids. However, the percentage differences between the surfaces calculated in this way are much greater than those between the volumes, so that the supposition of a monomolecular layer offers no advantage here.

There are, however, many objections to the arguments of Lamb and Coolidge:

1. The net heat of adsorption, which is equal to the heat of wetting, cannot be always the same for one sort of charcoal, independent of the nature of the liquid. Since the charcoal takes up almost equal quantities at saturation, the heats of wetting per gram of charcoal should also be nearly equal. However the heats of wetting indicate that this is not true at all, even for those organic liquids tested by Lamb and Coolidge.

Gurvic made determinations with bone black, Gaudechon with sugar charcoal dried at 100°C., and Bartell and Ying Fu with sugar charcoal, dried at 1200°C.; their results for the heat of wetting per gram of charcoal are shown in table 20.

From this it is evident that the percentage differences are very great, especially for Gaudechon's sugar charcoal. For bone black (which has a larger ash content) they approach, save for a single exception, the order of magnitude found by Lamb and Coolidge for the differences between the net heats of adsorption, (i.e. about 25 per cent).

2. Heat of adsorption cannot be caused merely by compression, as shown by Coolidge (13) in a more recent article, since it is greatest for the first quantities of gas, which do not find anything to compress. The loss of potential energy at the near approach of the charcoal is not equivalent to a heat of compression from all sides. An adsorbed layer can be compressed only by the layers lying above it, which are also attracted by the charcoal. Here we have to do not only with the attraction between adsorbent and adsorptive, but also with the mutual attraction between molecules of the adsorptive. This influence will be especially evident in the case of a vapor condensing on the charcoal.

We shall try to develop this idea quantitatively, in order to come to an estimate (a rather approximate one, perhaps) of that part of the heat of adsorption which we can explain by compression.[3]

We therefore suppose a constant volume, to which we gradually admit more vapor, for instance by communication with a volume in which the pressure is somewhat higher. The differences in

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[3] Of course this heat of compression has nothing to do with the heat which we calculated for the compression of the unadsorbed gas.

pressure must always be very small, so that we can disregard the heat of expansion of the gas admitted. Heat of compression is then continually developed, and the total quantity of heat, U (from the initial condition with no volume up to a quantity A), is exclusively a function of A.

For the heat of compression of 1 gram-mol, we may write the formula of Maxwell:

$$\left(\frac{dQ}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v,$$

if v represents the molecular volume and Q the heat absorbed. The heat of compression of A gram-mols,

$$dU = -A\,dQ = -AT\left(\frac{dp}{dT}\right)_v dv.$$

If V is the constant total volume, $v = \frac{V}{A}$, consequently

$$dv = -\frac{V}{A^2}\,dA$$

and

$$\frac{dU}{dA} = T\frac{V}{A}\left(\frac{dp}{dT}\right)_v = T\left(\frac{dp}{dT}\right)_v v.$$

As long as the gas laws are applicable,

$$\frac{dp}{dT} = \frac{R}{v},$$

consequently

$$\frac{dU}{dA} = RT.$$

As soon as the vapor is saturated, p does not change any more, and as $v = \frac{RT}{p}$, we find

$$\frac{dU}{dA} = RT^2\frac{\delta \ln p}{\delta T},$$

and consequently the heat of condensation. As v is always the molecular volume of the vapor admitted, $\frac{dU}{dA}$ remains constant until everything is condensed and the volume is filled with liquid. Then $\left(\frac{dp}{dT}\right)v$ immediately rises rapidly, the compressibility of a liquid being very small. In order to follow the adsorption process as closely as possible, let us suppose that saturated vapor, which immediately condenses, is admitted; then $\frac{dU}{dA}$ equals the heat of condensation of the vapor admitted plus $T\left(\frac{dp}{dT}\right)v$, in

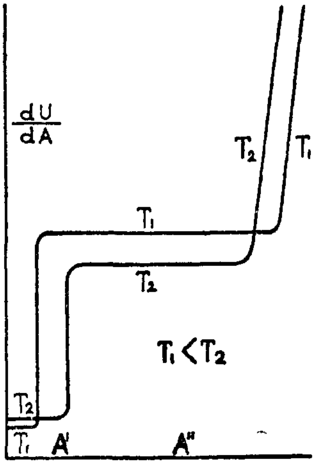


FIG. 12. CHANGE OF $\frac{dU}{dA}$ WITH A AT TWO TEMPERATURES

which v is now the molecular volume of the liquid. If we now calculate the curve for ether at 0°C., $\frac{dU}{dA}$ per normal cubic centimeter is at first 0.024 calorie, at condensation it is 0.297 calorie and afterwards, when the liquid is being compressed, it is $0.297 + 0.506 = 0.803$ calorie per normal cubic centimeter.

The value of A, at which condensation appears, is $A' = \frac{p'V}{RT}$, in which p' is the saturated vapor pressure. For higher values of T, A' is larger, since p' increases more than T. The heat of condensation falls with increase of temperature; RT however has increased. The point A'', where the volume is entirely filled with liquid, is situated at higher T at lower A, owing to the dilatation of the liquid. The curves for two temperatures will therefore intersect twice, and will have the course as shown in figure 12.

If we now place the constant volume of our derivation on a par with the volume taken up by the first layer, we see that the heat of compression will increase strongly as soon as the first layer is filled. The value of 0.8 calorie per normal cubic centimeter of ether will not be reached however, for when the liquid is compressed in the first layer, the point is reached at which a newly admitted quantity of vapor forms a second layer more easily than it attains a place in the first layer. This second layer is subjected to forces from the adsorbent as well as from the first layer and therefore compresses the latter. The heat of compression thus liberated cannot be calculated quantitatively; that it may be important is shown from the following reasoning.

The second layer does not evaporate (for the sake of convenience we consider the equilibrium as being static) in spite of the fact that the pressure is smaller than the saturated vapor-pressure. If, however, the same liquid were present in place of the charcoal, the second layer would evaporate immediately. The force exercised by the charcoal on this second layer must therefore be so much greater than that of the liquid itself at the same distance, that it neutralizes the lowering of the vapor-pressure. If, for instance, the pressure is one-tenth of the saturated tension, the attraction of the charcoal is ten times greater than that of the liquid at the same place. The first layer, therefore, is situated between two layers which attract each other ten times more strongly than in the normal liquid; therefore the compression will be about ten times the normal inner pressure. If we estimate the inner pressure for ether at 0°C. according to van der Waals to be 1400 atmospheres, the compression of the first layer is 14,000 atmospheres. The heat liberated when one cubic centimeter of liquid is compressed, is for ether at 0°C. equal to 0.00298 calorie per atmosphere (average between 1 and 12,000 atmospheres). (This value was calculated by Lamb and Coolidge from Bridgeman's measurements.) For 14,000 atmospheres this becomes 41.7 calories. If, for instance, 0.2 cc. of liquid is present in the first layer, 8.3 calories of heat of compression are liberated when the second layer has been formed. If also 0.2 cc. of liquid = 44.4 normal cubic centimeters of vapor have come in the second layer, about 0.19 calorie per normal cubic centimeter has been contributed to the heat of adsorption by the heat of compression of the first layer.

