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K. VETENSKAPSAKADEMIENS NOBELINSTITUT
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ON ADSORPTION FROM SOLUTIONS

BY

A. M. WILLIAMS

(1851 EXHIBITION SCHOLAR OF THE UNIVERSITY OF EDINBURGH)

WITH 4 FIGURES IN THE TEXT

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When a substance in a state of fine division, such as charcoal or silica, is shaken up with a solution a change in the concentration of the solution is often observed although no *chemical* action has taken place. If the concentration of the solution has decreased — as in the majority of cases hitherto studied — the phenomenon is termed *positive* adsorption, while if the concentration of the solution has increased, *negative* adsorption is said to have occurred.

At constant temperature the relation between the amount adsorbed (a) and the concentration (c) outside the adsorbing body is usually expressed by the exponential formula extensively employed by FREUNDLICH[1]

$$a = k c^n \tag{1}$$

where k and n are constants varying with adsorbent, solute, solvent and temperature. But more recently G. C. SCHMIDT[2] has advanced new formulae based on observations which led

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[1] Z. f. P. C. *57*, 385.

[2] Z. f. P. C. *74*, 689; *77*, 641; *78*, 667.

him to conclude an adsorption maximum where the adsorbent seemed incapable of gathering up more of the solute however great the concentration outside should be. It is obvious that such a contingency is not provided for in formula (1).[1]

It was with a view to investigate the variation or non-variation of this *maximum* with the temperature that the present investigation was undertaken. The results, critical more than experimental, were unexpected. In the first place let us consider how the experiments on adsorption from solution are usually carried out.

The method is very simple. A known quantity of solution of known concentration is added to a known mass of adsorbent. After adsorption is judged to be complete a measured quantity of the solution, freed from the adsorbent, is withdrawn and the concentration determined by titration or otherwise. The calculation then proceeds as exemplified. — Let 50 ccm. of solution containing a grams solute be shaken up with 1 gram charcoal. When adsorption is completed, 25 ccm. are withdrawn and found to contain $(a-x)/2$ grams of solute. Then 50 ccm. would contain $(a-x)$ grams, and therefore the charcoal has adsorbed x grams, while the concentration outside is now $(a-x)/50$ grams solute per ccm. Now this calculation is based on the assumption that the volume of the solution outside the charcoal has remained constant, and this assumption is — *erroneous*. Nevertheless the faulty method of calculation will be found throughout the literature of the subject. Of course with dilute solutions the change in volume is negligible. SCHMIDT in his paper cited above makes a similar slip. He assumes the mass of the solution outside the charcoal to remain constant, even when several per cent is being taken up by the charcoal.[2]

To obtain therefore a correct estimate of the amount adsorbed we must base our calculation on something else which remains constant and which may be employed as a point of reference. The obvious thing to select appears to be the mass

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[1] (The formula is also applied to gaseous adsorption. In the case of solutions if c be expressed as, say, grams per gram *solution*, we get a »maximum», with $c = 1$, which was scarcely contemplated by the framers of the formula.)

[2] In the adsorption of gases such an error does not creep in. But it may be pointed out that here *the volume of the adsorbed gas is neglected.* The error thus introduced scarcely affects the value calculated for the amount absorbed more than 0,5 % at the most, e. g. in some of Miss HOMFRAY's results. Z. f. P. C., *74*, 129.

of the solvent. Let the original solution contain c_0 grams of, say, acetic acid per gram solution. Let the solvent be water. Let M grams of the solution be added to G grams charcoal, and let the final concentration be found to be c grams acetic acid per gram solution. Let u_0 denote the amount of acid adsorbed in grams per gram charcoal. Then if the mass of water be constant

$$\begin{aligned} u_0 &= \left\{ \mathrm{M} c_0 - \mathrm{M}(1 - c_0) \, . \, c/(1 - c) \right\} / \mathrm{G} \\ &= \frac{\mathrm{M}}{\mathrm{G}} \cdot \frac{c_0 - c}{1 - c} \end{aligned} \tag{2}$$

If we employ this formula to recalculate SCHMIDT's results it will be found that u_0 steadily increases, that is, a *maximum* u_0 was not found (see later).

But in calculating u_0 as the amount absorbed we have still made an assumption (which was included also in the »constant» volume or mass), namely we have assumed that the mass of the solvent does not change. But we have no ground for this assumption. In fact *the solvent is also partly adsorbed.*[1]

Let u denote the true amount of solute adsorbed in grams per gram absorbent, and w the corresponding value for the solvent. Then

$$u = u_0 + w \, . \, c/(1 - c) \tag{3}$$

Hence we cannot know the *true* amount of either solvent or solute adsorbed unless we can find another equation involving u or w or both.

We may, however, draw several conclusions from (3) and (2).

In the first place since u and w represent absolute amounts, and not excesses nor defects, neither u nor w can be negative. Nor can $c/1 - c$ be negative.

If we write (3) as

$$u/w = u_0/w + c/1 - c$$

we note in the second place that

$$u_0 = 0, \text{ or, } c_0 = c$$

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[1] The tendency has been to regard the solvent as a »space» in which the solute has play.

that is, no change in concentration is observed if

$$u/w = c/1 - c$$

again if

$$u/w > c/1 - c$$

u_0 is positive, $c_0 > c$.

This is »*positive*» adsorption.

Lastly if

$$u/w < c/1 - c$$

u_0 is negative, and $c_0 < c$.

This is »*negative*» adsorption, which takes place when the adsorbed surface layer is richer in solvent than the exterior solution. We may note yet another point of interest here. Let us calculate the amount of water adsorbed on the assumption that the mass of the acetic acid outside the charcoal has remained constant. We have

$$w_0 = \frac{M}{G} \cdot \frac{(1 - c_0) - (1 - c)}{c} = - \frac{M}{G} \cdot \frac{c_0 - c}{c}$$
$$= - u_0 . (1 - c)/c.$$

Thus so called *positive* adsorption of acetic acid is *negative* adsorption of water. It is well known that a very dilute solution is well nigh cleared of the solute by the adsorbent. If we interchange solute and solvent, e. g. take a dilute solution of water in acetic acid, we may expect the same process to take place, and to find nearly all the water adsorbed. If then we trace a (u_0, c) curve *we may expect u_0 to reach a maximum, pass through that value, pass through zero and proceed to negative infinity for $c = 1$.* The curve should be of the form presented in Figure 1.[1]

We proceed to apply these views to our experimental data.

Experimental part.

The materials chosen were blood charcoal as adsorbent, and solutions of acetic acid and water. The charcoal contained 6—7 % silica, and 0·1 % iron. Nothing could be extracted

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[1] Of course the liquids in the mixture are presumed to behave similarly throughout.

from it on digesting with boiling water and filtering hot. Acid extractions were also blank. Tests were made initially as to time of adsorption. These indicated a difference of about 0·1 °/₀ in the concentration of the acid outside the charcoal, between

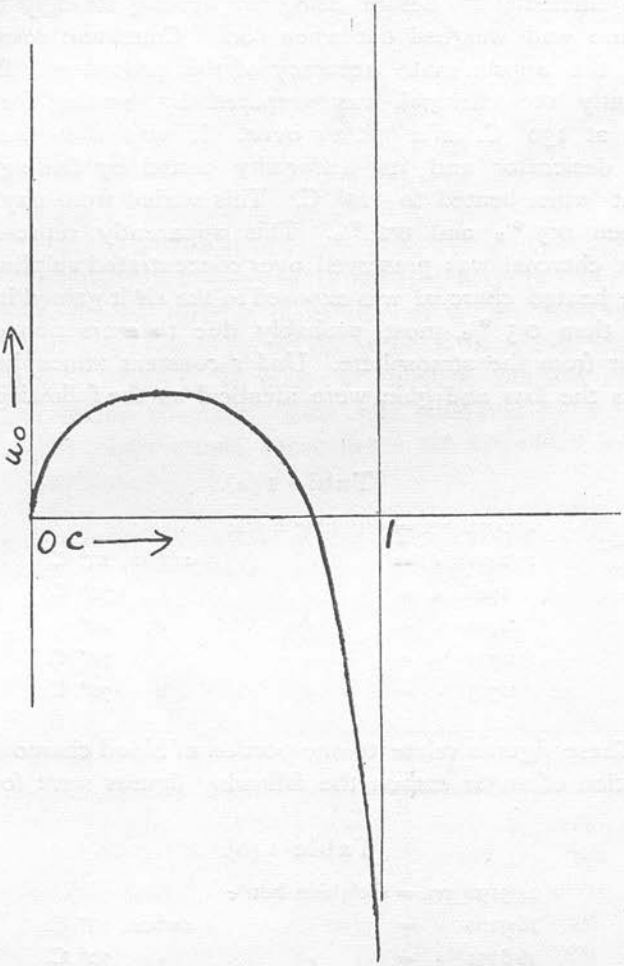

Figure 1.

observations taken after 30 minutes contact with charcoal and after 24 hours. The solutions plus charcoal were shaken up in sealed flasks in a thermostat for at least 48 hours, and in many cases 96 hours or more. It was found that rubber was acted upon by the acid solutions, so the bottles were closed with paraffined corks. The acid appeared rather to be adsorbed by the rubber than to attack it. There was no action with the paraffin wax.

For the first series of experiments the charcoal was prepared immediately before using by heating strongly to expel moisture and weighed out when cool. Consistent results indicated the approximate accuracy of this procedure. But subsequently the charcoal was prepared by heating for several hours at 130° C. in a hot air oven. It was then transferred to a desiccator and its uniformity tested by finding loss of weight when heated to 110° C. This varied from day to day between 0·3 $^0/_0$ and 0·2 $^0/_0$. This apparently represents air as the charcoal was preserved over concentrated sulphuric acid. If the heated charcoal was exposed to the air it gained in weight more than 0·5 $^0/_0$, most probably due to extraction of water vapour from the atmosphere. Under constant atmospheric conditions the loss and gain were identical as the following figures show.

Table 1 (a).

14·0932 grs. = weighing bottle
15·2421 » = » + carbon, 20° C.
·1708 » = » » 70° C.
·2420 » = » » 20° C.
·1710 » = » » 70° C.
·1705 » = » » 70° C.

These figures relate to one portion of blood charcoal. With a portion of sugar carbon the following figures were found.

Table 1 (b).

14·5190 grs. = weighing bottle
16·9120 » = » + carbon, 20° C.
16·8754 » = » » 70° C.
16·9137 » = » » 20° C.
16·8770 » = » » 70° C.
16·8778 » = » » 70° C.

The blood charcoal was not absolutely uniform. Though it was well mixed at the start analyses of different portions gave silica residues varying from 6 to 7 $^0/_0$. The solutions were titrated by means of three solutions of Barium hydroxide, of normalities $^1/_{80}$th, $^1/_{20}$th, and $^1/_7$th. (These were checked regularly by means of standard HCl solution.) In every case two readings were taken, and these seldom differed in value by more than $^1/_{10}$th $^0/_0$. With the higher concentrations the change due to adsorption even by a relatively large mass of charcoal sinks rapidly to a few per cent of the initial concentration, so that the error introduced into u_0, from a titration out $^1/_{10}$th $^0/_0$ — and no greater accuracy is claimed — is here very large.

The following tables show results at 18° C. and 25·6° C.

