0.0005 referred to a hydrogen electrode in the same acid. In 4 N acid we find 1.221 ± 0.001.

In either acid $[Br_2][Cl_2] = 3.2 \times 10^{-4} [BrCl]^2$. In 6 N acid $[Br']^2$, $[Cl_2] = 3.0 \times 10^{-12} [Br_2][Cl']^2$, but in 4 N acid this constant is 5.6×10^{-12}. The ratios $K_{2,6N}/K_{2,4N}$ can be predicted from the activity coefficients of hydrobromic and hydrochloric acids as found by other investigators. The two equilibrium constants were calculated in each acid by successive approximations. Two other constants are derived from them.

If e.m.f. is plotted against the logarithm of bromine concentration, the slope becomes very small at the smallest bromine concentrations, and approaches 0.0297 at the largest.

Given molal bromine, 2.4% reacts in 6 N hydrochloric acid to give bromide ion and bromine monochloride. In 4 N acid the percentage is actually larger and is 2.8%. With 0.01 M bromine the percentages are 20 and 18.5, respectively. At minimal bromine concentrations the reaction apparently would become complete.

Further measurements over other concentration ranges are in progress.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 140]

THE HEATS OF ADSORPTION OF SEVERAL GASES AND VAPORS ON CHARCOAL

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Introduction

Extensive measurements of the heat evolved when gases or vapors are adsorbed on charcoal and other substances have already been made. As early as 1874 Favre,[1] for example, determined the heat evolved for a large number of gases adsorbed on charcoal prepared from a variety of woods. The heat evolved per gram of gas adsorbed was found to be independent of the kind of charcoal, although the total amount adsorbed or the capacity was variable. The results of Favre were confirmed and extended later by Chappuis,[2] Titoff,[3] and Homfray[4] and recently by Lamb and Coolidge.[5] Homfray, however, instead of using a direct method, made an exhaustive study of the pressure-temperature concentration relation for argon, nitrogen, carbon monoxide, methane, carbon dioxide

[1] Favre, *Ann. chim. phys.*, **5,** 1 (1874).

[2] Chappuis, *Wied. Ann.*, **19,** 21 (1883).

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

[4] Homfray, *ibid.*, **74,** 129 (1910).

[5] Lamb and Coolidge, THIS JOURNAL, **42,** 1146 (1920).

and ethylene. The Bertrand vapor-pressure formula ($p = G(T - a)^n/T$) was used to represent the constant-concentration relation between the pressure (p) and the temperature (T), G, a and n being constants in the equation. The heats of adsorption may, of course, be computed from the experimental data and constants given by Homfray. The values indicate that the heat of adsorption diminishes with increasing amounts of gas adsorbed.

The later careful experimental work of Lamb and Coolidge on the adsorption heats for organic vapors, wherein the charcoal was pumped out at 350° and to a pressure of 0.01 mm., showed that the adsorption heat was reproducible and decreased in a definite manner with the amount adsorbed. It was further clearly demonstrated that the heats of adsorption were practically independent of the capacity of the charcoal to adsorb large amounts of fluid. Interesting relationships were also pointed out connecting the heats of adsorption with the latent heats of vaporization, and the heat of compression under high pressure.

About the same time it was shown by Harned[6] that the presence of residual gases on the surface of the charcoal, even after prolonged heating in a good vacuum, influenced in a remarkable manner the *rate* at which gases or vapors were adsorbed. Thus chloropicrin adsorbed on charcoal (which had been heated to 900° and pumped for several hours) gave a rate of adsorption which was slow initially. It was only after repeated alternate heating and saturation of the charcoal with chloropicrin that the rate characteristics became reproducible. This fact indicates that the adsorptive process may be considerably interfered with by the presence of previously adsorbed material on the surface of the charcoal. It appears, therefore, that it might be preferable to "clean up" the charcoal with the particular gas before initiating observations in connection with the measurement of adsorption heats. It is quite likely, however, that this "residual-gas" effect demonstrated by Harned may affect the heat of adsorption only for the heats attending the first minute quantities adsorbed and is "swamped out" as soon as any considerable quantity is adsorbed. This in fact seems proved from the measurements of Lamb and Coolidge, since in their measurements the first heat of adsorption was measured for an amount equal to roughly 20% of the whole quantity of gas admitted to the charcoal. Thus in most cases the heat of adsorption for the smallest quantity whose heat of adsorption was measured, corresponded to a surface of charcoal covered by one or several layers of the adsorbing molecules. That there would be, in view of Harned's results, a measurable influence on the heat of adsorption until a *first layer* on the surface was completed, starting initially with a surface partially covered with foreign molecules, is at present neither definitely proved nor dis-

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[6] Harned, THIS JOURNAL, **42,** 372 (1920).

proved, and the presence or absence of such an effect may be important in connection with the relation between surface catalysis and adsorption effects.

In a recent theory of adsorption due to Langmuir,[7] use is made of the hypothesis that the adsorbed molecule is held by either the "primary valence forces" or the "residual valence forces" of the atoms composing the adsorbing surface. At the surface of a piece of charcoal, for example, one of the primary bonds of each carbon atom would be unsaturated or at any rate partially free to exert an influence and one adsorbable atom or molecule would be bound for each surface carbon atom. Adsorption, therefore, Langmuir suggests, involves one layer only. On the other hand there is indication that very many layers of molecules must be attached in certain instances where substances are taken up by solids. Langmuir assumes in the latter cases that the material is condensed in the capillary spaces and only those molecules constituting the first layer are to be referred to as adsorbed. This layer, moreover, is to be considered as chemically or quasi-chemically united to the surface atoms of the adsorbent.