This estimate is only approximate, for: (*1*) the influence exerted by the charcoal on the second layer is partly indirect, owing to the changes brought about in the first layer; (*2*) if only the first layer is present, it is not under normal inner pressure; (*3*) the heat of compression will not be constant for each normal cubic centimeter which comes into the second layer.

We do not know at all how the formation of the second layer is effected, and cannot trace therefore, how the heat of compression will be distributed over the next quantity adsorbed. If, as soon as the second layer is filled, a third layer is formed, the attraction of the charcoal will have decreased much more than the compressible quantity of liquid has increased. The heat of compression will therefore be much smaller than at the formation of the second layer, and will always become smaller for possible following layers.

We shall now compare the curve calculated for $\frac{dU}{dA}$ with the curve for $\frac{dQ}{dA}$, found by Lamb and Coolidge at 0°C. for ether on cocoanut charcoal (figure 13). The straight part in the $\frac{dQ}{dA}$ curve must agree with the rise of the $\frac{dU}{dA}$ curve, and therefore shows us where the second layer is filled. This begins at about $A = 23$ normal cubic centimeters; this quantity of ether covers as monomolecular liquid layer a surface of 188 square meters, if we take for the thickness of the layer the cube root of the volume of one molecule.

As the ether molecules are probably orientated, it is more exact to take for the section of the molecule parallel to the surface of the charcoal, the value of about $0.20 m\mu^2$, found by Adam for many organic substances with straight chains. The surface of one gram of the charcoal of Lamb and Coolidge amounts then to 139 square meters. In the same way we calculate from the ether curve of Keyes for his charcoal a specific surface of 100 square meters.

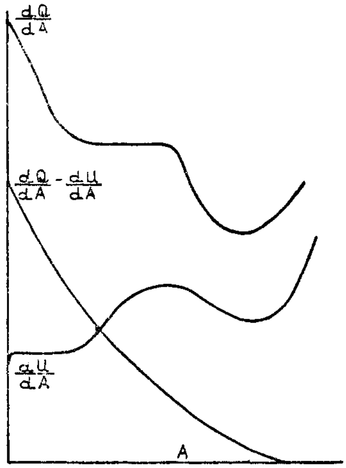


FIG. 13. ETHER ON CHARCOAL AT 0°C.

Heat of adsorption (measured by Lamb and Coolidge), heat of compression and real heat of adsorption. The value of $\frac{dQ}{dA}$ of the abscissa is 0.15 calorie.

If we now draw $\frac{dQ}{dA} - \frac{dU}{dA}$ against A, we get a curve which goes down regularly, and represents the heat of adsorption which we should find if we could avoid the heat of compression. We call this the "real heat of adsorption" (the expression "net heat of adsorption" would be preferable, if Lamb and Coolidge and many others had not used "net heat of adsorption" for the "heat of wetting"). The meaning of this "real heat of adsorption" will be discussed later on.

With ether the fall of the "real heat of adsorption" is compensated by the rise of $\frac{dU}{dA}$, whereby $\frac{dQ}{dA}$ remains constant therefore over a rather long distance. This is an exception. If the heat of compression is smaller in proportion to the real heat of adsorption, $\frac{dQ}{dA}$ will continue to go down slowly; if the heat of compression is greater in proportion to the "real heat of adsorption" than in the case of ether, $\frac{dQ}{dA}$ will rise slowly. Especially if $\frac{dU}{dA}$ is small, it is very difficult to deduce from the curve for the heat of adsorption where the second layer is formed.

Lamb and Coolidge have not continued their determinations up to the point of saturation. However, it is possible to deduce the further course of these curves from the isotherms measured by Goldmann and Polanyi (see figure 11). Just before saturation, $\frac{dQ}{dA}$ rises steeply and then falls to the heat of condensation. This rise cannot be attributed to heat of compression, but probably is due to the heat liberated when a large liquid-air interface disappears. For by filling a narrow capillary, which was coated by a thin liquid layer, the surface energy of the liquid will disappear and be converted into heat. From the quantity of heat liberated we can calculate the area of liquid surface which has disappeared, provided that the surface tension of the liquid is known.

From the figure the amount of heat which is due to the final rise of $\frac{dQ}{dA}$ can be estimated, although only approximately. This represents, for instance with ether at 10°C., a quantity of heat of about 0.5 calorie. The free surface energy per square centimeter of surface is for ether at 10°C. about 18 $\frac{\text{ergs}}{\text{cm}^2}$. Consequently the liquid surface must have been about 116 square meters. At -7°C. the amount of heat due to the rise of $\frac{dQ}{dA}$ is greater (see figure 11); also the free surface energy is then greater.

That exactly the same surface for the liquid should be found as we calculated for the charcoal of Lamb and Coolidge, was not to be expected. In the first place, the charcoal worked with was of a different kind; in the second place, the liquid surface must always be smaller than that of the charcoal, since the roughnesses of the surface and the very small cavities are filled sooner.

The fact that the values calculated for the liquid surface and for the charcoal surface are of the same order proves that the capillaries of the charcoal used do not differ much in diameter, and that they are first covered regularly with a liquid layer. Just before saturation a very small quantity of liquid will suffice to fill the pores entirely.

The maximum surface, which one normal cubic centimeter of ether can have at 10°C. as liquid, is 16.3 square meters (this is the total surface of both sides of the monomolecular layer). This is therefore also the largest surface, which can disappear by condensation of one normal cubic centimeter of ether, in case it finds liquid molecules on both sides. The heat which is liberated in that case is about 0.07 calorie per normal cubic centimeter, which therefore is the largest amount which the surface energy can attribute to $\frac{dQ}{dA}$ for ether at 10°C.

If we now look at the curves calculated for *n*-pentane from Goldmann and Polanyi's isotherms, we see here exactly the same thing as with ether. At 10°C. the filling of the second layer begins at a smaller value of A than at –7°C.; therefore at the lower temperature the real heat of adsorption had fallen more, before the rise of $\frac{dU}{dA}$ set in. The filling of the capillaries makes itself obvious here by the steep rise of $\frac{dQ}{dA}$. The curves are however not known up to saturation; neither do we know the surface tension of *n*-pentane. Consequently the liquid surface cannot be calculated here.