M . . . . mass of solution in grams.
G . . . . » » charcoal » »
c_0 . . . . original concentration of solution in grams per gram.
c . . . . . final concentration of solution in grams per gram.
u_0 . . . . acid adsorbed in grams per gram if no water adsorbed.
$u_0.(1-c)$ » » , if mass of solution outside charcoal remains constant. This was tabulated by SCHMIDT. His observations recalculated are appended for comparison.

The assumption is made throughout that the equilibrium is independent of the relative masses of charcoal and solution. This is true so far as these experiments are concerned.

Table 2 (a). 18° C.

G	M	c_0	c	u_0	$u_0\ (1-c)$
5·067	49·93	·000721	·0000325	·0068	·0068
4·067	»	»	415	834	834
5·032	99·86	»	928	·0124	·0124
3·590	»	»	·000146	160	160
2·683	»	»	214	189	189
4·010	49·96	·003578	832	343	343
5·012	99·92	»	·00144	426	425
2·065	49·96	»	172	451	450
3·007	99·92	2	208	495	494
2·028	»	»	250	532	530
1·001	»	»	300	570	568

G	M	c_0	c	u_0	u_0 (1 — c)
5·566	25·03	·01625	343	579	577
3·405	»	»	650	722	719
8·184	50·18	·03337	·01742	995	978
7·640	25·22	·06487	3081	·116	·112
5·079	»	»	4026	·127	·122
7·696	25·30	·08903	5046	·134	·127
5·036	»	»	6263	·142	·133
6·049	25·45	·1348	·1010	·158	·142
4·483	»	»	·1093	·162	·145
3·652	»	»	·1141	·162	·144
2·181	»	»	·1223	·166	·145
8·239	25·93	·2944	·2464	·200	·151
5·334	»	»	·2633	·205	·152
—	—	—	(·2827	·209)	(·150)
7·092	26·32	·4242	·3882	·218	·134
5·080	»	»	·3984	·222	·134
—	—	—	(·401	·25)	(·150)
—	—	—	(·410	·24)	·141)
—	—	—	(·413	·20)	(·118)
—	—	—	(·416	·23)	(·134)
—	—	—	(·417	·21)	(·124)

The figures in brackets were obtained in determinations where measured volumes were titrated, densities being read off from tables. They are therefore less reliable than the others, where weighed amounts were titrated.

Table 2 (b). 25·6° C.

G	M	c_0	c	u_0	u_0 (1 — c)
3·245	69·98	.000752	·000157	·0128	·0128
4·102	53·00	·001651	275	178	178
4·063	72·06	1243	278	171	171
2·949	69·00	»	343	204	204
3·493	63·69	1651	421	224	224
1·178	64·32	1243	698	297	297
2·251	72·63	1651	738	294	294

G	M	c_0	c	u_0	$u_0\,(1 - c)$
1·293	59·84	1651	920	338	338
6·309	28·27	·04981	·0253	·113	·108
4·045	46·48	»	391	·129	·124
5·339	36·75	·1014	801	·153	·141
4·066	37·12	»	858	·156	·143
7·334	30·97	·2049	·1700	·178	·148
5·557	30·95	»	·1787	·178	·146
4·087	18·945	·3408	·3128	·189	·130
5·656	44·89	»	.3246	·190	·128
—	—	—	·3193	·191	·130
—	—	—	·3329	·195	·130
—	—	—	·3733	·196	·123
—	—	—	·3815	·202	·125
6·396	36·23	·5193	·5015	·202	·101
4·710	55·43	»	·5097	·229	·112
6·238	24·25	·9240	·9143	·44	·038
5·144	26·41	»	·9180	·38	·031

In the following table are given the observations of SCHMIDT, taken from his tables, 11, 12, 15, 16. The results are treated as above, the acid »adsorbed» being reckoned on a gram of charcoal, not on the total amount of charcoal present. The notation is as above.

The substances employed were sugar charcoal and acetic acid.

Table 2 (c).[1]

c	u_0	$u_0\,(1 - c)$
·000088	·0053	·0053
·000322	·0107	·0107
372	·0121	·0121
66	·0145	·0145
·00212	·0319	·0318
265	·0307	·0306
362	·0373	·0372

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[1] Z. f. P. C. *74*, 689 etc.

c	u_0	$u_0(1-c)$
·01115	·0489	·0484
1161	·0610	·0603
165	·0627	·0617
375	·0838	·0807
376	·0836	·0805
381	·0780	·0750
559	0907	·0856
577	·0877	·0826
919	·0990	·0899
·1055	·1018	·0912
·1264	·108	·0944
·1664	·105	·0875
·2348	·115	·0880
·257	·118	·0877
·294	·129	·0911
·306	·130	·0902
·350	·149	·0969

The curves in Figure 2 illustrate the results in table 2 (b). It will be seen that no maximum has yet been attained for u_0, while $u_0(1-c)$ passes through a maximum turning point then decreases. This maximum turning point SCHMIDT has apparently mistaken for a maximum with $c = 1$, or $c/1 - c = \infty$. It may be noted that the second equation he employs, has not a maximum at infinity as he supposes. but a maximum turning point as above.

$$\mathrm{I} = \text{curve of } (c/1 - c,\ u_0)$$

$$\mathrm{II} = \text{ » » } (c/1 - c,\ u_0(1-c)).$$

Four other observations fall under Table 2 (b). These were obtained from 96·3 $^0/_0$ acid by titration methods reading to one part in four thousand at uniform temperature. Two results show distinct negative adsorption, two distinct positive adsorption within the limits of observational error. Apart from the considerable error introduced by an inaccurate reading, moisture carried in by the charcoal at high concentrations of the acid brings in a very serious error. Thus if W grams water per

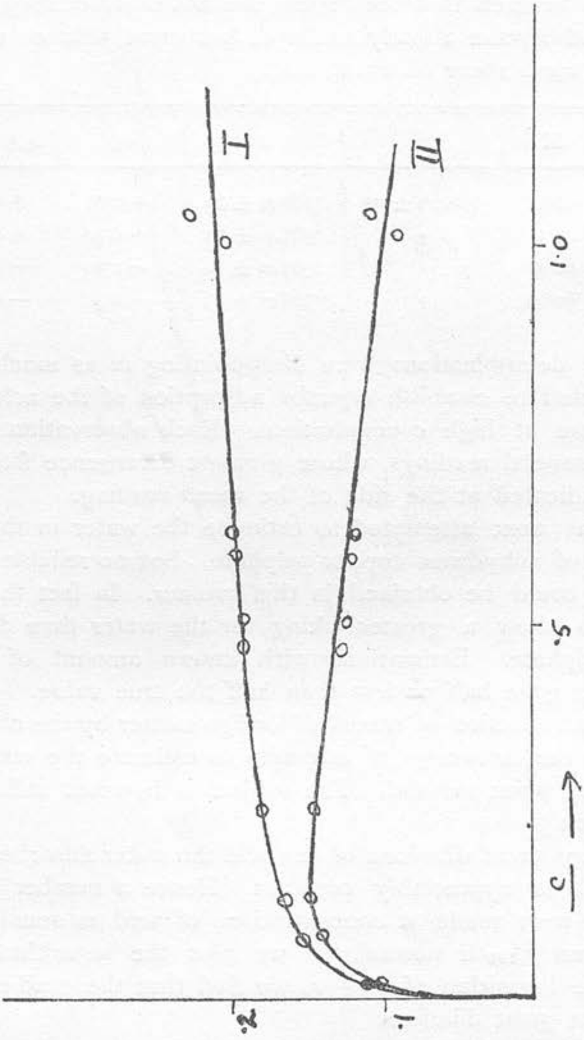

Figure 2.

gram charcoal are brought into the solution, the value u_o^1 we obtain in place of the true u_o is given by

$$u_o^1 = u_o + Wc/1 - c$$
$$= u_o + 26\ W$$

in the case above. As about this region we expect a very small negative adsorption of the acid such an error may have a great influence on the value u_o^1 found for u_o.

It will be seen that the results are not contradictory to the ideas on adsorption already outlined, but great reliance cannot be placed upon these observations.

G	M	c_0	c	u_0	$u_0(1-c)$
6·065	32·34	·962,$_{75}$ ± 20	·960,$_{75}$ ± 20	+ 0·27	+ 0·011
5·229	42·15	»	·961,$_{30}$ ± 13	+ 0·30	+ 0·012
2·720	60·47	»	·963,$_{26}$ ± 10	— 0·30	— 0·015
3·988	60·69	»	·963,$_{75}$ ± 19	— 0·42	— 0·011

These determinations were disappointing in as much as it was expected to establish *negative* adsorption of the acid with greater ease at high concentrations. Each observation is the mean of several readings, whose greatest divergence from the mean is indicated at the side of the mean reading.

(It was next attempted to estimate the water in the acid by means of anhydrous copper sulphate. But no reliable determinations could be obtained in this manner. In fact the acid seemed to show a greater liking for the water than did the copper sulphate. Estimations with known amount of water persistently gave half or less than half the true value.

The introduction of traces of foreign matter by the charcoal destroyed the accuracy of attempts to estimate the water by the freezing point method. The subject is however still under investigation.)

At very great dilutions of the acid the water adsorbed may be treated as appreciably constant. Hence a number of observations were made at concentrations of acid as small as or smaller than $^1/_{100}$th normal. If we plot the logarithm of u_0 against the logarithm of $c/1-c$, we find that the gradient becomes $\frac{1}{2}$ at great dilutions,

This is seen in Figure 3.

The upper curve refers to the observations at 18° C., the lower to those at 25·6° C. The straight line is the line of gradient $\frac{1}{2}$. The last two observations in the first part of Table 2 (b) are not on the diagram. The lower curve if continued would pass some distance beneath them. If the ($\log c$, $\log u_0$) curves were drawn they would not fall so much from the straight line in the diagram, but would still be concave to the horizontal axis.

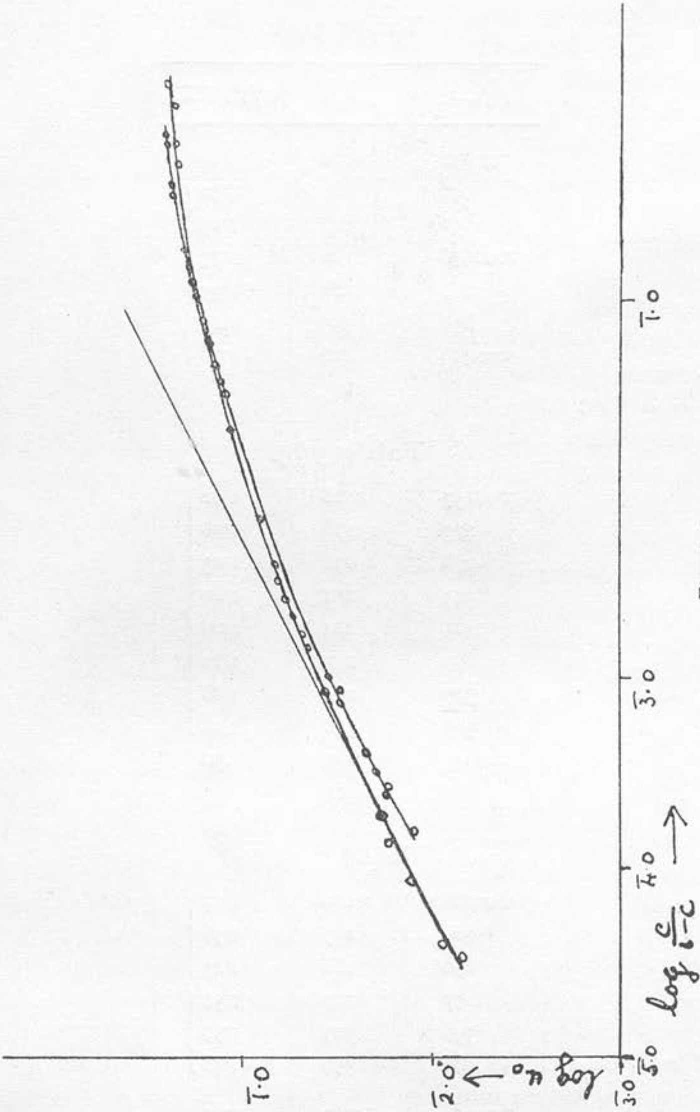

Figure 3.