It may be supposed, however, that if, for example, oxygen molecules (or atoms) are attached to the surface carbon atoms by virtue of even secondary valence forces, the molecules, as such, will be in a special state of "valence strain" such as to enable this first layer to constitute of itself an adsorbing surface for a second layer of molecules of the same or of a different species. The state of "valence strain" in the second layer might, of course, be less in degree than for the first layer, but still conceivably sufficient to adsorb a third layer and succeeding layers similarly, until finally a layer was held attached in which the state of the molecules differed but little from the free state.

Even if it is conceived that the magnitude of the adsorption forces is sufficiently great to disrupt the oxygen molecules and cause the atoms to be held by the surface carbon atoms, it still appears likely that the second layer adsorbed would adsorb as a modified molecule and succeeding layers attach in a state of "valence strain" of continuously lessened degree. The point of view here suggested amounts then to accepting the thought that possibly primary[8] valence forces or secondary valence forces are involved in the phenomenon of adsorption but that the first adsorbed layer constitutes in itself a layer of molecules or atoms in a very special

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[7] Langmuir, THIS JOURNAL, 40, 1361 (1918).

[8] A certain hesitation is felt in using the terms "primary valence," "secondary valence," and "residual valence forces," for it is evident that the terms refer to qualities of atoms and molecules which cannot at present be precisely described or measured. The terms are used in this paper in the sense only of referring to qualities, a knowledge of which would permit an understanding of the manner of action of atoms one with another and, moreover, by what means molecular structure is maintained.

state (due to immediate proximity of the adsorbent), upon which additional molecules may adsorb to form a second layer, this layer and succeeding layers similarly partaking of the "special state" in a continuously lessened degree.

It is clear in any event that adsorption phenomena may be due to tremendous forces at the adsorbent surface which involve what is known as primary valence, or more feeble "residual valence" which manifests itself in a manner scarcely to be distinguished in its action from a uniform and homogeneous attractive force. As examples of the former, reference is made to the striking experiments of Langmuir, wherein oxygen atoms are held at extremely low pressures on the surface of tungsten and carbon filaments at very high temperatures. The other extreme is exemplified in the adsorption of substances such as water vapor or argon on charcoal.

Allusion has already been made above to the case wherein for an adsorbed substance the primary valence of, for example, a surface carbon atom was wholly or partially engaged, and the state of the resultant surface such as to enable the single layer of adsorbed molecules to exert an attraction for other molecules either of the same or different kind. It may well be that the state of strain of the molecular structure of the molecules in the adsorbed state is related to the phenomenon of surface catalytic action, since conditions favoring chemical reaction are thereby induced as a consequence of disturbing the normal conditions of equilibrium of atomic forces involved in preserving the existence of the molecule in the unadsorbed state.

The supposition has also often been made that in the adsorbed condition the molecules are attached to the surface by the same kind of forces as are called cohesional in the equation of state. If this were the universal fact the energies of adsorption of different species of molecules on the same adsorbing material should be some regular function of the cohesive constants in the equation of state of the respective species. Sufficient data are now available to enable a comparison of the cohesive constants with the adsorptive energies of different molecular species. It does not appear, however, that the simple cohesive pressure explanation of adsorptive action can account generally for adsorptive behavior. The adsorption of oxygen, for example, presents peculiarities which find no counterpart in the known adsorptive behavior of argon or water vapor.

In the experimental work described in the present paper the attempt has been made to measure the heats of adsorption for a variety of gases on the same sample of charcoal. Particular attention was paid to the case of oxygen due to the high chemical activity which oxygen manifests in the presence of carbon. Chlorine is of special interest also in this connection since Lamb and Coolidge, in their heats of adsorption work, found that compounds containing chlorine produced a "poisoning" effect on the charcoal such as to yield lower heats of adsorption when other substances were adsorbed on the chlorine-treated charcoal. The energies of adsorption for small concentrations[9] are therefore of particular interest.

Experimental Method and Apparatus

The ice calorimeter was employed in all the measurements and the charcoal used was contained in a quartz tube which could be heated to 1000° and exhausted by means of a diffusion pump. Fig. 1 represents the disposition of apparatus used in the measurement of all substances except ether, chloropicrin and water, which were vaporized into the calorimeter from the liquid state. To measure the amounts the liquids were contained in calibrated capillary tubes.

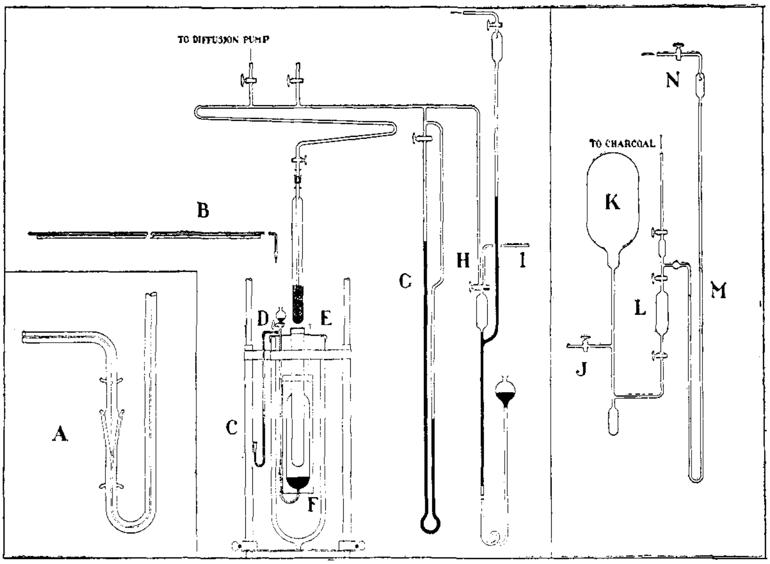

Fig. 1.

The first measurements were made by weighing the mercury displaced due to the melting ice within the calorimeter.[10] Later, a calibrated capillary tube B was employed which made connection with the calorimeter by means of a joint ground in such a manner as to cause practically no interruption of the capillary bore. The calorimeter was submerged in finely crushed ice, contained, in a 7.5-cm. Dewar tube set into a sliding

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[9] The term concentration will be used hereinafter to denote the number of moles of substance adsorbed per gram of adsorbent.