We now can draw for both temperatures the "real heat of adsorption" (see figure 14). These are smooth curves, which in the beginning fall very steeply, later on more slowly; they do not coincide for two temperatures, although the difference is not great.

In the systems dealt with heretofore, the kink in the $\frac{dU}{dA}$ curve, where this curve rises from RT to the heat of condensation, lies at a concentration too small to be noticed. However it appears again in the SO_2 line from Polanyi and Welke (figure 10) where the rise after $A = 0.33$ cc. shows the condensation into liquid.

The NH_3 line determined by Titoff at 0°C. (figure 2) begins to rise at $A = \pm 90$ normal cubic centimeters, which indicates that the second layer is built up there. (If it meant that the capillaries were filled, the rise would be steeper and much nearer to saturation.) The surface, which is covered by 90 normal cubic centimeters of NH_3 in a monomolecular layer, is 306 square meters. The charcoal of Titoff therefore has a greater specific surface than that of Lamb and Coolidge.

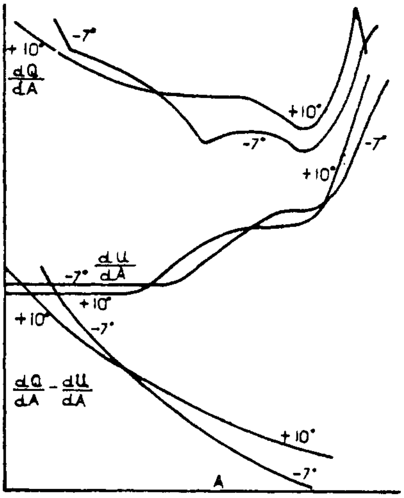


FIG. 14. n-PENTANE ON CHARCOAL AT 10°C. AND −7°C.
Heat of adsorption, heat of compression and real heat of adsorption.
The value of $\frac{dQ}{dA}$ of the abscissa is 0.07 calorie.

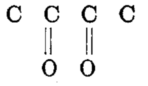
Titoff is of the opinion that the rise of $\frac{dQ}{dA}$ is due to the formation of liquid, and concludes from the difference between the value of the minimum and the higher values at subsequent volumes, what part of the adsorbed quantity condenses. This cannot be correct, for should 90 normal cubic centimeters be present on the charcoal in non-fluid condition, they would take up a volume of at least 21 cc. per gram of charcoal (the saturated vapor-pressure of NH_3 at 0°C. is 4.3 atmospheres). This is impossible, certainly for the compact cocoanut charcoal used by Titoff.

The argument of Tryhorn and Wyatt, who measured the rate of adsorption of saturated vapors on cocoanut charcoal, is erroneous for the same reason. They hung one gram of charcoal above the surface of a pure liquid at 20°C., and determined the increase in the weight of the charcoal with time. They found that $\frac{dA}{dt}$ (t = time) against t always gave a curve with a kink, and ascribed this kink to the sudden formation of a liquid layer on the charcoal. The difference in concentration between the surface of the pure liquid and that of the charcoal covered with a small layer of liquid would then be so small, that the rate of adsorption would also be very small. In most curves the kink is situated in the neighborhood of 2/3 to 5/6 of the saturation-quantity, for instance for ethyl alcohol at 53.6 normal cubic centimeters adsorbed. The assumption that a liquid layer is formed suddenly when this large amount has been adsorbed, is evidently absurd. The cause of the apparent discontinuity of the $\frac{dA}{dt}$ against t curve may probably be found in the form of the isotherm, for the rate of adsorption is proportional to the difference in pressure above the pure liquid and above the charcoal. At smaller values of A, p is so small that, compared with the saturated pressure, it may be neglected, but at $A = \pm 2/3$ of the saturation-quantity, p is increasing strongly. There is apparently a sudden change in the pressure, but a liquid layer had previously been formed on the charcoal.

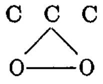
It is true that above the critical temperature of the adsorbed substance the heat of condensation disappears, but not the heat of compression, which remains equal to RT, except for the deviations from the laws for ideal gases. Whether more layers will form on the charcoal cannot be said with certainty; probably this will be the case at a lower temperature.

Of course it is not correct to ascribe each rise in a $\frac{dQ}{dA}$ curve to a heat of compression. When we recall the curves which have been found for O_2 on charcoal and for H_2 on nickel and on copper catalysts (figure 6), we understand that the cause of the rise can be quite different. The curve for O_2 rises from $A = 0$ to a value eleven times larger than its initial value. However, there is here no longer any question of real adsorption, but chemical interaction with the charcoal takes place. This is evident from the fact that in case of desorption only part of the oxygen can be recovered, and that when evacuating at a higher temperature, CO and CO_2 are set free (McLean). The quantities which are first adsorbed occupy the most active places of the surface and should therefore give the greatest heat effect, provided that no heat had been used to dissociate the O_2 molecule.

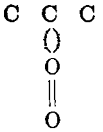
Each oxygen atom then combines with the charcoal to form one or more complexes, Garner and McKie distinguish three complexes which are possible, *viz.*:



(I)



(II)



(III)

(I) gives CO with desorption, (II) gives CO_2 and (III) gives unchanged O_2.

When evacuating at a higher temperature charcoal which had previously adsorbed O_2, it appears that the maximum evolution of CO_2 lies between 300°C. and 400°C., that of CO between 600°C. and 700°C. (Rhead and Wheeler). Over a large range of temperatures CO and CO_2 both appear; the surface of the charcoal will therefore always be dissimilar. The supposition is that at very small concentrations complex (I) is formed. This implies a complete dissociation of the O_2 molecule. Only the most active spots of the charcoal are able to cause such a dissociation; the liberated heat is therefore small. At larger values of A, complex (II) is formed; here the connection between the oxygen atoms is loosened but not broken; the liberated heat is great. If A becomes still larger we get complex (III), real adsorption, whereby the O_2 molecule remains intact; the liberated heat is here of the same order as the heat of adsorption of other gases.[4] For H_2 on catalysts the situation is essentially the same. We have no real adsorption here either, but chemical action interferes. At the most active points on the surface the hydrogen will be bound atomically, and heat is used for the dissociation of the H_2 molecule.

The third case of a rising $\frac{dQ}{dA}$ curve was that of H_2O on charcoal. Here the heat of adsorption has a smaller value than the heat of condensation. This might be due to the fact that the heat of compression for H_2O at 0°C. is negative, at least for the first 200 atmospheres. The condensation of water vapor into a compressed liquid therefore gives a smaller heat than the normal heat of condensation; at higher pressures the difference becomes smaller.