The constancy of $u_0/c^{\frac{1}{2}}$ in dilute solutions is shown by the numbers in the following tables. The first two refer to 2 (a) and 2 (b), the third to observations on acetic acid and sugar charcoal, at 25·6° C.

Table 3 (a).

$c/1-c$	u_0	$u_0/\sqrt{c/1-c}$
·0000325	·0068	1·19
415	834	1·30
928	·0124	1·29
·000146	160	1·33
214	189	1·29
833	343	1.19
·00145	426	1·12

etc.

Table 3 (b),

·000157	.0128	1·02
275	178	1·08
278	171	1·03
343	204	1·10
421	224	1·09
697	297	1·12
737	294	1·08
919	338	1.11
·0260	·113	.70

etc.

Table 3 (c).

·000081	·0140	1.53
109	155	1·56
150	188	1·43
257	229	1 54
396	305	1·55
503	350	1·48
·00324	·0599	1·05
497	678	·96
631	829	1·04
720	914	1·08
·0418	·109	·54
491	·117	·53
·1193	·131	·38

It is of course quite possible that if still greater dilutions had been examined the gradient of the curve of logarithms might have increased to unity. In this case we should expcct $u_0/c^{\frac{1}{2}}$, which is equal to $(u_0/c) . c^{\frac{1}{2}}$, to decrease with c. So far as we have investigated, $u_0/c^{\frac{1}{2}}$ increases as c decreases, and we have no evidence of a subsequent decrease of $u_0/c^{\frac{1}{2}}$.

The very slight tendency to decrease shown in the first observations in 3 (a) und 3 (b) may be attributed to errors of manipulation.

Some observations on *silica* are of interest. The silica had been previously ignited and should not therefore have been able to become hydrated. It was fairly pure, containing no metallic salts, and the extract with boiling water showed only a slight opalescence with silver nitrate solution. The results are as follows.

Table 4. Temp. 25°·6 C.

G	M	c_0	c	u_0	$u_0 + \frac{3}{10} \frac{c}{1-c}$
4·783	75·08	·0007516	·0006829	·00108	·00128
3·182	78·69	·0007516	·0007102	·00102	123
2·346	65·90	·0012429	·0011922	·00146	182
1·197	74·59	·0012429	·0012177	·00157	193
3·111	65·52	·003867	·003822	·00093	208
3·414	94·13	·006108	·006071	·00102	284
4·110	75·70	·013941	·013904	·00068	491
2·349	31·66	·05588	·05597	— ·0016	·0162
2·745	31·05	·3502	·3512	— ·017	·145
2·783	26·80	·3502	·3520	— ·027	·136

Owing to the inconsiderable differences in concentration the values of u_0 are only correct to about 10 $^0/_0$. The form of the (c, u_0) curve is evidently somewhat like that shown in Figure 1.

If, however, we assume that a chemical reaction, such as

$$SiO_2 + H_2O = H_2SiO_3 \qquad (\alpha)$$

takes place, then we must increase u_0 by $\frac{18}{60} . c/1 - c$. This is done in the last column and no negative adsorption is then indicated. There was, however, no evidence of such a hydration of the silica. There was no apparent change in the condition of the silica on addition of the solutions, and silica exposed to water vapour did not adsorb by any means the quantity of water demanded by equation (α).

Returning to a consideration of the observations on charcoal, we have already noted that in dilute solutions $u_0/c^{\frac{1}{2}}$ is a constant, and as c increases $u_0/c^{\frac{1}{2}}$ decreases.

Professor ARRHENIUS suggested that if I exposed charcoal to water vapour in a desiccator, I would be able by direct weighing to estimate the amount of water adsorbed in absence of acetic acid. The equilibrium between charcoal and water vapour is of course the same as that between charcoal and water at the same temperature. I therefore put into a desiccator a beaker of water and a weighing bottle containing a known weight of charcoal and after a week found the increase in weight of the charcoal was constant.

If we denote this increase in weight per gram charcoal by w_∞ then $w_\infty = \cdot 396$ grs, at room temperatures (18° C.) two determinations giving ·394 and ·398.

Now

$$\begin{aligned} u_0 &= u - w \, . \, c/1 - c \\ &= u - w_\infty c/1 - c \quad \text{at very great dilutions} \\ &= u \quad \text{to 1st approximation.} \end{aligned}$$

Hence we have found that at great dilutions

$$u/c^{\frac{1}{2}} = \text{constant.}$$

This equation and the observations suggest that the general law governing adsorption of water and acetic acid in the case examined may be

$$(4) \qquad u/w = \mathrm{A}\left\{c/1 - c\right\}^{\frac{1}{2}}, \text{ where A is constant.}$$

For at great dilutions this becomes

$$u_0 = \mathrm{A}\, w_\infty c^{\frac{1}{2}},$$

which has been found above.

Also $u/w = u_0/w + c/1 - c$

so that $u_0/w = \mathrm{A}\{c/1 - c\}^{\frac{1}{2}} - c/1 - c$

or $$u_0 \Big/ \left(\frac{c}{1-c}\right)^{\frac{1}{2}} = \left\{\mathrm{A} - \left(\frac{c}{1-c}\right)^{\frac{1}{2}}\right\} . w. \tag{5}$$

Now w will evidently decrease, it is most natural to suppose, with increase of u and c. Hence $u_0 \Big/ \left(\frac{c}{1-c}\right)^{\frac{1}{2}}$ will decrease with increase of c, as has been found. If, therefore, as the observations suggest, equation (4) holds, it supplies us with a second equation connecting u and w in terms of measurable quantities, so that we can then determine u and w. For A is easily determined. Thus at 18° C.

$$u/c^{\frac{1}{2}} = \mathrm{A} . w_{\infty} = 1{\cdot}3$$

and

$$w_{\infty} = {\cdot}396, \therefore \mathrm{A} = 3{\cdot}3.$$

Unfortunately results at greater concentrations of the acid do not confirm this suggestion. For equation (5) shows that $u_0 = 0$ when

$$\mathrm{A} = \{c/1 - c\}^{\frac{1}{2}}$$

$$\text{or } c/1 - c = 10{\cdot}8$$

$$\text{or } c = {\cdot}913.$$

And positive adsorption was found at greater concentrations (at 25·6° C. however). If it had been possible to obtain observations of adsorption of small quantities of water with great excess of acid, — observations corresponding to those with greatly diluted acid — such information would have been very useful in deciding this point. But information was obtained by another method. This was simply to leave the charcoal in contact with the vapour of a solution of acetic acid. Two known quantities of the charcoal under investigation contained in weighing bottles were put into a desiccator along with a beaker containing about 50 ccm. of solution whose concentration was roughly known. At first the charcoal was weighed every day as it was believed that the increase in weight due to adsorption of the vapour would be complete in about ten days — the time found for adsorption of water vapour and acetic acid vapour. The desiccators were also evacuated by an air pump at first. Equilibrium however was only found after a very long period — namely a hundred days or so.

The weighing bottles had ground glass stoppers which were inserted when the bottle and contents were weighed, as it was found that the adsorbed vapour readily escaped from the charcoal into free air. When the successive weighings on different days gave the same value, it was assumed that equilibrium had been attained.

The concentration of the solution in the beaker was then accurately determined and the charcoal containing the adsorbed vapour dropped into the solution. After being well shaken up, the concentration of the solution was redetermined after 24 hours. No change in concentration indicated equilibrium.

Let $i =$ increase of weight per gram charcoal.[1]

$$\left.\begin{aligned}&\text{Then } u + w = i\\&\text{Also } u = u_0 + w \,.\, c/1 - c\end{aligned}\right\}$$

These two equations enable us to determine both u and w. A row of desiccators containing solutions of different concentrations were set up. Of these, the weaker solutions were destroyed by the development of a fungus before equilibrium was attained. The same fungus grew upon the charcoal in some of the more concentrated solutions. In other cases the true equilibrium had not been attained when the charcoal was emptied into the corresponding solution. But there survived the following results.

Table 5 (a). (Room Temperature 18° C.)

(1) $c = 0$ (Pure water)

$$i = \left.\begin{matrix}\cdot 394\\ \cdot 398\end{matrix}\right\} \text{after 7—14 days.}$$

$$i = \cdot 396.$$

---

[1] The amount of *air* adsorbed is ignored. If 1 % air be adsorbed originally this is probably almost entirely displaced by the water and acid. i should be corrected by ·01, and u, w, and u_0, i then refer to ·99 gms charcoal.

(2) $c = \cdot963$
$i = \cdot548$, after 7—14 days.

(3)

Days	Mass
0	1·000
25	1·360
60	1·435
71	1·444
113	1·457
118	1·456
125	1·457

$i = \cdot457 \qquad c = \cdot0519 \qquad \frac{c}{1-c} = \cdot0548.$

(4)

Days	Mass	Mass
0	1·000	1·000
25	1·424	1·429
60	1·500	1·515
68	1·498	1·514
71	1·496	1·513
77	1·493	1·509
81	1·494	1·510

$i = \cdot502 \qquad c = \cdot2628 \qquad \frac{c}{1-c} = \cdot356.$

(5)

Days	Mass	Mass
0	1·000	1·000
25	1·413	1·387
60	1·481	1·482
68	1·484	1·485
71	1.482	1·488
77	1·482	1·487
81	1·4828	1·4877

$i = \cdot485 \qquad c = \cdot4073 \qquad \frac{c}{1-c} = \cdot687.$

From (1) we get

$w_\infty = .396$

» (2) $u_\infty = \cdot552$ approx.

» (3) $\left.\begin{array}{ll} u + w & = \cdot457 \\ u & = \cdot135 + \cdot0548\, w \end{array}\right\}$

$\left.\begin{array}{ll} u & = \cdot152 \\ w & = \cdot305 \end{array}\right\}$

From (4) $\left.\begin{aligned} u + w &= \cdot 502 \\ u &= \cdot 205 + \cdot 356\, w \end{aligned}\right\}$

$\left.\begin{aligned} u &= \cdot 283 \\ w &= \cdot 219 \end{aligned}\right\}$

» (5) $\left.\begin{aligned} u + w &= \cdot 485 \\ u &= \cdot 223 + \cdot 687\, w \end{aligned}\right\}$

$\left.\begin{aligned} u &= \cdot 330 \\ w &= \cdot 155 \end{aligned}\right\}$

The values of u_0 are interpolated from Table 2 (a).

The change in concentration of solution on pouring in saturated charcoal was about $\frac{1}{10}$th %.

The (u, w) diagram is shown in Figure 4 (I).