[10] The ice may be very conveniently deposited in a uniform layer by placing a tube containing liquid ammonia inside the calorimeter. The mercury rises to the height of the ice mantle desired and serves to distribute the flow of heat very evenly. A tight rubber stopper and connecting rubber tube must be employed to lead away escaping ammonia gas, otherwise it will dissolve in the ice water within the Dewar tube.

support which permitted the calorimeter to be raised to receive the quartz tube containing the charcoal. To secure good heat conductivity between the charcoal and the calorimeter tube, mercury was placed in the ice-mantle tube sufficient to fill the space between the calorimeter tube and the former to a height above the level of the charcoal. The technique of using the ice calorimeter has been so fully developed and described elsewhere that further details will be omitted.

In the cases of chloropicrin, water and ether, the liquids were freed from permanent dissolved gases by repeated distillation and the amounts adsorbed determined by noting the volume of liquid which disappeared from the capillary tube containing the liquid, immersed in a constant-temperature bath.

The method of measuring and introducing the gases varied somewhat with the conditions encountered. The ammonia and carbon dioxide were measured by means of an ordinary water-jacketed gas buret sealed *in situ*. The constant volume gas pipet H served for the oxygen, and the manometer G was used to measure the residual gas pressures over the charcoal. For chlorine, contained in K, sulfuric acid manometers had to be employed. The purified chlorine was frozen with liquid air and Bulb K pumped. The freezing and pumping process was repeated several times to insure the separation of dissolved air.

The charcoal used was a sample of that employed by the French government for gas masks during the war. It was graded to pass a screen having meshes 0.162 cm. and retained on a screen of mesh 0.132 cm. To remove the ash as completely as possible the charcoal was extracted in a Soxhlet extractor with hydrochloric acid for 24 hours and then with water for 48 hours. The charcoal was then warmed with hydrofluoric acid on a steam-bath and, after drying at 100°, extracted with water for 400 hours, during which time the water was changed every seven hours. The charcoal was finally dried at 150°. The reduction in ash content was as follows: ash content, original charcoal, 6.9%; after treatment with hydrochloric acid, 0.62%; after treatment with hydrofluoric acid, 0.36%.

The charcoal, before being used for the measurements, was baked at about 900° in the quartz tube until the pressure fell to about 0.0004 mm. This required in general from 12 to 20 hours. During the course of measurements with a given gas or vapor the charcoal was never allowed to come in contact with the air or any gas other than that under measurement. The weight of charcoal used amounted to 2.365 g. in the chloropicrin-water-ether series and 2.248 g. was employed for the remaining gases.

The pure substances whose heats of adsorption were measured were as follows: oxygen, chlorine, carbon dioxide, ammonia, ether, chloropicrin and water. In each instance, a measured amount of substance was admitted to the fixed quantity of charcoal, and the amount of heat evolved computed from the displacement of the mercury corresponding to the volume displacement due to the melting of the ice mantle of the calorimeter.

After equilibrium had been obtained, a further quantity of vapor was admitted to the charcoal. A continuation of this portion-wise process of adding fluid was followed until the desired total quantity had been added. The amounts adsorbed will be given in moles per gram of charcoal. Moles will be in every case designated by c while the integral heat of adsorption per g. charcoal actually measured will be denoted by q. The variation of the heat of adsorption per mole of substance at any particular ratio of substance to charcoal will be denoted by $(\partial q)/(\partial c)$.

The quantity $(\partial q)/(\partial c)$ was obtained graphically from large-scale plots using q and c as coördinates.

The Experimental Results

Tables I–VII summarize the measurements carried out on the substances oxygen, chlorine, carbon dioxide, ammonia, ether, chloropicrin and water.

TABLE I

OXYGEN

Series 1		Series 2		Series 3		Series 4		Series 5	
$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	q
1.08	2.92	0.18	1.25	0.055	0.38	0.052	0.24	0.043	0.32
2.46	3.51	.36	2.12	.12	.84	.15	.80	.11	.77
4.53	4.53	1.00	3.00	.20	1.36	.38	1.71	.32	1.99
..	..	1.41	3.21	.57	2.62	..	..	.63	2.83
..	..	2.31	3.70	1.15	3.10	..	..	1.39	3.29
..	..	3.78	4.37	..	..	..	..	2.33	3.74
..	..	4.55	4.77	..	..	..	..	..	..

$c \times 10^4$	$(\partial q/\partial c)_{\text{obs.}}$	$(\partial q/\partial c)_{\text{calcd.}}$	$c \times 10^4$	$(\partial q/\partial c)_{\text{obs.}}$	$(\partial q/\partial c)_{\text{calcd.}}$	$c \times 10^4$	$(\partial q/\partial c)_{\text{obs.}}$	$(\partial q/\partial c)_{\text{calcd.}}$
0	72000	72000	0.3	43470	43000	1.0	5830	8370
0.1	67850	72000	.4	27910	26500	2.0	5120	5710
.2	61850	66000	.5	20070	18420	4.0	4360	4575
						∞	4000	4000

TABLE II

CHLORINE: 315 CC. PER G., N. T. P.

Series 1		Series 2		Series 3		Series 4	
$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	q
0.06	0.107	0.09	0.19	0.071	0.25	0.072	0.22
.123	.21	.168	.38	.15	.48	.14	.43
.185	.31	.29	.70	.32	.98	.33	.90
.247	.42	.60	1.55	.48	1.35	2.47	6.64
.42	.79	..	..	.64	1.76	..	..
.77	1.60	..	..	1.78	4.89	..	..
1.14	2.25	..	..	..	..	..	..
1.54	2.98	..	..	..	..	..	..
1.92	3.78	..	..	..	..	..	..