However, the behavior of H_2O with regard to charcoal, which in many respects is different from that of the organic liquids, may also be considered from another standpoint, which at the same time shows us a quite different side of the problem of adsorption.

In case the heat of adsorption of a substance is smaller than its heat of condensation, the substance is adsorbed more at a higher temperature and at the same relative pressure. (By relative pressure we mean the pressure p, divided by the saturated vapor-pressure p_s). For,

$$\frac{dQ}{dA} = RT^2 \frac{d \ln p}{dT} = RT^2 \frac{d \ln \frac{p}{p_s}}{dT} + RT^2 \frac{d \ln p_s}{dT}.$$

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[4] In a recent paper Marshall and Bramston Cook publish heats of adsorption for O_2 on charcoal at 0°C; here the initial values are very high. The course of the curve they find is quite different from that of Garner and McKie, although at greater pressures the values coincide. Especially at very small concentrations do different kinds of charcoal behave quite differently.

The last term is the heat of evaporation. When this is greater than $\frac{dQ}{dA}$, then $\frac{d\ln\frac{p}{p_s}}{dT}$ must be negative. At a higher T, $\frac{p}{p_s}$ is smaller at the same A; and at the same $\frac{p}{p_s}$, A is consequently greater. The shape of the isotherms is different here from those in the case of the organic liquids.

Coolidge (14) has determined isotherms of water on charcoals with different ash contents and has found that the influence of the ash content was great, especially at small concentrations.

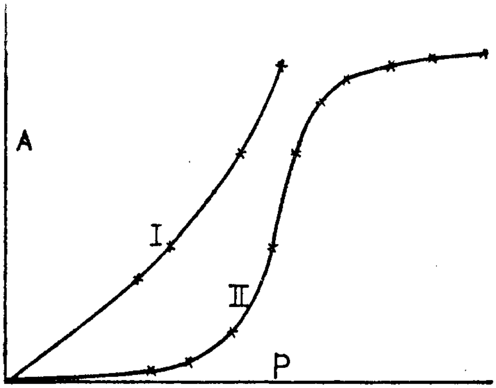

FIG. 15. ISOTHERMS OF H_2O ON CHARCOAL AT 0°C.
I—cocoanut charcoal; II—sugar charcoal

The isotherms at 0°C. on cocoanut charcoal, which contains rather many inorganic impurities, and on sugar charcoal, which does not contain them, are shown in figure 15. At small values of p, the course of the curves is quite different. (An analogous diagram has been found by Trouton and Miss Poole for the isotherms of water on glass wool, which has been dried in various ways.) With pure sugar charcoal hardly anything is adsorbed between $p = 0$ and $p = 1.5$ mm. Hg; at higher pressures, A at once increases steeply. The equilibria were all reversible; the same p was found whether working at decreasing or at increasing pressure (with cocoanut charcoal such was not the case). The shape of the isotherm of H_2O on sugar charcoal is indeed quite different from that of an organic liquid, where in the stretch of pressures $p = 0$ up to $p = 1.5$ mm. Hg, more than half of the quantity necessary for saturation is adsorbed.

This difference is explicable, because the adhesion between charcoal and an organic non-polar liquid is so much greater than that between charcoal and water. Charcoal is wetted spontaneously and completely by an organic liquid, and the angle of contact is 0°; with water the wetting is not complete, and the contact angle is between 0° and 180°. Bartell and Osterhof have worked out a very ingenious method to determine quantitatively the adhesion tension even when the contact angle is 0°. They found that the work of cohesion of benzene is much smaller than the work of adhesion with charcoal; for water it is just the opposite.

Therefore work is required to replace a water-water interface by a charcoal-water interface, and consequently the heat of condensation of water on a surface of charcoal must be smaller than that on a water surface. If the surface of the charcoal is covered, we once more get the normal heat of condensation.

This consideration enables us to calculate the specific surface of the charcoal, for instance in the system H_2O on charcoal, according to Keyes. Considering the point where the normal heat of condensation is reached as the beginning of a second layer, we calculate for the surface of the charcoal 60 square meters per gram, i.e. a somewhat smaller value than that derived from Keyes' diagrams for ether on charcoal.

The course of the isotherms on various kinds of charcoal can now be explained too. Large ash contents of the charcoal, i.e. many inorganic impurities, make the work of adhesion for water greater, and therefore the adsorption at small pressures will also be greater. With increasing temperature, the cohesion decreases more than the adhesion. (At the critical point there is no longer any surface tension, but there is still adsorption.) Consequently at small pressures the isotherm for higher temperature is situated above that for lower temperature, and at the same relative pressure A increases with increase in T.

Bartell and Osterhof assume that the inner pressure of a liquid is a function of the surface tension, and that the relation between the pressure in the adsorption layer and the inner pressure of the liquid is the same as that between the work of adhesion and that of cohesion. Therefore the pressure of adsorbed H_2O will be smaller than the normal inner pressure, while the opposite is true with organic liquids.

Coolidge (14) found the same behavior as that of H_2O for the adsorption of Hg vapor on charcoal. With nitrogen on charcoal at 15°C. and at very small pressures, Rowe found an analogous behavior; but the curvature of the isotherms was smaller in this case; at -183°C., however, the curve ran normally. As we are here above the critical point, the comparison with the heat of condensation is impossible and the terms "work of adhesion" and "cohesion" have lost their usual meaning. The fact, however, that $\left(\frac{dA}{dp}\right)_T$ increases when the charcoal has already condensed some nitrogen on its surface, proves that the attraction of the charcoal for a nitrogen molecule is smaller than the mutual attraction between two nitrogen molecules (at the same distance). Figure 9 for the calculated heat of adsorption of nitrogen shows that at different temperatures the curves first rise and then run nearly horizontally; near 0°C., however, the heat of adsorption has the usual course, as appears from isotherms of Titoff and Miss Homfray. Evidently these relations are very dependent on the temperature.

The behavior of H_2O, of Hg vapor and of N_2 with charcoal emphasizes the chemical forces between adsorbent and adsorptive, just as well as does the adsorption of O_2 on charcoal and of H_2 on metals. In the latter cases the chemical forces are dominating; in the first cases they are failing.

These results contradict the idea that the adsorption is not specific; in the case of O_2 we can still say that we have nothing to do any more with real adsorption, but with H_2O and N_2 this is surely the case. The part played by the chemical forces at adsorption would be much clearer, if most investigators had not experimented exclusively with charcoal, and especially with a kind having a high ash content.