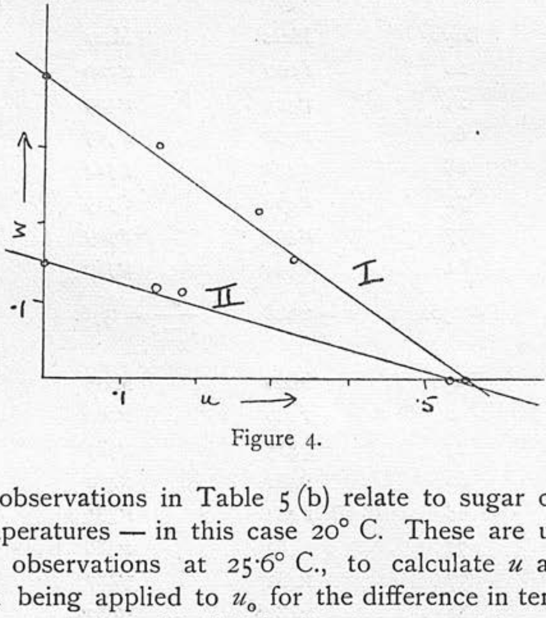

Figure 4.

The observations in Table 5 (b) relate to sugar charcoal at room temperatures — in this case 20° C. These are used along with the observations at 25·6° C., to calculate u and w, no correction being applied to u_0 for the difference in temperature. Such a correction would slightly increase u_0 and hence increase the value found for u and decrease that found for w. The values of u_0 are taken from Table 3 (c) through extrapolation.

Table 5 (b).

(1) $c = 0$
$i = \cdot 1450, \cdot 1466, \cdot 1445,$ (10—15 days)
$= \cdot 1482$ (40—45 days)

(2) $c = \cdot 963$
$i = \cdot 510, \cdot 530$

(3) $c = \cdot 1129$
$i = \cdot 2647, 2681$

(4) $c = \cdot 1998$
$i = \cdot 2947, 2974$

These give (1) $w_{\infty} = \cdot 147$

(2) $u_{\infty} = \cdot 53$ (approx.)

(3) $$\left.\begin{aligned} u + w &= \cdot 266 \\ u &= \cdot 134 + \cdot 127\, w \end{aligned}\right\}$$

$$\left.\begin{aligned} u &= \cdot 149 \\ w &= \cdot 117 \end{aligned}\right\}$$

(4) $$\left.\begin{aligned} u + w &= \cdot 296 \\ u &= \cdot 152 + \cdot 250\, w \end{aligned}\right\}$$

$$\begin{aligned} u &= .181 \\ w &= \cdot 115 \end{aligned}$$

The $(u,\ w)$ curve is shown in Figure 4 (II).

Table 5 (c). 20° C.

(1)	(2)	(3)	(4)
$c = 0$	$c = \cdot 963$	$c = \cdot 218$	$c = \cdot 490$
$i = \cdot 486$	$i = \cdot 587$	$i = \cdot 546$	$i = \cdot 565$

These observations are on blood charcoal used in 25·6° determinations.

It may be noticed that the points lie near the line joining the points on the axes. The curve is apparently slightly concave towards the origin, and the straight line $\dfrac{u}{u_{\infty}} + \dfrac{w}{w_{\infty}} = 1$ may be taken as a first approximation to it.

The information given by the observations on this point and on the previous suggestion that the relation $u/w = \mathrm{A}\,.\,(c/1-c)^{\frac{1}{2}}$ might exist is presented in the table following.

Table 6 (a).

c	u	w	$\dfrac{u}{w}\Big/\left(\dfrac{c}{1-c}\right)^{\frac{1}{2}}$	$\dfrac{u}{u_{\infty}} + \dfrac{w}{w_{\infty}}$
0	0	·396	3·30	1·00
·0519	·152	·305	2·13	1·05
·2628	·283	·219	2·17	1·07
·4073	·330	·155	2·57	1·00
1·000	·552	0	—	1·00

Table 6 (b).

0	0	·147	10·5	1·00
·1129	·149	·117	3·57	1·08
·1998	·181	·115	3·15	1·12
1·000	·53	0	—	1·00

Table 6 (c).

c	u	w	$\frac{u}{w}\Big/\left(\frac{c}{1-c}\right)^{\frac{1}{2}}$	$\frac{u}{u_\infty}+\frac{w}{w_\infty}$
0	0	0·49	2·2	1·00
·218	0·26	0·28	1·8	1·01
·490	0·39	0·18	2·2	1·02
1·000	0·59	0·	—	1·00

The fifth column of this table shows that *at least as a first approximation*

$$\frac{u}{u_\infty}+\frac{w}{w_\infty}=1 \tag{6}$$

may be taken as a second relation connecting u and w.

Solving (3) and (6) which are both linear in u and w we thus can easily obtain a set of values of u and w corresponding to values of c or $c/1-c$. It might thus be possible to obtain the true relation connecting u and c, and w and c. Specimen values of u, w and c are so presented in Table 6 above. But it has not been thought advisable to present a (c, u) curve so constructed until more accurate observations on the adsorption from the vapour phase of the acetic acid — water mixtures are completed.

The observations so far lead to the following obvious conclusions. At great dilutions the acetic acid is adsorbed directly as the square root of the concentration of the acid outside the charcoal. With increasing concentration of the acid in the solution, the amount adsorbed per gram of charcoal tends to a maximum which is attained with the pure acid.

Summary.[1]

(1). It has been shown that the usual method of calculating adsorption results leads to inaccurate conclusions, and in moderately concentrated solutions neither the volume of solution nor its mass outside the charcoal may be regarded as sufficiently constant.

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[1] Some of these conclusions were mentioned by Professor ARRHENIUS in a lecture at Göttingen, June 8 1912, in cognisance of my results.

(2). It is pointed out that not merely the solute but also the solvent must be regarded as being adsorbed.

(3). A method is indicated whereby in the case where the vapour phase gives the same adsorption equilibrium as the liquid phase, the amounts of solvent and solute adsorbed may be calculated.

(4). An explanation is offered of »negative» and »anomalous» adsorption.

(5). A second relation (approximate at least) connecting the amounts of solvent and solute adsorbed is indicated.

(6). A true adsorption maximum is indicated which is the same as the amount of vapour adsorbed of the substance under investigation at the given temperature. Hence it may be expected that gases under their critical temperature will also have this maximum of adsorption.

(7). It is suggested that at great dilutions n in $a = kc^n$ becomes a whole number or simple fraction.

It must of course be pointed out that these remarks apply only to solutions and more particularly to the case studied. The case of salts, for example, which have no vapour pressure is not considered.

In conclusion I would seek to express my deep gratitude to Professor ARRHENIUS who first directed my attention to this most interesting study, and who has throughout given me every possible assistance in its prosecution and in the presentation of the results. And to my fellow students in the laboratory are also due my sincerest thanks for many acts of kindness and assistance.

Nobel Institute for Physical Chemistry,

Experimentalfältet, 1st July, 1912.

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Tryckt den 5 mars 1913.

Uppsala 1913. Almqvist & Wiksells Boktryckeri-A.-B.

On "Negative" Adsorption.

BY

A. M. WILLIAMS, M.A., B.SC., 1851 Exhibition Scholar
of the University of Edinburgh.

(From the Muspratt Laboratory of Physical and Electro-Chemistry,
University of Liverpool.)

(*A Paper read before the Faraday Society, Wednesday, April* 22, 1914,
PROFESSOR ALFRED W. PORTER, F.R.S., *in the Chair.*)

Reprinted from the *Transactions of the Faraday Society,* 1914.

ON "NEGATIVE" ADSORPTION.

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INTRODUCTION.

In 1898[*] Lagergren[†] observed that on shaking up solutions of electrolytes with charcoal or silica the concentration of the salt in the solution *increased* instead of decreasing. This "negative" adsorption fitted in very well with the deductions from Gibbs's[‡] well-known formula. Hägglund[§] repeated Lagergren's experiments with "pure" charcoal and failed to obtain anything save indications of slight positive adsorption. Lachs and Michaelis[‖] also cite experiments interpreted as contradicting Lagergren's results. Evans[¶] using filter paper as adsorbent, found an adsorption maximum passing to zero, but not negative adsorption. More recently numerous examples of "anomalous" adsorption[**] have appeared, where the adsorption passes through a maximum and decreases instead of continuously increasing with increase of concentration, while Schmidt[††] believed he had observed a maximum of adsorption with acetic acid solutions, but this appears to the author to be erroneous.[‡‡] In studying adsorption by crystals, Marc[§§] also appeared to find a maximum, but his interpretation of it differed from Schmidt's.

Several experimenters[‖‖] have obtained maxima and minima of adsorption and also negative adsorption working with more than one substance in solution. But, in such cases, the possibilities of chemical action are not excluded (and the method of calculation is open to the same criticism as is directed against Schmidt).

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[*] After this was written I found a paper by Gore, *Chem. News* (1894), 69, pp. 23, 33, 44, containing numerous cases of negative adsorption by silica. Trouton, B.A. Report, 1911, p. 328, seems to have repeated some of Gore's work.

[†] *Bihang till K. Svenska Vet.-Akad. Handlingar*, 24, ii., 4.

[‡] Works, I, p. 336. See also J. J. Thomson, *App. of Dyn. to Phys. and Chem.*, p. 191.

[§] *Koll. Zeitsch.*, 7, p. 21.

[‖] *Zeitsch. f. Elektroch.*, 1911, p. 1.

[¶] *Journ. Phys. Chem.*, 10, p. 290.

[**] Biltz u. Steiner, *Koll. Zeitschr.*, 7, p. 112. Herzog u. Adler, *Koll. Zeitschr.*, I, Suppl. Heft 2. Michaelis u. Rona, *Bio. Zeitschr.*, 15, p. 196, etc. Freundlich, *Zeitsch. f. physik. Ch.*, 73, 385. Dreyer and Douglas, *Proc. Roy. Soc.*, 82 (B), p. 185. Morawitz, *Koll. Beihefte*, 1, p. 301. Lottermoser, *Zeitsch. f. physik. Ch.*, 62, p. 377. Moore and Ryland, *Bio. Journ.*, 5, p. 32, etc.

[††] *Zeitsch. f. physik. Ch.*, 74, p. 689 ; 77, p. 641 ; 78, p. 667 ; 83, p. 674.

[‡‡] Williams, *Medd. fran K. Vet.-Akad., Nobelinstitut*, 2, 27.

[§§] *Zeitsch. f. physik. Ch.*, 76, p. 58.

[‖‖] Estrup, *Koll. Zeitsch.*, 7, 299 ; *Oversikt, K. Danske Vid-Sels. Förh.*, 1912, No. 4 ; 1913, No. 1. Oryng, *Koll. Zeitsch.*, 13, pp. 9, 14, etc.

If M grams of solution of, say, a salt in water be shaken up with G grams adsorbent, and if the concentration of the salt be c_0 grams per gram solution initially and c finally, then the amount adsorbed in grams per gram adsorbent (if no water is adsorbed) is

$$u_0 = \frac{M}{G} \cdot \frac{c_0 - c}{1 - c}.$$

But if w grams water per gram adsorbent be adsorbed then the amount should be

$$u = u_0 + w \, . \, c/1 - c.$$

(Also, if the area of one gram adsorbent be A then we may put in Gibbs's equation:

$$\left.\frac{u_0}{A} = \Gamma = -\frac{c}{RT} \cdot \frac{d\sigma}{dc}.\right)$$

It has been generally found that if c is small, u_0 is positive.* As long as no chemical action takes place and the relative adsorption of the two substances, salt and water, appears to depend on their relative masses present, it seems natural to assume that with c nearly equal to unity more water than salt will be adsorbed. Hence we may expect that u_0 will at first increase to a positive maximum, decrease, pass through zero and become negative (probably being equal to $-\infty$ when $c = 1$). This would explain and reconcile the results of Lagergren, Evans, Lachs and Michaelis, etc.