$c \times 10^4$	0	0.1	0.5	1.0	2.0
$\partial q/\partial c$	31900	31000	28100	25900	24600

Table III

Carbon Dioxide: 505.6 cc. per g., N. T. P.

Series 1		Series 2			
$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	$\partial q/\partial c$
1.69	1.36	1.71	1.36	0	8410
3.55	2.72	3.64	2.61	1	7940
5.26	3.58	5.41	3.86	5	6588
8.41	4.81	7.37	5.09	∞	6000
13.94	6.85	9.34	6.47	..	..
...	..	11.13	7.67	..	..
...	..	13.96	9.67	..	..

Table IV

Ammonia: 1300 cc. per g., N. T. P.

Series 1		Series 2		Series 3			
$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	$\partial q/\partial c$
1.55	2.28	1.81	2.06	1.67	2.24	0	16940
3.39	4.00	3.75	3.45	3.97	3.99	1	13160
5.17	5.43	5.79	4.83	6.74	6.24	5	7500
7.78	7.65	7.53	5.91	11.18	9.78	15	7160
11.38	10.64	9.16	6.85	15.56	13.15	∞	7000
14.32	12.42	11.95	9.42	...	...	..	...
...	...	15.57	11.57	...	...	..	...

Table V

Ether: 289 cc. per g., N. T. P.

Series 1		Series 2				
$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	$\partial q/\partial c$	$\partial q/\partial c$, L. and C.
1.75	2.64	3.23	5.24	0	15830	...
4.37	6.28	6.56	10.13	2.5	15340	15850
8.49	12.18	10.37	15.09	5.0	14370	...
12.79	17.49	13.98	19.26	10.0	12470	...
16.85	21.46	17.30	22.56	15	9550	13800
21.75	24.96	22.12	25.72	∞	7800	...

Table VI

Chloropicrin

Series 1		Series 2		Series 3			
$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	$\partial q/\partial c$
3.22	5.21	3.07	4.98	3.17	4.54	0	16600
6.68	10.14	6.72	10.15	6.34	8.94	5	14280
10.03	14.39	10.12	14.31	9.51	12.26	10	12130
12.30	17.51	...	...	11.44	14.17	..	...

Table VII

Water

Series 1				Series 2	
$c \times 10^4$	q	$c \times 10^4$	q	$c \times 10^4$	q
9.21	7.86	45.6	46.42	9.04	7.67
17.94	17.18	54.9	56.01	18.20	16.40
27.10	26.85	64.2	65.88	26.68	26.01
36.6	36.81	..	...	36.31	33.52
$\partial q/\partial c = 10510$				$\partial q/\partial c = 9460$	

Attempts were made also to measure the heat of adsorption of hydrogen, but sufficient accuracy was not attained with the present apparatus. The values of $(\partial q)/(\partial c)$ were in each case obtained from large-scale plots of the q, c values listed in the tables.

There is no known functional relation between q and c except the two constant empirical equation $q = mc^n$ which sufficed to represent the results of Lamb and Coolidge. This equation gives for $(\partial q)/(\partial c)$, $mn(1/c^{1-n})$ or $n(q/c)$. It has been found that for the present results this equation rectifies the data tolerably well except for oxygen. A rational equation is very much needed, however, and even an empirical equation of greater generality than the log q–log c equation is much needed.

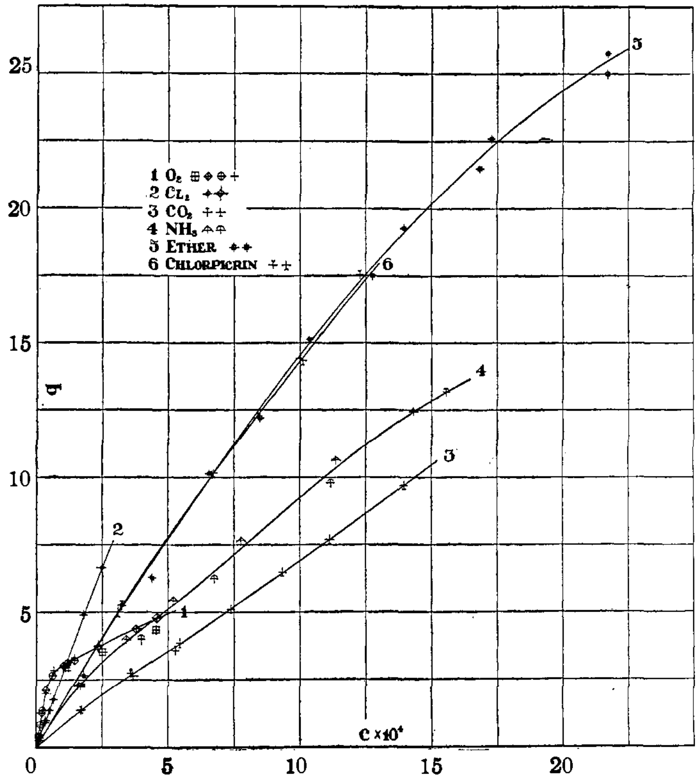

Fig. 2.

The data of the tables are plotted directly in Fig. 2 and again in Fig. 3, using as coördinates log q and log c. The latter figure indicates that particularly for oxygen log q is not proportional to log c except at the smaller concentrations or again at the larger. In fact an inflexion exists. In the case of carbon dioxide on the other hand, the range of the data is not badly represented by a linear equation between the variables. There appears to be in this case, however, a trend slightly convex to the log *c* axis. Ammonia exhibits a similar behavior, and also chlorine. Oxygen and ether, however, are concave to the axis of log *c*, although oxygen exhibits an inflexion at the higher concentrations. Chloropicrin is measured over too short a range to make comment of any value.