For the adsorption of H_2O the influence of such inorganic impurities has already appeared clearly; for SO_2 and NH_3 it will also make a difference what kind of charcoal is used. As for the adsorption of organic liquids on charcoal, the first layer will probably be orientated in such a way that in the first instance we shall have always to do with the forces between the charcoal and the carbon atoms of the liquid layer. Great divergencies may consequently not be expected there, and the conclusion as to whether adsorption is specific or not may not be drawn from the results.

V. CONCLUSIONS FROM THE HEAT OF ADSORPTION AS TO SOME THEORIES ABOUT GAS ADSORPTION

The heat of adsorption is often used to calculate other quantities, chiefly the specific volume of a gas in the adsorbed condition.

In accordance with the principle of Maxwell-Boltzmann, the entropy of a state is proportional to the logarithm of its probability. For the difference of entropy between free and adsorbed gas the heat of adsorption q (per gram-mol) is taken. The probabilities of the two states are assumed to be proportional to the molecular volumes V_V (in free) and V_A (in adsorbed condition)

$$\frac{V_V}{V_A} = e^{\frac{q}{RT}}$$

From this we shall try to calculate V_A in some cases:

Case I. For CO_2 at 0°C., Titoff finds, at $p = 2.4$ mm. Hg, the value of q to be $\frac{dQ}{dA} \times 22{,}400 = 7773$ calories. $V_V = \frac{760}{7.4} \times$ 22400 cc. Then V_V becomes = 4.39 cc. The molecular liquid-volume at 0°C. for CO_2 is ± 48.9 cc.

Case II. For NH_3 at 0°C. Titoff finds, at $p = 2.6$ mm. Hg, the value of q to be $0.501 \times 22{,}400$ calories. V_A then becomes 0.0067 cc. The molecular liquid-volume at 0°C. for NH_3 is ± 27 cc.

Case III. For benzene at 0°C., Lamb and Coolidge find at $p = 2$ mm. Hg, the value of q to be $0.75 \times 22{,}400$ calories. V_A then becomes 0.00004 cc. The molecular liquid-volume of benzene at 0°C. is ± 88.5 cc.

From these examples it appears that no real meaning may be attributed to the volumes found, which are so much smaller than the liquid-volumes. The compressibility of liquids is small; therefore the specific volume even at high pressures cannot differ much from that at one atmosphere.

Polanyi and Welke, who have determined the adsorption of SO_2 on charcoal at very small concentrations, calculated the density in the adsorption layer according to Maxwell-Boltzmann, and also found impossible values. They therefore introduced the term "apparent density," and determined the change of this quantity with increasing concentration. If they applied the formula to a vapor-liquid equilibrium, when q is the heat of evaporation and V_V the specific volume of the saturated vapor, it appeared that the apparent density of a pure liquid was ±3 × the real density.

Jacquet and Hückel write the formula of Maxwell-Boltzmann:

$$\frac{AV_V}{V} = e^{\frac{q}{RT}},$$

in which V is the adsorption volume of one gram of charcoal. The density of the gas is $n = \frac{1}{V_V}$, and consequently

$$\frac{A}{n} = V\, e^{\frac{q}{RT}}.$$

If $\ln \frac{A}{n}$ (at constant n) is drawn against $\frac{1}{T}$, a straight line must be found, from which $\frac{q}{R}$ and $\ln V$ can easily be found graphically.

For SO_2 and NH_3 the curves appeared not to be straight, and therefore the results are inaccurate; but for various gases Hückel obtains in this manner values for V and q. These q values are smaller than those determined directly. Hückel finds for N_2 3200 calories (±4500 calories is determined); for CO_2, 5560 calories (6750 calories is determined) etc. For the adsorption volume per gram of charcoal he finds ± 0.05 cc.

That the deviations between the values found and those calculated according to Maxwell-Boltzmann are not as great here as in the calculation of the specific volume of the liquid layer, is due to the form of the equation, but does not prove anything at all for its validity.

Iliin thinks it possible to determine the surface of an adsorbent by means of the *e*-formula. If r be the thickness of the adsorption layer and S the surface of one gram of adsorbent, then

$$\frac{A}{Sr} = \frac{1}{V_V} e^{\frac{q}{RT}}.$$

At the same pressure, temperature and heat of adsorption the quantity adsorbed per square centimeter of surface must always be equal (as Iliin takes account only of monomolecular layers, r is always the same for the same adsorptive). The conclusion is that adsorption is not specific at all! If we know q and A for one adsorptive at the same p and T on two adsorbents, of which one has a known surface, S can be calculated for the other adsorbent. This Iliin does for charcoal.

Without using an adsorbent with a known surface, Iliin's conclusions can easily be tested. If we have two adsorbents with specific surfaces S_1 and S_2, on which A_1 and A_2 have been adsorbed per gram at the same p and T, whereby the heats of adsorption are q_1 and q_2 then:

$$\frac{\frac{A_1}{S_1}}{\frac{A_2}{S_2}} = \frac{e^{\frac{q_1}{RT}}}{e^{\frac{q_2}{RT}}} \quad \text{or} \quad \frac{S_2}{S_1} = \frac{A_2}{A_1} e^{\frac{q_1 - q_2}{RT}}$$

Now $\frac{S_2}{S_1}$ must be independent of the adsorptive with which the relation is determined, as otherwise there would still be a question of a specific effect. However $\frac{S_2}{S_1}$ is not constant at all. In calculating from Chappuis' measurements the relation between the specific surface of the charcoal and that of the meerschaum used, with SO_2 as adsorptive, we find, if S_2 is the charcoal surface, that

$\frac{S_2}{S_1} = 3.08$ (calculated at 0°C. and 30 mm. Hg). With NH_3 as adsorptive at the same T and p, $\frac{S_2}{S_1}$ becomes 169. In other cases the agreement is just as bad.

It is generally known that the principle of Maxwell-Boltzmann does not exactly represent the facts in many cases, especially when we have to do with weak bonds between atoms or molecules, as, for instance, with the specific heat of polyatomic gases. In adsorption we often have to do with weak bonds and chemical forces between the molecules of the adsorbent and the adsorptive; the more these specific influences prevail, the greater the error made when using the *e*-formula. With the systems studied by Kälberer and Mark (for instance, argon on silicic acid), the formula gives useful results, but there the requirement that the number of degrees of freedom of the molecule in free and adsorbed condition must be equal, is fulfilled (Sementschenko). If this is not the case, the known smooth curve of Maxwell for the distribution of energy can not be applied, but must be replaced by the stepped figure, as calculated by means of the quantum theory.