EXPERIMENTAL PART.

Blood charcoal from Merck was being purified by washing for certain experimental purposes and the opportunity of testing the above idea suggested itself. The charcoal was cleaned by boiling up with distilled water, and finally by repeated washings in the cold. The conductivity of the washings fell from 120×10^{-6} mhos to $4 - 5 \times 10^{-6}$ mhos at 25° C.,† where it remained steady. The conductivity of the water employed was 2×10^{-6} mhos. This final preparation was used with solutions of several electrolytes. The changes of concentration in the solutions, after treatment with the charcoal, were found to be small. In general about five grams of charcoal were shaken up with 100 grams solution in a Jena flask closed with a paraffined cork. Along with every experiment a blank was performed, a hundred grams of solution being shaken up without charcoal. The flasks were rotated for 24 to 48 hours in a thermostat at 25° C. The concentration of the solutions was determined as follows: Similar amounts were withdrawn from the original solution, the blank and the test solution (free from charcoal of course). They were then diluted down to the same extent. All dilutions were done by weighing. The concentrations of the resulting solutions were then determined from their conductivities, employing the telephone method. No change was observed between the blank and the original solution.

Alternate readings were then taken with the diluted blank and test solutions. Thus first the diluted blank solution, then the diluted test solution, then again the former, then again the latter were placed in rotation in the same conductivity cell (washing out, of course, with the replacing solution each time), with the same resistance out in the box and hence reading near the same place on the bridge. When the two pairs of readings were found concordant, they were accepted. The ratio c_0/c was

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* See, however, Gore, *loc. cit.*, Trouton, *loc. cit.* Instances are given of negative adsorption at low concentrations becoming positive adsorption at higher concentrations.

† Allowing 10 grams water to 1 gram charcoal.

thus determined with as great accuracy as the method and the apparatus employed allowed. The readings on an ordinary metre bridge were taken to the nearest tenth of a millimetre. Assuming an error of ·1 mm. in opposite directions in the two readings, the error in c_0/c would be 8 in 10,000.

It is possible that, since Kohlrausch and Holborn's tables were used for interpolation to determine the concentration in the diluted solutions, the values of c_0 and c may be out in the same ratio by a small percentage. But this is unimportant, and c_0/c is unaffected. A sharp minimum was always obtained by diluting sufficiently—generally 25 c.c. were made up to 2 litres with the more concentrated solutions. The error introduced into calculation by error in dilution would be less than 1 in 10,000. The solutions were also tested with methyl orange, phenolphthalein, and in some cases rosolic acid, but no change in their behaviour to these reagents occurred after being shaken up with charcoal. The salts employed were the purest preparations.

The observations are as follows :

	KCl.	
c.	c_0/c.	u_0.
·00044	1·027	+ ·00032
·00266	1·021	+ ·00128
·00616	1·018	+ ·00230
·0205	1·0061	+ ·0025
·0398	1·0014	+ ·0011
·0563	1·0014	+ ·0017
·0680	0·9988	— ·0017
·0721	·9990	— ·0018
·101	·9995	— ·0012
·128	·9990	— ·0026
·170	·9981	— ·0077
	NH_4Cl.	
·0122	1·0060	+ ·0015
·0229	1·0077	+ ·0034
·0489	1·0114	+ ·0119
·0992	1·0035	+ ·0074
·152	1·0013	+ ·0045
·191	1·0007	+ ·0033
	$BaCl_2$.	
·095	1·0123	+ ·026
·153	1·0070	+ ·028
·220	1·0055	+ ·036
	$CuSO_4$.	
·067	1·020	+ ·033
·114	1·007	+ ·024
	$MgSO_4$.	
·00043	1·101	+ ·00089
·00123	1·072	+ ·0024
·0257	0·991	— ·0044
·0516	·987	— ·014
·0528	·986	— ·016
·1001	·986	— ·034
·1538	·990	— ·039

It will be seen that with KCl and $MgSO_4$ maxima of u_0 were found, and u_0 afterwards became negative; with NH_4Cl a maximum was found, but at great concentrations negative adsorption had not yet been found. With $BaCl_2$ even at great concentrations the adsorption was still increasing; and nothing can be said about $CuSO_4$.

SUMMARY.

It has been experimentally found with some electrolytes in water that the "adsorption" is at first positive, increases to a maximum, decreases, passes through zero, and becomes negative.

Attention is therefore drawn to the fact that with different concentrations of the same solution both positive and negative "adsorption" of the solute may be observed. Hence both solvent and solute must be regarded as being adsorbed.

These experiments were performed in May and June in the Muspratt Laboratory. To Professor F. G. Donnan, F.R.S., are due the thanks of the author for interest, encouragement, and advice.

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NEGATIVE ADSORPTION.

By A. M. WILLIAMS, M.A., B.Sc.

DISCUSSION.

The Chairman remarked that though the recognition of the simultaneous adsorption of water and salt served to clear up much of the behaviour in cases of anomalous adsorption, he was very doubtful whether it was competent to explain everything. For example, it threw no light on the experimental results obtained by Professor Trouton and referred to in the paper. He added, further, that the correction to be made for the water adsorption depended upon the relative quantities of solution and adsorbent taken; and in most of Professor Trouton's work the amount of solution taken was so large that the correction necessary could only be very small. This was fortunate, because it was very difficult to estimate the amount of water adsorbed.

Mr. A. M. Williams: The correction on u_0 for water adsorption for any given equilibrium concentration depends solely on that concentration, and hence is *independent* of the volume of solution relative to one gram adsorbent. For suppose a gram of adsorbent is in equilibrium with a solution containing equal masses of solvent and solute. Then, if the adsorbent has taken up one gram solvent, the correction on u_0 is one gram also, whether there be 50 or 500 c.cms. of solution. As written above, the correction is $wc/1-c$, and w is evidently a function of c only. If, however, the calculation has been based on the volume concentrations, the correction is somewhat different, but still approximately independent of the volume of solution taken. For if we denote by u_v the adsorption reckoned on the assumption that the initial volume of the solution v_0 does not change and v be the final volume, we have, using a notation similar to above—

$$u_v = v_0(c_0 - c).$$

But—

$$\begin{aligned} u &= v_0c_0 - vc = v_0(c_0 - c) + (v_0 - v)c. \\ &= u_v + (v_0 - v)c. \end{aligned}$$

Let the specific volumes in solution of concentration c be s_1 and s_2 for solute and solvent respectively. Then—

$$v_0 - v = us_1 + ws_2$$

Hence the correction on u_v is $(us_1 + ws_2)c$, which is independent of v_0 and dependent on c only, s_1 and s_2 being regarded as approximately constant near c. The correction *cannot* therefore be altered in *magnitude* for any equilibrium concentration c by varying the *volume* of solution in contact with one gram adsorbent. (It is assumed, of course, that the mass of solution is large compared with $u + w$.) It can only be ignored provided $u - u_v/u$ or $(s_1 + s_2w/u)c$ is small relative to unity in the case of volume concentrations, or $u - u_0/u = wc/u(1 - c)$ is small in the case of mass concentrations as employed by the author.

Until a second equation is deduced connecting u, w, and c, we are not entitled to say that the correction is small, unless other considerations indicate this clearly, *e.g.* with dilute aqueous solutions of acetic acid and charcoal it was found (Williams, *loc. cit.*) that $u_0/c\frac{1}{2}$ was nearly constant and w about ·5. Hence the correction being proportional to $c\frac{1}{2}$ could be made very small by decreasing c. (By taking observations on the adsorption from the vapour phase u and w were determined. So far as the author knows, this is the only case in which they have actually been measured.)

It is obvious that if there was a relation of the type $u/w = kc/1 - c$, then provided k is less than unity, we would obtain negative values of u_0, that is, "*negative* adsorption."

It may further be pointed out that since s_1 and s_2 are not certainly constants if c varies much, u_v will vary with v_0, unless v_0 is very great. Professor Trouton has perhaps found this, but no data are given in such of his results as are published.

The author does not put forward any *mechanism* to explain the phenomenon of adsorption, but merely wishes to emphasise the fact that *both* solute *and* solvent are removed from the main body of the solution—that is, both are in some degree adsorbed.

The Adsorption of Vapours

BY

A. M. WILLIAMS, M.A., B.Sc.

(1851 Exhibition Scholar of the University of Edinburgh.)

(A Paper communicated to the TRANSACTIONS *of the Faraday Society, June* 1914.)

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By A. M. WILLIAMS, M.A., B.Sc., 1851 Exhibition Scholar of the University of Edinburgh.

(*A Paper communicated to the* TRANSACTIONS *of the Faraday Society, June* 1914.)

An investigation by Professor F. G. Donnan and the author on the thermodynamics of adsorption suggested that instead of using log a and log p as variables in plotting adsorption curves (a is the number of c.cm.'s at N.T.P. adsorbed per gram adsorbent at the pressure p) it might be of interest in the case of gases below their critical point to use log a and log p/P, where P is the saturation vapour pressure of the adsorbed vapour in liquid form. This has been done before by Trouton,* who showed that a does not vary greatly with T if p/P is constant, in the case of water vapour adsorbed by flannel.

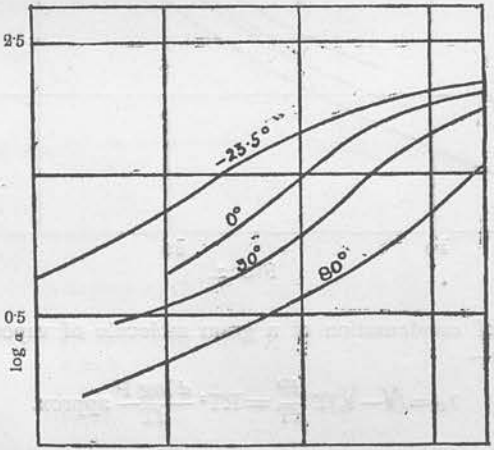

FIG. 1.

The graphs given show the curves for ($\log_{10} a, \log_{10} p$) and ($\log_{10} a, \log_{10} p/P$) from the observations of Titoff † on the adsorption of ammonia by charcoal. It will be seen that the apparently dissimilar curves of Fig. 1 become more obviously curves of the same type in Fig. 2, and provided there is no sudden change in the curvature near log $p/P = 0$, there is a *finite maximum* of adsorption for $p/P = 1$. Titoff's observations with carbon dioxide may be similarly treated and lead to the same conclusions. Arrhenius ‡ by extra-

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* *Proc. Roy. Soc.*, 1905, A, 77, 292.

† *Zeitsch. f. Physik. Chemie*, 1910, 74, 641.

‡ *Meddelanden fran K. Veten. Akad.*, Nobel Institut., 1911, 2, 7.

polating from an empirical formula suggested by the work of Schmidt on solutions deduced a maximum of adsorption which he suggests to be independent of the temperature and supposes to exist even above the critical point.