The case of oxygen is particularly striking when the quantity $(\partial q)/(\partial c)$ is considered. Fig. 4 indicates that as zero concentration is approached, about 72,000 cal. is evolved for one mole (32 g.) of oxygen adsorbed. The heat of formation of carbon dioxide from the monoxide and oxygen is about this magnitude (69,000 cal.). There can be little doubt that the heating of the charcoal to 900°, however long, would not suffice to remove completely the unimolecular layer.[11] However, Blench and Garner[12] found from measurements carried out from 18° to 450° and at a concentration of 0.06×10^{-4} moles of oxygen per g. charcoal that the molecular heat of adsorption at the **higher** temperature amounted to almost $3\frac{1}{3}$ times the heat at 0° while at 280° it is more than double.[13]

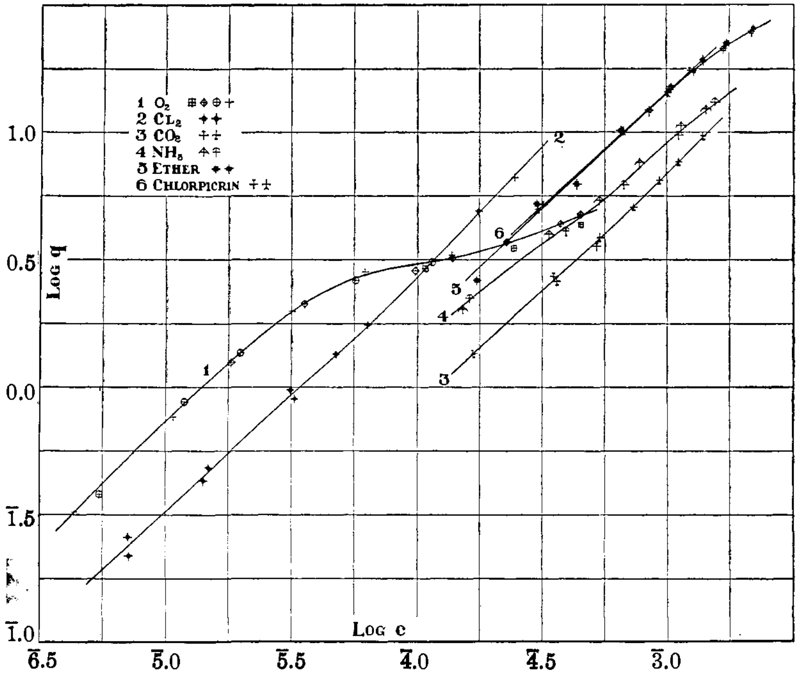

Fig. 3.

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[11] Langmuir, This Journal, **38,** 2221 (1916).

[12] Blench and Garner, *J. Chem. Soc.,* **125,** 1288 (1924).

[13] Extrapolating the results of Blench and Garner at 18° to zero concentration, we find a number only slightly greater than 72,000 cal. for the heat of adsorption.

The huge temperature coefficient for the heat of adsorption as zero concentration is approached (340 cal. per degree) may be due to better experimental realization at the higher temperatures of a gas-free surface. The initial amounts of oxygen adsorbed would, in this case, first interact in such a way as to complete the first layer as oxygen atoms with the liberation of a large quantity of heat per mole of oxygen. An estimate of the heat of formation of carbon dioxide from gaseous carbon, for example, is approximately 400,000 cal. (heat of vaporization of carbon 287,000 cal., Fajans).[14] The difficulty with which Langmuir found carbon monoxide to be evolved from carbon filaments at 1300° to 2100° would seem to indicate that perhaps there would not be sufficient unattached adsorbent carbon atoms (46%) to account in this manner for the 224,000 cal. found by Blench and Garner at 450°.

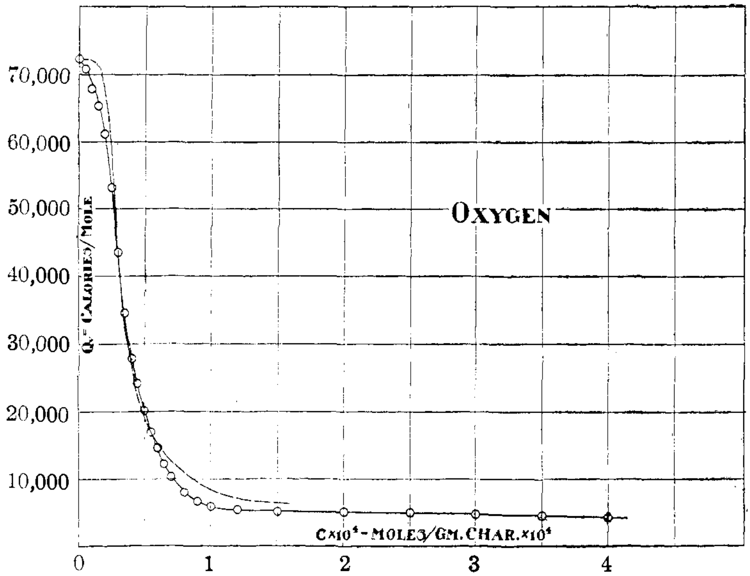

Fig. 4.

The general form of the curve (Fig. 4, for example) relating q to c indicates that many adsorbed layers are involved in passing from zero concentration at the ice-point temperature to the highest concentrations here measured (4.5×10^{-4} moles). It might be anticipated on the basis of the view of successive adsorbed layers herein assumed that a constant heat of adsorption should be obtained for each successive layer until completed. It is evident that after the formation of the first layer or even before its completion, a second or successive layers would begin to form at certain portions of the surface and instead of a broken curve a con-

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[14] Fajans, *Z. Physik*, **1**, 101 (1920).

tinuous diminution of heat of adsorption would result. The tendency to complete one layer at a time would depend on the intensity with which each layer was held, greatest for the first layer and less as the successive layers were less firmly bound. The kinetic energy of the particles approaching a surface in process of formation would also be a factor in the distribution of adsorbing particles. A rapidly moving particle, for example, impinging on a molecule belonging to a layer in the process of formation would tend to remain contributing to the next layer, whereas a slow-moving particle might be deflected under the attractive force and occupy a position in the layer being completed.