A somewhat exaggerated metaphor enables us to explain why we always find too small a value, when calculating the specific volume in adsorbed condition by the *e*-formula. The force exerted by the charcoal diminishes very markedly with increase in the distance from the surface. If we suppose that the adsorbed molecules are situated on the charcoal as are pins on a pin-cushion, the field at the point of the pin determines the adsorption and the heat of adsorption. This value of q is used in the formula, and therefore we calculate in reality the volume of the pin-point. About the volume of the pins themselves, however, we cannot conclude anything; a conception such as Polanyi's "apparent density" is therefore of no value.

The potential theory also tries to explain the adsorption from a purely physical standpoint. According to this theory, developed for gases below the critical temperature by Polanyi (later on also by Berenyi, Lowry and Olmstead and others), the potential ϵ of a point is determined only by the distance from the adsorbing surface, and is independent of whether the interjacent space is filled or not. This distance being determined by the quantity already adsorbed, ϵ depends exclusively on A; this relation is called the characteristic function. Polanyi, assuming that the equation of state is applicable, finds

$$\epsilon = RT \ln \frac{p_s}{p_A},$$

in which p_s is the saturated vapor-pressure. For the heat of adsorption

$$\epsilon = q + T \frac{d\epsilon}{dT}$$

holds, but according to Polanyi $\frac{d\epsilon}{dT} = 0$ over a large range of temperatures above 0°K, therefore $\epsilon = q$, and the net heat of adsorption, drawn against A, gives the characteristic function. Polanyi and his collaborators do not calculate the latter from calorimetric data, but from isotherms, and they then find curves, which indeed fall in the beginning but afterwards run rather flat.

Hückel has calculated that this cannot be correct, since a potential which depends only on the distance from the surface must fall abruptly to 0. The curves which we found for the heat of adsorption show clearly that this opinion of Polanyi cannot be correct, for then the potential would increase again with an increase of the distance from the surface.

If $\frac{d\epsilon}{dT} = 0$, then $\frac{dQ}{dT}$ must be 0. This is not correct either, although $\frac{dQ}{dT}$ is sometimes small. The potential and the heat of adsorption cannot be identified therefore, and the mutual action of the molecules of the adsorptive contributes considerably to the heat of adsorption.

Goldmann and Polanyi have tried to improve the theory without throwing overboard the good results obtained in many cases. They assume that the adsorption layer is monomolecular at small concentrations, and that the difference of the potential arises from the roughness of the charcoal surface. Around the most active spots isles of liquid are first formed, and the potential depends exclusively on the adsorbed volume. Goldmann transforms the isotherms to affinity curves, i.e. he draws the affinity F against A

$$F = RT \ln \frac{p_s}{p_A}$$

The different curves do not coincide, but run very close to each other. Although the potential is independent of T, according to Goldmann and Polanyi, the affinity indeed changes with T at constant A, owing to the dilatation of the adsorptive. In general the following holds:

$$F = q + T \frac{dF_A}{dT} = q - T \left(\frac{dF_A}{dA}\right)_T \left(\frac{dA}{dT}\right)_F.$$

The heat of compression of a liquid is proportional to the pressure and to the dilatation of the liquid. Now $-\left(\frac{dF_A}{dA}\right)_T$ represents the gradient of the potential at right angles on the equipotential surface F_A, and is therefore a measure of the force with which the liquid is compressed, and $\left(\frac{dA}{dT}\right)_F$ is proportional to the dilatation of the liquid. The second term to the right in the equation above represents the heat of compression of the adsorbed liquid owing to the quantity just admitted, and the affinity is the difference between the heat of adsorption and the heat of compression. The curves which we have drawn in figures 13 and 14 for the "real" heat of adsorption, therefore represent the same as Goldmann's affinity. This "real" heat of adsorption however arises not only from the direct influence of the adsorbing surface, but also from the attractive power exercised by the first layer on newly admitted molecules. We may not say therefore that the affinity on a certain point is independent of the fact whether the space between the adsorbent and that point is filled or not. Moreover, it is not correct that the potential is independent of the temperature and that the reason why the affinity curves for different values of T do not coincide must be sought only in the dilatation of the liquid. Goldmann himself finds that this dilatation is different, when calculated from affinity curves, or when determined experimentally. The difference is considerable especially at small concentrations. If Goldmann had also determined isotherms of water on pure charcoal, he would have found, for instance between 10°C. and 20°C. a shrinking of the liquid at increasing temperature instead of a dilatation. For with water, A increases with T at constant $\frac{p_s}{p_A}$; consequently at the same A, F is greater at higher T.

This shows clearly the one-sidedness of the potential theory. Its hypotheses are approximations, which however in many cases can represent the facts with sufficient accuracy, at least beneath the critical temperature and at higher concentrations, where chemical forces are of less influence.

According to Patrick and his collaborators Greider, McGavack, Davidheiser and Long, adsorption is based upon condensation of liquid in the pores of the adsorbent. Indeed, the vapor-pressure over a highly curved surface is smaller than above a plane one. The relation between the radius of curvature of the surface and the vapor-pressure above it is expressed in Lord Kelvin's equation.

If vapor is admitted to an adsorbent, for which Patrick usually takes silica gel, at small values of p the narrowest pores will be the first to be filled with liquid and then gradually wider ones will fill. For the same gel, the relative vapor-pressure $\frac{p}{p_s}$, according to Patrick, depends only on the volume already filled. (Just as in the case of Polanyi's work, the molecular liquid-volume is of great importance here.) From the knowledge of one isotherm and the change of density of the liquid with the temperature, it is possible to calculate the other isotherms.

However, the adsorbed liquid-volume at constant relative pressure appeared to be smaller at higher temperature, except for $\frac{p}{p_s} = 1$; there the liquid-volume is about constant. According to Patrick the liquid is submitted to a negative pressure, in that the surface tension will try to make the interface liquid-vapor as small as possible by filling the capillaries as far as possible. The density is smaller than the normal value and approaches the latter as $\frac{p}{p_s}$ approaches 1.

Lord Kelvin's equation not being applicable to radii of curvature of molecular dimensions, Patrick used an empirical formula

$$V = K\left(\frac{p\sigma}{p_s}\right)^{\frac{1}{n}}.$$

in which V represents the liquid-volume, σ the surface tension and K and $\frac{1}{n}$ are constants. The formula corresponds to the facts fairly well except at small relative vapor-pressures and near the critical temperature. The formula does not show, however, that the influence of σ on V must be different at different relative vapor-pressures and that at $\frac{p}{p_s} = 1$, V is constant. Since V becomes smaller with increasing T at the same $\frac{p}{p_s}$, multiplication by a quantity, which decreases at higher temperature, will improve the agreement. Gregg (32) therefore tried $\frac{1}{T}$ instead of the surface tension, used by Patrick, and found that, in general, this was more satisfactory.