It can easily be shown from the graphs that $\left(\frac{\Delta \log p/P}{\Delta T}\right)_a$ steadily decreases as p/P approaches unity. This suggests that $\left(\frac{\partial \log p/P}{\partial T}\right)_a = 0$ when $p/P = 1$. Now it may be shown that if a small quantity of gas be adsorbed at *constant* temperature and pressure (not necessarily *equilibrium* pressure) the heat evolved per gram molecule would be—provided the volume of the gaseous phase per gram charcoal is negligible, etc.—

$$\lambda_p = (v - v_0)T\left(\frac{\partial p}{\partial T}\right)_a = RT^2\left(\frac{\partial \log p}{\partial T}\right)_a \text{ approx.}$$

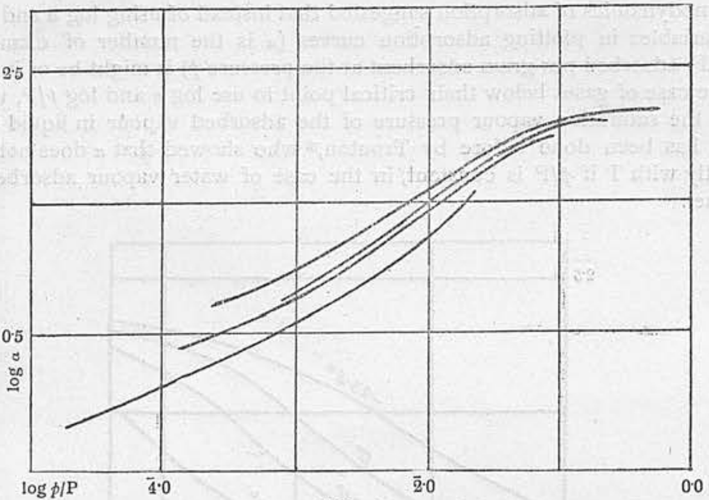

FIG. 2.

The heat of condensation of a gram molecule of vapour at the same temperature is—

$$\lambda_P = (V - V_0)T\frac{dP}{dT} = RT^2\frac{d \log P}{dT} \text{ approx.}$$

Here—

v = volume of one gram molecule of gas at p and T.
V = " " " " P and T.
v_0 = " " " of adsorbed gas at p and T.
V_0 = " " " of liquid at P and T.

Hence if *liquid* were adsorbed the corresponding heat would be—

$$\lambda = \lambda_p - \lambda_P = RT^2\left(\frac{\partial \log p/P}{\partial T}\right)_a \text{ approx.,}$$

which is, of course, the well-known formula for the heat of dilution.

Let us consider two curves for log p/P, log a at temperatures T and T + ΔT near $p/P = 1$. The difference in abscissæ (Fig. 3) is proportional to λ. It may be expected that this sinks to zero as was previously indicated. Thus

Bellati and Finazzi * experimenting on silica found that the heat of immersion in water sank to zero as the silica was saturated with water vapour. The author found that specimens of charcoal saturated with 70 per cent. benzene and 130 per cent. chloroform by weight respectively evolved no heat on dropping into the corresponding liquids at the same temperature, though ·4 calories per gram charcoal could easily have been detected. (On the other hand air-saturated charcoal evolved per gram more than 25 calories in benzene and 40 calories in chloroform.) Hence, since λ is zero when $p/\mathrm{P}=1$, the difference in abscissæ is zero when $p/\mathrm{P}=1$. That is both the curves cut the line $\log p/\mathrm{P}=0$ at the same place, or *the adsorption when* $\mathrm{p}=\mathrm{P}$ *is independent of the temperature.*

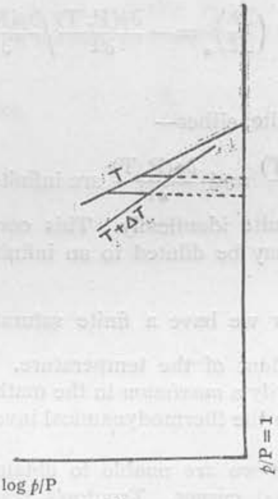

FIG. 3.

Otherwise—

$$\lambda=(v-v_{\circ})\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{a}-(\mathrm{V}-\mathrm{V}_{\circ})\mathrm{T}\,\frac{d\mathrm{P}}{d\mathrm{T}}.$$

Ultimately, when $p=\mathrm{P}$,

$$v=\mathrm{V},$$

$$v_{\circ}=\mathrm{V}_{\circ}\ \text{(very likely)},$$

$$\lambda=0,$$

$$\therefore\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{a}=\frac{d\mathrm{P}}{d\mathrm{T}}\ \text{when}\ \frac{p}{\mathrm{P}}=1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Suppose the relation between a, p, and T can be represented as—

$$a=\phi(p,\mathrm{T}),$$

then the value of $\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{a}$ is determined by—

$$0=\left(\frac{\partial \phi}{\partial p}\right)_{\mathrm{T}}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{a}+\left(\frac{\partial \phi}{\partial \mathrm{T}}\right)_{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

---

* *Atti del R. Istituto Veneto*, 1900, lix., II., and 1902, lxi., II., p. 507.

The relation between the amount adsorbed for the saturation vapour pressure and the temperature is given by—

$$a_\infty = \phi(\mathrm{P}, \mathrm{T}),$$

where P is a function of T.

The gradient of this curve, that is, the variation of a_∞ with the temperature, is given by—

$$\frac{da_\infty}{d\mathrm{T}} = \frac{\partial\phi(\mathrm{P}, \mathrm{T})}{\partial \mathrm{P}} \cdot \frac{d\mathrm{P}}{d\mathrm{T}} + \frac{\partial\phi(\mathrm{P}, \mathrm{T})}{\partial \mathrm{T}};$$

but, finally, we have from above (1) and (2)—

$$\frac{d\mathrm{P}}{d\mathrm{T}} = \left(\frac{\partial p}{\partial \mathrm{T}}\right)_a = -\frac{\partial\phi(\mathrm{P}, \mathrm{T})}{\partial \mathrm{T}} \Big/ \frac{\partial\phi(\mathrm{P}, \mathrm{T})}{\partial \mathrm{P}},$$

when $p = \mathrm{P}$.

Hence, since $\frac{\partial \mathrm{P}}{\partial \mathrm{T}}$ is finite, either—

(i) both $\frac{\partial\phi(\mathrm{P}, \mathrm{T})}{\partial \mathrm{T}}$ and $\frac{\partial\phi(\mathrm{P}, \mathrm{T})}{\partial \mathrm{P}}$ are infinite, whence a_∞ being equal to $\phi(\mathrm{P}, \mathrm{T})$ is infinite identically. This corresponds to the case of solutions which may be diluted to an infinite extent.

or—

(ii) $\frac{da_\infty}{d\mathrm{T}} = 0$, or we have a finite saturation pressure adsorption which is independent of the temperature. It should be noted that this is not necessarily a *maximum* in the mathematical sense, so far as we can judge from the thermodynamical investigation above.

It is unfortunate that we are unable to obtain more information concerning a_∞ from $(p/\mathrm{P}, a)$ curves. Trouton's results * show a change of curvature comparatively early. This was also found by Masson and Richards † who concluded that a_∞ was infinite. The only other observer who has taken the adsorption up to the vapour pressure (excluding the case of gels) is Hunter ‡ who, indeed, gives finite adsorptions at pressures greater than the saturation vapour pressure, *e.g.* his cyanogen figures. His results do not clearly show such a change of curvature. It is uncertain whether they are explicable on the ground that he did not allow the adsorption at the given pressure to be complete when he took readings (the rate of adsorption slows down very considerably near $p/\mathrm{P} = 1$ as is easily found experimentally) or whether he obtained supersaturation of the charcoal. Several experiments of the author point to this as a possibility. If charcoal originally *in vacuo* is put into contact with the vapour from the pure liquid in another part of the same vessel and is saturated or nearly so and some of the liquid be dropped upon the charcoal, it has invariably been found that the charcoal + adsorbate loses weight till it approaches " saturation " again. §

These facts support the idea of a finite " saturation pressure " adsorption. The curves from Titoff's observations seem indeed to indicate a *maximum* of adsorption at the saturation pressure of the vapour. But the author has found with sulphur dioxide at − 10° C. that when p/P approaches unity, in fact

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* *Loc. cit.* † *Proc. Roy. Soc.*, A, 78, 412.

‡ *Jour. Chem. Soc.*, 1865, p. 285; 1867, p. 160; etc.

§ Compare, however, contra, Masson and Richards, *loc. cit.*

after $p/P = \cdot 9$, the adsorption curve suddenly bends up, as was easily found by Trouton[*] and Masson and Richards[†] after $p/P = \cdot 2$ in the case of water vapour. It may therefore be unwise to extrapolate from Titoff's observations.

SUMMARY.

From considerations relating to the heat of adsorption near the saturated vapour pressure of a fluid (the adsorption being reversible) it is deduced thermodynamically that the adsorption is either infinite or finite and independent of the temperature.

Evidence is adduced as to the adsorption being finite, but nevertheless not necessarily a *maximum* in the mathematical sense.

In conclusion the author would seek to express his indebtedness to Professor A. W. Porter, F.R.S., of the Physics Department, University College, for his kindness in reading and assisting him in the presentation of this paper.

UNIVERSITY COLLEGE,
LONDON.

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[*] *Loc. cit.*

[†] *Loc. cit.*

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The Adsorption of Sulphur Dioxide by Charcoal at −10° C.

By **A. M. Williams**, M.A., B.Sc.

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XI.—The Adsorption of Sulphur Dioxide by Charcoal at $-10°$ C.

By A. M. Williams, M.A., B.Sc., 1851 Exhibition Scholar of the University of Edinburgh, 1911–14. *Communicated by* Professor JAMES WALKER, F.R.S.

(MS. received December 2, 1916. Read February 5, 1917.)

THE object of this research was to find how the heat evolved on the adsorption of a vapour varied with the amount adsorbed. Work in this direction had already been done by Chappuis,[*] and more recently by Titoff.[†] Neither of these experimenters carried out the adsorption till the adsorbent was even approximately "saturated," with simultaneous measurement of the heat effect. To do this, then, was the aim of the author.

The adsorbent selected was blood charcoal (puriss. Merck). Similar charcoal had been employed before by the author and no further purification by means of acids, etc., was attempted. Its relative density had been found to be 1·628. The adsorbate selected was a vapour whose liquid boiled not far from room temperature, namely, sulphur dioxide with boiling-point at $-10{\cdot}1°$ C. The sulphur dioxide was prepared by redistillation of the liquid from a siphon. The gas was passed through sodium sulphite solution to free it from traces of sulphur trioxide, and through bulbs containing concentrated sulphuric acid to dry it thoroughly. It then passed into a spiral glass worm surrounded by a freezing mixture. The exit from the condensing flask led to another sulphuric acid bubbler and finally to a caustic alkali solution which prevented the gas escaping into the air.

Instead of a Bunsen ice calorimeter such as was employed by Chappuis and by Titoff, the author used a gas calorimeter after the manner of Dewar[‡] and of Estreicher.[§] The dimensions of the calorimeter were determined with reference to a large vacuum vessel possessed by the University College, London, Chemical Laboratory. This vessel was used to contain the freezing mixture in which the calorimeter was immersed. The calorimeter is shown in fig. 1. It consists of a Dewar's vessel, silvered save for a narrow

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[*] *Wied. Ann.*, xix (1883), p. 21.

[†] *Zeits. f. physik. Chem.*, lxxiv (1910), p. 641. See also Joulin, *Ann. Chim. phys.* (5), xxii (1881), p. 398; and Favre, *Ann. Chim. phys.* (5), i (1874), p. 209.