The attempt to deduce an equation connecting the molecular heat of adsorption in the successive layers as a function of the concentration has not been sufficiently successful to be worth recording. Empirically it may be observed, however, that $(Q_i - Q)/Q$ is zero initially and a constant when the heat becomes independent of the concentration. Thus the equation may be written, where Q_i is the value of $\partial q/\partial c$ as zero concentration is approached and Q_f the final value of $\partial q/\partial c$: $Q_i - Q = Q_i - Q_f f(c)$. The $f(c)$ is some function of the concentration which reduces to zero for $c \doteq 0$ and unity for $c \doteq \infty$. One form for $f(c)$ is $a/[c(e^{a/c} - 1)]$. The equation for q then becomes

$$q = Q_i \int_0^c \frac{\mathrm{d}c}{1 + \frac{Q_i - Q_f}{Q_f} \frac{a}{c(e^{a/c} - 1)}}$$

This equation satisfies the terminal requirement of the q, c curve, for when $c \underset{\cdot}{=} 0$, $q \underset{\cdot}{=} Q_i c$, the heat evolved as the first layer is filled up for an amount of charcoal sufficient to be covered with a unimolecular layer or 32 g. of oxygen. Also when $c \underset{\cdot}{=} \infty$,[15] $q \underset{\cdot}{=} Q_f c$, which is the heat similarly given out as the final layers are completed. The $f(c)$ is unfortunately of such a form that the integral cannot be expressed in terms of ordinary functions. With $a = 1.44 \times 10^{-4}$ the values given in Table I under the column $(\partial q)/(\partial c)$ cal. have been computed. The dotted line in Fig. 4 is a graphic representation of the same computations.

The accord between the observed and calculated curves is perhaps as good as the present data warrant. Attention is directed to the fact that the part of the curve corresponding to small values of c is relatively flat. As a rough approximation, assuming that this portion corresponds to the first layer, a value may be given for the active surface of the charcoal. The curve begins to fall at $c = 1 \times 10^{-5}$. If this in fact corresponds to the amount of oxygen per g. of charcoal required for the first layer, the active surface would be 5100 sq. cm. (the diameter of an oxygen molecule being taken as 2.9×10^{-8} cm.). This estimate is far under previous

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[15] The designation $c \underset{\cdot}{=} \infty$ is herein used as an abbreviated means of denoting a concentration of adsorbed substance sufficiently large to give Q values substantially independent of the concentration.

estimates by Lamb, Wilson and Chaney,[16] 1 × 10^7 sq. cm.; Williams,[17] 0.131 × 10^7 sq. cm.; or Lowry and Hulett,[18] (0.16 to 0.44) × 10^7 sq. cm.

It is worth noting that if the carbon atoms themselves were extended in a unimolecular layer, there would be 0.5 × 10^7 sq. cm. per g., or double this number if both sides of a carbon atom were available as an adsorbing surface.

The energy of adsorption for chlorine is likewise large initially, but the drop with increasing amounts adsorbed is not nearly as large as for oxygen. No special comment need be made beyond noting that charcoal is a good catalyst for the synthesis of phosgene from carbon monoxide and chlorine. It is not unlikely that a study of the heat of adsorption of both carbon monoxide and phosgene would provide sufficient data, with the energy of adsorption of chlorine gas, to suggest the mechanism of the catalytic action in this simple synthesis. The necessary measurements were originally planned as a part of the present investigation but could not be completed.

The substances carbon dioxide, ammonia and ether would not be expected to unite chemically with the carbon atoms in the first adsorbed layer. The energy of adsorption for the first exhibits a comparatively slight fall with increasing concentration, while ammonia shows a relatively large drop. The values for ether agree in the main with the results obtained by Lamb and Coolidge except that the decrease in the heat is greater at the higher concentrations. Thus at $c = 2.5 \times 10^{-4}$, Q is 15,340 as compared with 15,850 obtained by Lamb and Coolidge, whereas at $c = 15 \times 10^{-4}$ Lamb and Coolidge find a value over 4000 cal. greater. The values for carbon dioxide and ammonia agree as well as may be expected with previous measurements by Chappuis and Titoff but the data of the latter are very much lower at the smaller concentrations.

The heat of adsorption of water is distinctly different in its relation to the concentration from the known behavior of other substances. The measurements recorded in Table VII are not as concordant as would be desirable since the second series gives a considerably lower average value of $\partial q/\partial c$ as compared with the first. The mean of both values of Q although lower, does not differ greatly from the heat of evaporation of liquid water (10,600). There is an apparent tendency, it should be also noted, for Q to increase with rising concentration rather than decrease.

Reference has already been made to the old idea that the cohesional forces of the normal gas or liquid phase may be the cause of adsorption phenomena. It has already been shown that in the case of oxygen the adsorption energy is enormous for the first small amounts adsorbed. The

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[16] Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, **11,** 430 (1919).

[17] Williams, *Proc. Roy. Soc.*, **96A,** 287 (1919).

[18] Lowry and Hulett, THIS JOURNAL, **42,** 1393 (1920).

ordinary heat of evaporation of liquid oxygen is, in fact 45 times smaller. Even in the case of carbon dioxide, ammonia or ethyl ether the initial heats of adsorption are more than double the usual heat of evaporation of the liquids at 0°. The case of water is by comparison an apparent anomaly, for the heats of adsorption and evaporation are about the same.