Patrick explains the decrease in V at constant $\frac{p}{p_s}$ with higher T from the abnormal density of the liquid. However, this argument is completely refuted by Coolidge (13). He pointed out that V must change with T, as V depends on σ and on the density of the liquid and the dependencies of those quantities on T do not neutralize each other.

It is not logical to try to attribute adsorption at small concentrations to capillary condensation. This appears only when the surface is completely wetted by the liquid, i.e. when the cohesion is much smaller than the adhesion. If the cohesion is greater, the meniscus is lower in a capillary than in a wide tube (Hg in glass) and the vapor-pressure over the curved surface is greater than the normal one. When the adhesion is greater, Patrick explains everything by means of cohesion, or what comes to the same thing, by means of surface tension.

As long as the influence of the surface is mainly a direct one, we have to do with adsorption. We speak of capillary condensation only when, owing to the form of the surface, an arriving molecule comes into the field of force of more adsorbed molecules than it would in the case of a plane surface, and is then held by them. The influence of the surface is then entirely indirect.

This is also the case, when the electric conditions of the surface cause an induced cohesion. De Boer has given a beautiful example of this kind. He determined the quantity of iodine adsorbed at different pressures by a small layer of calcium fluoride on a glass surface. The surface of the CaF_2 layer being larger than that of the glass covered by it, the thickness of the adsorption layer cannot be calculated with absolute accuracy from the quantity adsorbed; probably it has the thickness of many molecules. When the iodine vapor was saturated, a layer of iodine could be perceived on the uncovered glass.

The explanation for the thickness of the layer is that the first layer of iodine is bound by the field of force of the calcium and fluoride ions; consequently the atoms of iodine become dipoles, which in their turn can adsorb a next layer. As a matter of fact the polarizing effect becomes weaker in following layers. This induced cohesion, which is important in many cases, cannot be separated from pure adsorption.

Moreover, the limit between capillary condensation and adsorption is also very difficult, if not impossible, to stipulate. In fact, we ought to unroll the curved surface and see whether the same quantity remained on it; if so, we have to do with adsorption.

In section IV we have seen that sometimes one can conclude from the curves for the heat of adsorption, where the capillaries are filled. In the cases discussed above (ether and pentane on charcoal), the adhesion was great with regard to the cohesion, so that each molecule was drawn as near as possible to the surface of the charcoal. With the cocoanut charcoal of Lamb and Coolidge it appeared that at about $A = 23$ ncc. the second layer began; at saturation, about 100 normal cubic centimeters were adsorbed; the thickness of the layer will therefore be four to five molecules, i.e. the average diameter of a capillary is that of nine ether molecules. It is now evident from the curve for the heat of adsorption, that the charcoal surface is covered almost entirely and regularly on all sides with a layer which has the thickness of four molecules, and only when the pressure is almost equal to that of the saturated vapor does the last layer come into the capillary. In such cases one is not justified in making a distinction between capillary condensation and adsorption.

However, this may be important when the pores of the adsorbent differ very much in width, or when the adhesion is not as great in proportion to the cohesion as in the cases above. Then at increasing concentration pores will be filled gradually and the surface energy will be gradually liberated as heat, i.e. the heat of adsorption will not show a steep rise near saturation and will possibly not rise at all (compare for instance the curve for SO_2 on blood charcoal, figure 5). Therefore the influence not only of the inner volume, but of the whole structure of the adsorbent appears to be great.

Langmuir alone calls adsorption a chemical phenomenon; crystallization and evaporation also belong, according to his opinion, to this category. Langmuir holds the unsaturated valences of the surface atoms responsible for the adsorption. On the surface a number of equivalent spaces, "elementary spaces" are available, which, in the most simple case, can contain one molecule of the adsorptive each. Langmuir works with adsorbents of known surface and considers the equilibrium from the standpoint of the kinetic gas theory: the number of molecules leaving the surface per unit of time is equal to the number clinging upon it. The number of molecules which collide depends on the pressure, the temperature and the molecular weight of the substance; the number which cling depends on the probability of adhesion and on the occupation of the surface; the number which evaporate also depends on the occupation and on the rate of evaporation. From this Langmuir comes to the formula for the isotherm $A = \frac{abp}{1 + bp}$, in which a is a constant, depending on the number of elementary spaces per unit area, and b a constant, depending on the probability of adhesion and the rate of evaporation from a fully occupied surface. Then

$$\frac{p}{A} = \frac{p}{a} + \frac{1}{ab}.$$

$\frac{p}{A}$ drawn against p must give a straight line, from which a and b can be found graphically. If Langmuir draws his determinations (at 90°K and 155°K) in this way, the curve is indeed straight, if the pressures are not situated far from each other (the greatest pressure applied by him is 172 bar = 0.13 mm. Hg). Moreover, Langmuir finds, in two or three control series, other constants in his formula, so that, when calculating A at determined p, using the various constants, we find values which differ by 30 per cent. If Langmuir calculates from the constants found the number of elementary spaces per unit area, he finds at 90°K for mica sometimes 9×10^{13}, sometimes six times as much. For glass the differences are still greater.

Langmuir himself disregards the quantity adsorbed in a blank experiment (possibly on the wall of the apparatus), which amounts to 10 to 30 per cent of the quantity found in the real experiment, since this amount does not surpass the experimental error. The cause of these large experimental errors and the poor agreement between control determinations is in the first place due to fluctuations in the temperature (against which no precautions were taken), and further to the inaccuracy of A, which was calculated from a small difference of pressure in a large volume.

The accuracy of Langmuir's experiments is not greater than up to 30 per cent; probably it is hardly possible to obtain a greater accuracy at these very small pressures, but the question arises as to whether such determinations are adequate to prove a theory.

The cases where the curve of $\frac{p}{A}$ against p is not at all straight, Langmuir ascribes to the existence of various kinds of places on the surface. For this case he derives a complicated formula, which contains two constants for each kind of place. Also the possibility that an elementary space can contain more than one molecule, is considered; this also leads to a formula with many constants. In this manner indeed values calculated and found can be brought to agreement, but the practical usefulness of such a formula is then strongly reduced.

Zeise finds that for his determinations on glass the formula must be $A = \sqrt{\frac{abp}{1 + bp}}$, which means that two spots of adsorption hold one gas molecule. However, he also uses in control determinations other constants, which differ much. Zeise (as well as Langmuir) thinks the theory also applicable on charcoal as an adsorbent and he calculates data of Miss Homfray, Titoff and Richardson with Langmuir's formula, and finds the agreement very satisfactory.