[‡] *Proc. Roy. Soc.*, lxxiv, A (1904), p. 122, and lxxvi, A (1905), p. 325.

[§] *Zeits. f. physik. Chem.*, xlix (1904), p. 602, and *Anz. Akad. Wiss. Krakau*, 1910 A, p. 345.

strip up the side. The outer wall is extended into a ground-glass collar with a side tube at the base. A ground-glass stopper fits into the collar and the combination is sealed with mercury. Through the stopper which is also evacuated passes a capillary ending inside the calorimeter in a bulb which holds the charcoal. The gas to be adsorbed is led in through the capillary and the heat of adsorption causes evaporation of the calorimetric liquid — sulphur dioxide — and the gas evolved is collected through the side tube.*

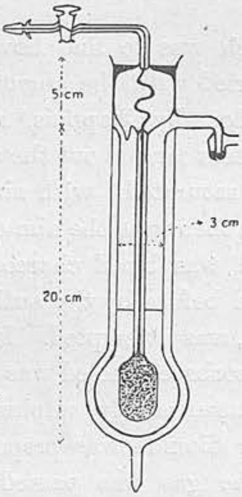

FIG. 1.

In Estreicher's experiments the rate of leak of sulphur dioxide from his vessel due to heat passing inwards was about 20 c.cm. of gas per minute, but only 5 per cent. of the total gas collected—2000 c.cm. In the author's case the leak was never more than 4 c.cm., and generally about 2 c.cm., per minute, but in some measurements it was as much as 80 per cent. of the total gas collected. Estreicher collected the gas evolved in a large aspirator containing water with a layer of white oil in which the dioxide is not so readily soluble as in water. The author was compelled to substitute mercury, as the gas was sufficiently soluble in any oil at his disposal to interfere seriously with the collection. An oil gauge was then used to indicate the pressure. It was now found that the leak appeared steadily to diminish. This was traced to cooling of the liquid sulphur

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* The calorimeter was made to the author's design by Baumbach of Manchester. The first calorimeter which subsequently broke was resilvered and evacuated by the author, the second by the maker. The rate of leak was less in the first calorimeter. The author is indebted to Dr Whytelaw-Gray for many hints as to manipulation here.

dioxide owing to rapid evaporation into the atmosphere, and was obviated by joining on a mercury bubbler to the delivery tube from the calorimeter. When the mouth of the calorimeter was closed the gas bubbled through this and the atmosphere above the liquid soon became entirely gaseous sulphur dioxide, and the temperature remained steady at that, corresponding to (say) 0·5 mm. more than the barometric pressure.*

The greatest difficulty was the adjustment of the temperature of the freezing mixture round the vacuum vessel. The observations were taken during a spell of hot weather, which no doubt contributed to the steady rise in temperature of the mixture from $-10°$ C. The variation of the leak due to radiation inwards showed that the liquid sulphur dioxide was very sensitive to changes in temperature of the surrounding bath. The leak varied also with the level of the dioxide in the calorimeter. In itself the leak was small, but when the measurement was spread over two or three hours it soon amounted to a considerable percentage of the volume of the gas evolved during the experiment. As a result, observations of the leak had to be taken from (say) two hours before the gas was let in to be adsorbed till some time after the adsorption was adjudged complete. The author is convinced that the substitution of a freezing mixture for a bath of the calorimetric liquid itself—as used by Dewar—was a grave mistake, and impaired the ease and accuracy of the observations.

The apparatus made and devised by the author for the study of adsorption is shown in fig. 2, and is essentially a constant-volume apparatus. It consisted of a large bulb whose one end was attached to the ground-glass join to which fitted the charcoal bulb part of the calorimeter. The other end joined on to a capillary tube passing into ordinary quill tubing containing a fine tip of blue glass. From below this ran a side tube with a tap connecting with the mercury pump and the gas reservoir.†

The main tube continued downwards, then upwards parallel to the blue-point tube, and constituted with its connections a manometer, pressure readings being taken in the mirror scale behind. The volume from the blue point (marked *b* in the figure) to the tap of the charcoal bulb was found from the weight of mercury of known temperature required to fill it; and the volume from the tap to the bulb (including the hole in the tap) was similarly found before joining on the filled bulb to the capillary.‡

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* It would have been possible by means of a tap to adjust the mercury so that the pressure was always (say) 78·0 cms., and so keep the dioxide at a fixed temperature.

† A two-way tap above the charcoal bulb would have been simpler.

‡ A change in volume on joining of 0·1 c.cm. would affect all the calculated values of the amount adsorbed 0·03 per cent., and the change must have been less.

The volume of the charcoal was known from its density and weight after complete evacuation.

The complete evacuation of the charcoal bulb took six days. The initial evacuation was accomplished by the water pump, the final by the mercury pump when the bulb was immersed in a bath of the vapour of boiling sulphur. At the end the last traces of adsorbed gas were removed by means of the second evacuated charcoal bulb immersed in liquid air. The evacuation was a very tedious process. The condition of the charcoal in a state of fine powder added to the difficulty, as it was borne upwards by the air leaving it. To prevent it going through all the tubes and connections a tiny plug of cotton-wool was placed in the head of the ground-glass join. The fine powder occasionally stuck in the capillary tube, and had to be brought back to the bulb by repeated tapping, or even, after disconnection at the join, by vigorous knocking on the bench. Though the volume of the bulb was 17 c.cm., it was "filled" by 4·5 gm. charcoal (density 1·63).

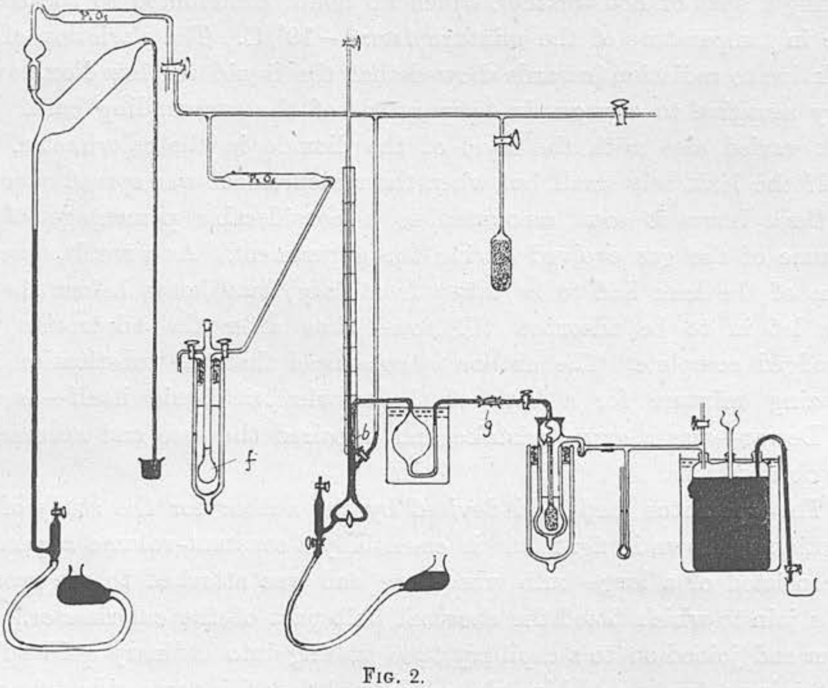

FIG. 2.

Sulphur dioxide to be adsorbed was kept in the bulb *f*, immersed in a freezing mixture of alcohol and carbon dioxide snow. When freshly made up this mixture froze the sulphur dioxide. The air was removed by freezing the dioxide in liquid air and evacuating the bulb, the solubility of the gas evolved being then 99·99 per cent. When the gas was required the mercury in the manometer was lowered, the requisite taps opened, and the freezing mixture removed until the manometer indicated the approximate pressure required. The taps were then closed, the freezing mixture replaced, and the mercury adjusted to touch the blue tip again. Mercury was also run through the tap behind the manometer before it was shut. The tap between the manometer tubes was now closed and that above the charcoal bulb opened, and the adsorption proceeded at *constant volume.* At the close the mercury was first roughly adjusted, and then on opening the closed manometer tap the pressure was accurately found with the mercury touching the fine blue point.

The heat of the adsorption vaporised some of the liquid dioxide around the charcoal bulb. This gas passed through the mercury bubbler and caused an increase in pressure, indicated on the oil gauge. Mercury was run out of the reservoir to keep the pressure constant. The volume thus collected every ten minutes was found by weighing to the nearest gram. A small correction was made for the volume of liquid dioxide and the thistle funnel tube; and another when necessary was applied for change in temperature of the initial volume of gas in the aspirator. The security of the joins, corks, etc., in the collection apparatus was regularly tested by pouring in mercury through the thistle funnel and finding if the amount recovered on adjusting the pressure was the same plus the natural leak during time of adjustment. When the gas was not being collected it passed through the tap shown above the reservoir into absorption vessels.

A short initial run was made, but owing to the fact that the liquid in the calorimeter had fallen below the shoulder of the charcoal bulb the heat effect registered was much less than it should have been. Two other complete runs were made, taking the pressure of adsorbed gas up to atmospheric. The comparison of the two sets of readings gives some idea of the accuracy of the calorimeter and method employed.

It is now necessary to indicate what calorimetric quantity is measured—that is, what is meant in this case by the "heat of adsorption." There may be defined, following Donnan,* three *isothermal* heats of adsorption, viz.: (1) *equilibrium*—the adsorption proceeds so that the vapour phase is constantly in equilibrium with the adsorbed phase; (2) *at constant pressure*—the gas at constant pressure, but not necessarily at equilibrium pressure is picked up by the adsorbent; (3) *at constant volume*—the total volume of the system is constant, and the gas is adsorbed with a fall of pressure. The heat effect registered by the author's arrangement was the *isothermal*

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* The treatment by Freundlich, *Kapillarchemie*, pp. 107–11, is confused and erroneous.

heat of adsorption at constant volume plus the heat introduced by the gas entering the adsorption chamber at a temperature higher than that of the chamber.

Sulphur dioxide does not accurately obey the law $pV = RT$. In correcting, the author made use of the data obtained by various observers.

(1) In correcting for temperature he used the data given by Leduc[*] in the deduced form

$$V_t = V_0(1 + \cdot 00396t),$$

when t is near 20° C. and the pressure is constant and not more than two atmospheres.

(2) The pressure correction was calculated from the data of Jacquerod and Pintza,[†] and of Baume.[‡] From their measurements of density at 0° C. a table was drawn up giving the values p' to be read for p the observed pressure, so as to make the gas conform to the equation $p'V = \text{constant} = RT/ 1{\cdot}023$. Specimen values thus found are given below.

p	76·00	60·00	40·00	20·00	10·00	0·00
p'	76·00	59·70	39·55	19·65	9·79	0·00

The application of the above corrections refers all volumes of gas to actual c.cms. at N.T.P., where the density of the gas is 1·023 times that calculated from the simple gas law $pV = RT$.

The observations are now given in the tables below, where

p = final pressure in cm. mercury;
a = c.cm. adsorbed measured at N.T.P.;
Δa = „ „ „ „ during an experiment;
β = c.cm. evolved from the calorimeter and measured at N.T.P.;
Δt = excess temperature of gas in reservoir over gas in adsorption bulb;
P = vapour pressure in cm. mercury.

As after a certain amount was adsorbed the rate of adsorption fell considerably, the stopcock was closed after forty minutes or so, and such non-equilibrium readings are given in brackets. In the course of work, however, opportunity was allowed for the adsorption to proceed for twenty-four hours or longer, and such readings are not enclosed in brackets. After the stopcock was closed a very small additional amount of gas would be adsorbed, but too small to affect appreciably the calculations.