During recent years investigations have been under prosecution in this Laboratory which have aimed to determine among other things the cohesive constants of certain selected substances. Of course for many years the constants a and b of van der Waals' equation have been available derived from "critical data," but since the equation is quantitatively inaccurate little use can be made of the constants. An equally grave difficulty has resided in the circumstance that the origin of the forces of cohesion has received no rational explanation until recently.[19] It appears clear as a consequence of Debye's work that the origin of these important forces lies (at least for certain types of molecule) in the induced polarization due to the displacement of the electric charges constituting the molecule by the electric field of the environing molecules. The force of attraction for the simpler molecules (no natural electrical moment) was shown to vary inversely as the ninth power of the distance and as the square of a function of the principal electrical moments of inertia of the molecule while the A of the equation of state of one of the authors[20] is equal to $6\pi N^2\tau^2\alpha/5d^5$, where τ is the electrical moment of inertia function, α the polarization, d the diameter of the molecule and N the Avogadro number. At present too little is known of the actual structure of atoms or molecules to enable the quantitative development of these important ideas to proceed much further, but considerable insight may be obtained relative to adsorptive phenomena by a comparison of the A and β constants of the equation of state[21] with adsorptive energies.

Table VIII contains in Col. 4 the value of 4 A/β which, per mole, may be considered to be the energy required to separate the molecules from their "actual volume" $\beta/4$ to infinity. The quantity β since van der Waals' original work has been considered in its physical significance to be four times the volume of the molecules. There are many reasons for believing that the "volume" of a molecule is by no means the simple concept supposed before the development of the electrical theory of atomic and molecular structure. The quantity β has, however, the dimensions of a volume, and for the present purpose may be considered as four times

[19] Debye, *Physik. Z.*, **21,** 178 (1920).

[20] Keyes, *Proc. Am. Acad. Sci.*, **3,** 323 (1917).

[21] The equation of state referred to is $p = \dfrac{RT}{v - \beta e^{-\alpha/v}} - \dfrac{A}{(v + l)^2}$ where A, β, α and l are constants and A and β are qualities analogous to A and β of van der Waals' equation. The constants given in Table VIII are taken in part from the published work of one of the authors and in part from investigations completed but unpublished.

Table VIII

Substance	$A \times 10^{-6}$ $\frac{\text{cc.} \times \text{atm.}}{\text{mole}}$	β cc./mole	$4\,A/\beta$, cal. per mole	$(Q_f)_v$ obs./0°	P_d
Ether	31.3	460	6600	7250	54.1
H_2O	19.0	230	8000	8914 9964	52.4
NH_3	8.5	136	6060	6456	61.5
CO_2	6.2	128	4680	5450	7.35
CH_4	2.4	58.4	3980	4600	6.35
A	1.6	51.2	3032	3450	4.17
O_2	1.5	44.5	3260	3454	4.10
N_2	1.3	49.5	2540	3654	4.35
H_2	0.16	19.3	804	1870	2.00
He	.026	13.0	194	387	0.55

the apparent "volume effect" of the molecules. The fifth column contains what are believed to be the most reliable values for the energy[22] of adsorption at large concentrations. The first five values together with those for oxygen are taken from the measurements contained in this paper. The Q_f values for argon, nitrogen, methane, hydrogen and helium have been selected from a consideration of the direct heat of adsorption measurements of Titoff and the p, T, c data of Homfray. The number for helium (665 cal.) was taken from the very meager data of the latter and corresponds to a temperature interval 83° to 195°K. or a mean temperature of 139° instead of 273° to which all the other values refer. The work of Harned and the experimental findings in the present work, indicate that the outgassing or heating of the charcoal with frequent treatment of the adsorbent with the substance being investigated, should be a part of the procedure in securing data bearing on adsorption. Data for the monatomic gases are especially important since these, of all molecules, are most nearly without a natural electrical moment.

The sixth column contains a list of the constants of the dielectric-constant equation $V = 4N\pi\alpha/3 = P_d, (D - 1)/(D + 2)$ where D is the dielectric constant, V the volume of a mole and α the electrical polarization per molecule. It will be noted that the first three entries in the table are large numbers compared with those that follow. The former are molecules which possess natural electrical moments and do not accord with Maxwell's refractive-index relation $n^2 = D$. The last seven substances have no appreciable natural moments except carbon dioxide, whose moment is small (ten-fold less than that for ammonia).

In Fig. 5 a graphical representation of the data of Table VIII is presented in which $(Q_f)_v$, $4\,A/\beta$; $4\,A/\beta$, P_d; and $(Q_f)_v$, P_d have been plotted. All three plots indicate simple relations between the variables. Of first im-

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[22] The term "adsorption energy" is a convenient term for the heat of adsorption less the external work and will be used to denote this quantity throughout the paper.

portance is the close relation between the final energy of adsorption and the energy which the equation of state cohesive-pressure constant A (dimensions, energy × specific volume) and the β constant would indicate as the amount of energy required to separate the molecules from contact to infinity. It is clear that the final layers of molecules in the adsorbed state are not strained or in a state, from the point of view of inherent properties, which is very different (except for close packing) from that of the normal molecule. On the other hand this should not be taken as evidence that the so-called capillary theory of adsorption is favored.

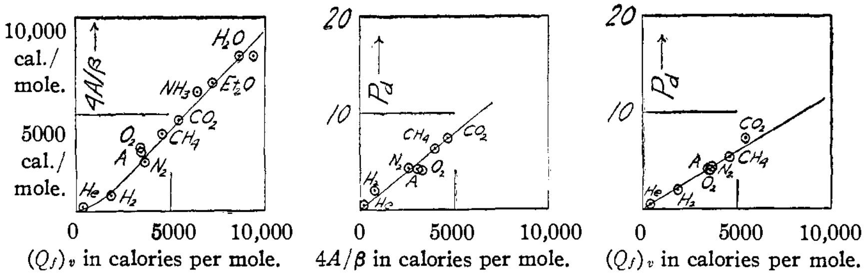

Fig. 5.—Plots showing relations among final heats of adsorption, dielectric properties and p-v.T properties.