Polanyi (71) observes that the way in which the constants depend on the temperature should be quite different from what it really is, if the constants had the meaning ascribed to them by Langmuir. He is of the opinion that the assumption that the number of elementary spaces per square centimeter of surface varies strongly with the temperature, is unjustified.

Probably from the agreement with the facts, resulting from Langmuir's formula of adsorption on charcoal and at higher pressures, we may conclude that the formula has a great flexibility and therefore is able to represent the facts fairly well, even in the cases where the hypotheses of Langmuir seem to be not quite correct.

Originally Langmuir assumed that the adsorbed molecules had no influence on each other. Later on (51) he reversed his opinion on this, and he agrees with Clausing when the latter states "that there is more work required to have a molecule (of a metal vapor) evaporated, when it is situated quite close to another one on the glass wall, than if it is present there individually. The rate of evaporation is greatest for isolated molecules." The difference will be greater in proportion as the cohesion is greater and the adhesion smaller. Only when the adhesion is greatest, may one neglect the influence of the adsorbed molecules on each other at small pressures.

The fact that the thickness of the layer is no more than that of one molecule at the small pressure at which Langmuir worked, does not mean anything as to the condition at greater pressures. The quantities of gas obtained by Langmuir when evacuating his adsorbents, are often much too large for a monomolecular liquid layer on the known surface. Here we must draw attention to the fact that according to experiments made by Frazer, Patrick and Smith the surface of glass is usually not smooth. Glass which has been in contact with a trace of water is covered with a layer of silica gel, which has a large inner surface so that the active surface of glass is unknown in most cases.

Langmuir does not prove that the adsorption layer is monomolecular, but he assumes that only the quantity present in the first layer is bound by adsorption. Against this hypothesis many objections can be raised.

Reichenstein (74) has come to the same form for the isotherm as found by Langmuir, but in a quite different way. He considers the adsorption volume as if it were a solvent between two other solvents (solid and gas). The relation between the concentrations depends on Henry's law and on the distribution coefficients. According to Reichenstein's "displacement principle," the sum of the concentrations of all substances in the adsorption layer is constant. In this the concentration of the adsorbent is also included, i.e. a certain number of molecules of the solid which cause adsorption.

If the concentration of one gas in the adsorption space is expressed in terms of the other concentrations with the aid of the distribution coefficients and the constant sum in question, the formula obtained in the case of one adsorptive has the same form as Langmuir's isotherm. The theory cannot be right however, as it has appeared from various experiments that at adsorption of a mixture of two gases, the sum of the quantities adsorbed is greater than the quantity of one of the two gases, which would be adsorbed if it were present separately with the same pressure (Bergter and others). Therefore the concentration of the solid in the adsorption volume must be smaller than in the case of only one gas being present, i.e. fewer molecules of the adsorbent participate in the adsorption. We meet with a similar case when only one gas is adsorbed at increasing concentrations; the more there is being adsorbed, the less adsorbent should participate. This is inconceivable. In fact, Henry's law is applicable only at temperatures far above the critical one, and at not too great pressures. In such cases all relations are much simpler; here it is possible (Lorenz and Landé) to apply the law of the corresponding states to the adsorption, and to express the adsorption of various gases on the same adsorbent in one diagram, reduced to critical quantities.

What we have said above leads to this unsatisfactory conclusion; that there is neither an empirical equation nor a theoretical one which can account for all the data which experiments have given us. Everyone will be inclined to put this question: What is, in your opinion, the right equation for the adsorption isotherm —the empirical equation of Freundlich, or the theoretical one of Langmuir, or another one? We are obliged to reply that we cannot give a general answer to that question, since none of the experimental equations and none of the theoretical equations, given up to now, is correct.

The empirical equation of Freundlich $A = \alpha p_n^1$ cannot express saturation; moreover the initial slope is always infinite, which in reality is the case only at low temperatures and great adhesion.

According to Langmuir $\frac{p}{A}$ drawn against p must give a straight line, consequently $\frac{d\frac{p}{A}}{dp}$ must be constant. According to Freundlich this is the same as

$$\frac{1}{A} - \frac{p}{A^2}\left(\frac{1}{n}\,\alpha p^{\frac{1}{n}-1}\right) = \frac{1}{A}\left(1 - \frac{1}{n}\right).$$

This must be constant, therefore $1 - \frac{1}{n}$ must increase in proportion to the increase of A. Saturation can indeed be expressed by Langmuir's isotherm.

According as $\frac{1}{n} = \frac{d \ln A}{d \ln p}$ remains rather constant, or decreases at greater concentrations, either the formula of Freundlich or that of Langmuir is most fit for use. Titoff and many others always give the values for $\frac{1}{n}$, calculated from their figures. From this the insufficiency of both equations is evident at a glance. For N_2 at –79°C., $\frac{1}{n}$ falls from 0.74 to 0.40; on the contrary at +151.5°C., $\frac{1}{n}$ increases from 0.89 to 1.02. For NH_3 at 30°C., $\frac{1}{n}$ first increases with rising p from 0.42 to 0.79, and then falls again to 0.40.

Williams recommends as isotherm $\ln\frac{A}{p} = B_0 - B_1A$ (B_0 and B_1 are constants). The derivation is not at all convincing, but at small concentrations (up to ±30 per cent of the value of saturation) the formula represents the facts fairly well.

The formula of Arrhenius

$$K \frac{dA}{dp} = \frac{C - A}{A}$$

(K is a constant and C is the saturation-quantity) is useful, especially at great concentrations and near saturation. This equation is analogous to that used by Schmidt for adsorption from solutions.

All these formulas are equally adequate; each has a domain in which it is useful, but none of them is able to express a complete isotherm at lower temperatures.

This is not at all strange, because many different items are important for the various parts of the isotherm. The initial slope and the beginning of an isotherm are determined by:

1. The chemical forces between adsorbent and adsorptive,
2. The temperature and the duration of the activating and outgassing of the adsorbent,
3. The specific surface of the adsorbent,
4. The condensability of the adsorptive,
5. The electric qualities of the adsorptive (the di-electric constant, whether the adsorptive molecule is a dipole, etc.).

Moreover, at greater pressures, the following are important (besides what has been mentioned already under 3, 4 and 5):

6. The molecular volume of the adsorptive,
7. The inner volume of the adsorbent,
8. The compressibility of the adsorptive.

It is obvious that all these magnitudes cannot be expressed in one concise useful equation.

As is evident from this summary only in the very first part of the isotherm are the chemical forces very important.

The adsorption at greater concentrations may be expressed in a physical theory, such as that of Goldmann and Polanyi, but from this it may never be concluded that the adsorption is not specific and has nothing to do with chemical forces.

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