The high initial heats and their trend with increasing concentrations make it appear more useful to regard the adsorbed material as arranged in layers, the first of which partakes of a very special molecular state due to the combined electrical stresses set up by the close proximity of the adsorbent and adsorbed molecules. The second and succeeding layers are not under the direct influence of the adsorbent *per se* but of the already adsorbed molecules whose special state partakes in continually lessened degree of the state of the first layer.

The $(Q_f)_v$, P_d plot is of considerable importance both from the point of view of adsorption theory as well as the molecular theory. The values of P_d for the first three substances of Table VIII do not appear, since they are out of the scale of the plot. The remaining substances show proportionally between $(Q_f)_v$ and the induced polarization due to the field of the environing molecules. This may be taken as proof that for these substances the electrical moment of inertia function (τ^2) divided by the diameter of the molecules to the eighth power is a constant (helium excepted). This may be easily seen by writing

$(Q_f)_v = K P_d = K (4/3) \pi N \alpha$, where K is a constant;

$(Q_f)_v = F 4 A/\beta$, where F is a constant;

and $K (4/3) \pi N \alpha = F 4 A/\beta$

or $K/F = \text{constant} = 4 A/\beta \times 1/(4/3) \pi N \alpha$,

since $A = (6/5) \pi N^2 \tau^2\alpha/d^5$ and $\beta = (2/3) \pi N d^3$

$K/F = \text{constant} = 27 \tau^2/5\pi d^8$.

The quantity $216\tau^2\alpha/5\pi d^9$ would be the force with which two molecules of the non-permanent-moment type attract when the centers are at a distance equal to the diameter of a molecule. The high initial energy of adsorption would indicate that either τ^2 was increased or that d was diminished as a consequence of the adsorptive state. Tau is a function of the principal electrical moments of inertia (dimensions, charge $\times\ l^2$) and it is probable that both τ and d are altered in magnitude. From the viscosity data of oxygen the diameter of the molecule at infinite temperature is 2.9×10^{-8}, while from the β value it is 3.28×10^{-8}; thus, if τ^2 remained constant the increase in $(Q_f)_v$ due to variation in diameter would be only 2.5-fold instead of 18-fold for oxygen, as appears to be the fact at zero concentration. Such a large change, as is the case here ($18\ Q_f = Q_i$), would seem to call for a very profound change in the molecule.

The theory of the cohesive pressure of molecules with large permanent moments is in too incomplete a state of development to permit any observations regarding the relation of the constants of these molecular species to the adsorption energies to be of much value. It would be very desirable, in this connection, to have measurements of the heats of adsorption at higher temperatures where the special effects due to the presence of permanent electrical moments in the molecule should vanish.

Summary

1. Measurements of the heats of adsorption on charcoal as ash-free as possible have been made at the melting temperature of ice for oxygen, chlorine, carbon dioxide, ammonia, ether, chloropicrin and water.

2. In each case the heat of adsorption per mole is large initially (concentration $\doteq 0$) and falls rapidly to an apparently constant value with increasing concentration. In the case of oxygen the heat of adsorption is about eighteen times as great initially (72,000 cal.) as compared with the constant final heat (4,000 cal.).

3. The magnitudes of the final energies of adsorption have been shown to be proportional to the potential energy of the molecules from a state of "contact" to infinity based on a computation of the latter from the equation of state constants A and β.

4. For molecules of the non-permanent electrical moment type, the energy of adsorption has been shown to be proportional to the electrical polarization of the molecule derived from dielectrical-constant data.

5. It is concluded as a result of the present investigation that adsorbed material can in general best be regarded as in a special state in which the first layer alone is to be considered as under the direct influence of the adsorbent. The first and succeeding layers, because of their special state, constitute new adsorptive surfaces which may adsorb molecules of the same species as the first layer or molecules of a different species. Each suc-

ceeding layer (the adsorbing molecules all of the same species) partakes of the special state of the first layer in lessened degree until finally a layer is reached wherein the molecular state differs little from what may be imagined as a molecular "contact" arrangement.

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THE ACTIVITY COEFFICIENTS OF THE IONS IN CERTAIN PHOSPHATE SOLUTIONS

A CONTRIBUTION TO THE THEORY OF BUFFER ACTION[1]

BY EDWIN J. COHN

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The behavior of weak electrolytes furnished one of the earliest and most complete confirmations of the theory of electrolytic dissociation. The degree of dissociation of such weak acids as acetic acid was shown to follow the law of mass action in 1888, and was calculated from measurements of conductivity by means of Ostwald's dilution law. The constants obtained from such studies of solutions of weakly dissociated electrolytes have remained the most useful that we possess for their quantitative characterization.

The characterization of strongly dissociated electrolytes in terms of the mass law remained difficult until the electrical forces resulting from the charges borne by ions were taken into account. The theory of inter-ionic forces deduced by Debye and Hückel[2] appears to be adequate for the quantitative description of behavior in even moderately concentrated solutions of strong electrolytes.

Systems containing both weak electrolytes and strong electrolytes are of general occurrence and of great significance both in chemistry and biology. The conditions that obtain when a weak acid is in the presence of its salts are, however, less easily analyzed than those that obtain in dilute solutions of the pure acid. The characterizations of such mixed electrolyte solutions have advanced in recent years, but the successive approximations, though they have made accurate investigation possible, have suffered from want of an underlying theory. The theory of inter-ionic forces renders it possible to apply the mass law to weak electrolytes in the presence of other ions.

The dissociation of a weak acid, HA, into a hydrogen ion, H^+, and its characteristic anion, A^-, may be described in terms of the mass law. In

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[1] A preliminary account of this investigation was communicated to the Twelfth International Physiological Conference, Stockholm, 1926.

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). Debye and McAulay, *ibid.*, **26**, 22 (1925). Hückel, *Naturwissenschaften*, **3**, 199 (1924); *Physik. Z.*, **26**, 93 (1925).