---

[*] *Comptes Rendus*, cxlviii, p. 1173 (1907).

[†] *Ibid.*, cxxxix, p. 129 (1904).

[‡] *Journal de Chim. phys.*, vi, p. 1 (1908).

This was shown by the fact that the rate of leak with stopcock open and shut was the same within the limits of concordance of readings taken. The quantity of heat measured never exceeded 95 gram calories, and in general varied between 55 and 30 calories. 80 per cent. of the effect was recorded in the first half-hour and 95 per cent. in the first hour.

TABLE I.—MASS OF CHARCOAL = 4·428 GM. IN VACUO.

p.	α.	$\Delta\alpha$.	β.	Δt.	P.
0·10	94·6	94·6	165·5	28·6	76·1
(0·48) 0·36	240·0	145·1	219·9	28·6	,,
0·92	387·7	147·7	215·3	29·1	,,
(1·67) 1·64	547	159·0	213·1	28·6	,,
(3·11)	705	157·7	204·7	28·9	76·3
(5·09) 4·50	858	151·3	186·4	29·3	,,
(7·18)	1003	144·7	194·7	27·9	,,
(10·32)	1137	134·2	178·5	27·5	,,
(14·14) 13·64	1254	115·4	152·6	27·7	,,
(24·63)	1432	178·6	226·4	28·9	76·5
(39·73)	1559	126·6	156·5	29·9	,,
(54·02) 53·30	1637	77·3	91·9	30·4	76·4
(65·32)	1711	74·3	76·1	30·9	,,
(72·76) 72·05	1815	104·1	106·6	31·2	,,
(76·96) 75·50	1948	126·9	120·9	29·9	77·0
(77·73) 76·40	2065	114·8	110·6	30·5	,,

TABLE II.—MASS OF CHARCOAL = 4·428 GM.

p.	α.	$\Delta\alpha$.	β.	Δt.	P.
0·14	119·2	119·2	197·4	27·7	75·9
0·45	269·8	140·2	208·5	29·7	76·5
(1·06) 1·05	421·1	161·3	223·8	28·6	76·2
(2·67)	676	255·3	333·6	28·5	,,
(5·29)	923	246·3	317·5	28·4	76·8
10·80	1176	253·5	...	...	,,
(22·10)	1402	226·0	287·5	29·6	76·7
(43·82) 43·60	1584	181·8	226·2	30·6	76·6
(66·32)	1724	139·8	151·4	29·1	76·5
(73·20)	1837	113·1	113·8	30·5	,,
(75·79) 75·41	1961	124·6	118·1	31·1	76·6
77·12	2104	143·0	...	...	77·1

In Table III are given the equilibrium values of p and α, taken from Tables I and II. The values of p are referred to $-10·1°$ C., when the pressure of the calorimetric dioxide would be 76·0 cm. mercury, using the fact that for a given α, p/P is nearly constant. α is referred to one gram charcoal.

TABLE III.—MASS OF CHARCOAL=1·000 GM.

p.	a.	p.	a.
0·10	21·4	0·14	26·9
0·36	54·2	0·45	61·0
0·92	87·6	1·05	95·1
1·64	123·5	10·68	266
4·48	193·8	43·2	358
13·59	283	74·9	443
53·0	370	76·0	475
71·7	410		
74·6	440		
75·4	466		

In Table IV are found the calorimetric results. a is a mean value of a during the adsorption, and is usually calculated from a logarithmic interpolation formula. Save at the beginning, this value does not greatly differ from the arithmetic mean of the initial and final amounts adsorbed in any interval. Instead of expressing the heat of adsorption in calories per c.cm. adsorbed, the ratio λ_v/λ_i is given of the isothermal heat of adsorption at constant volume to the "internal" heat of vaporisation of liquid sulphur dioxide. Thus with a usual notation

$$\lambda_i = (V_G - V_L)T\frac{dP}{dT} - P(V_G - V_L).$$

Again, since

$$\beta\{\lambda_i + P(V_G - V_L)\} = \lambda_v \Delta a + C_v \,.\, \Delta t \,.\, (\Delta a + \Delta a'),$$

where C_v is the specific heat at constant volume of the gas and $\Delta a'$ is the gas entering the adsorption chamber and not adsorbed, we have

$$\frac{\lambda_v}{\lambda_i} = \frac{\beta}{\Delta a}(1·0934) - \Delta t\left(1 + \frac{\Delta a'}{\Delta a}\right)(·001436).$$

To obtain λ_v in terms of calories per c.cm. absorbed, the ratio must be multiplied by 0·250. Estreicher from the vapour pressure measurements of Matthias and Chappuis calculated that the heat of vaporisation of 1 gm. sulphur dioxide at −10° C. was 95·7 cal. Favre had found 88·2 cal. Estreicher as the mean of three very concordant measurements of volumes evolved on heating gives 95·9 cal. as the observed heat. Later, by *weighing* the gas after absorption by a liquid he gives 95·3 cal. at −11° C. The author from Regnault's vapour pressure figures calculated 95·5 cal. at −10° C., assuming with Estreicher the density of the dioxide to be normal, and using the equation

$$\lambda = RT^2\frac{d\log P}{dT}.$$

Correcting for the departure from the gas law, we get 93·2 cal. at −10° C.* Taking 93·2 cal. as the heat of vaporisation of one gram of the dioxide at −10°, the factor 0·250 is easily calculated.

TABLE IV.

a.	λ_v/λ_i.	a.	λ_v/λ_i.
8·0	1·870	9·9	1·770
33·9	1·616	40·7	1·576
68·9	1·554	75·7	1·469
103·5	1·426	120·4	1·395
137·8	1·381	177·5	1·370
176	1·306	291	1·350
210	1·443	337	1·318
242	1·417	374	1·142
270	1·407	402	1·049
303	1·349	409	0·989
338	1·310		
361	1·257		
378	1·075		
398	1·026		
424	0·993		
454	1·012		

The results of Table III are presented in graphical form in fig. 3. The curve is of the same type as that obtained by Trouton † for the adsorption of water vapour by flannel. In the present case the upward bend occurs much later than $p/\mathrm{P}=\cdot 2$, the inflexion occurring about $p/\mathrm{P}=\cdot 63$ and the bend being pronounced only after $p/\mathrm{P}=\cdot 9$. The gradient does not appear to be infinite near $p/\mathrm{P}=1$.

The calorimetric observations are shown in fig. 4. It will be seen that a *minimum* heat of adsorption is indicated. Such a minimum heat of adsorption is shown in Titoff's observations on the adsorption of ammonia by charcoal, and in Chappuis' results for the adsorption of sulphur dioxide by charcoal, etc. The author's curve then passes through a maximum and drops to run parallel to the horizontal axis, with the heat of adsorption equal to the heat of condensation, as might well be expected when $p=\mathrm{P}$. The inflexion in the last portion of the curve occurs near $a=370$, while in fig. 3 the inflexion is near $a=365$, so there appears to be some close connection between the final portion of the two graphs.

We may regard the heat of adsorption as the sum of at least two effects, namely, loss of potential energy of the adsorbate in yielding to the attrac-

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* Mills, *Journ. of Phys. Chem.*, x, 1 (1906), calculates $\lambda=94\cdot 7$ cal. at −10° C.

† *Proc. Roy. Soc.*, lxxviii, A, p. 412.

tion of (1) the adsorbent and (2) the gas already adsorbed. The first effect will probably be represented by a function which diminishes to zero as more and more is adsorbed, if only because the sphere of molecular action of the adsorbent is attained. The second effect, on the other hand, may be represented by some function which will increase with the amount adsorbed, since the attracting "layers" will thicken. In the case of a vapour these "layers" will be able to exist "outside" the adsorbing particles, so as to give the same final heat effect as condensation of vapour into liquid. (This effect, represented by the last portion of the curves above, will be absent in the case of a gas above its critical temperature, since the "outside layers" will never attain sufficient density to attract much of themselves after the sphere of molecular action of the adsorbent is passed.)

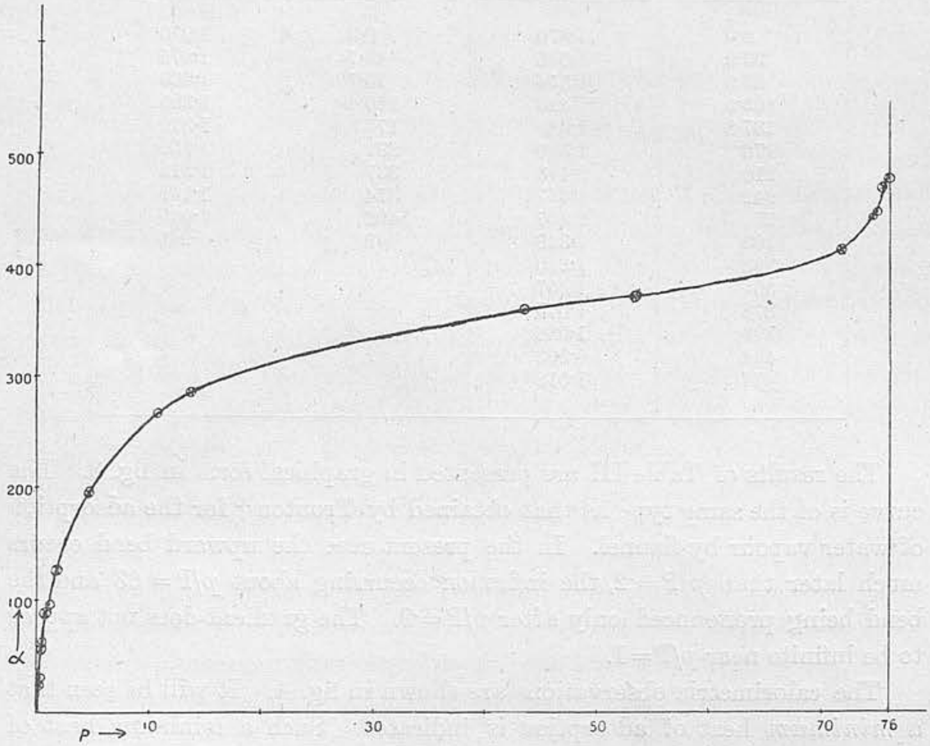

Fig. 3.

The sum of a steadily diminishing function and a steadily increasing function may quite well present a minimum, as found in the observations above.

It seems to the author that there should be a third term in the expression for the heat effect, namely, one representing the change in energy of the *adsorbent*. The Pouillet effect,* which is simply the heat given out on adsorption of a liquid by a powder, has been attributed to the compression of the "films" of liquid in contact with the powder. But in view of recent work on compression, the heat effect appears too large to be attributable solely to this cause. Thus the greatest loss of energy in compressing ether was found by Bridgman † to be 14 per cent. of the heat of condensation; and moreover, after a certain compression the total heat effect diminished. In the adsorption studied above (*cf.* also Titoff and Chappuis) the initial heat effect exceeds by more than 80 per cent. the heat of condensation, and only after a great amount is adsorbed does it fall much below an excess of 40 per cent. It seems, therefore, unlikely that it is only the adsorbate which loses a considerable amount of energy on adsorption, and it looks very probable that initially at any rate the adsorbent loses energy on what may be not *contraction* but *expansion of surface* in embracing the adsorbed particles. ‡

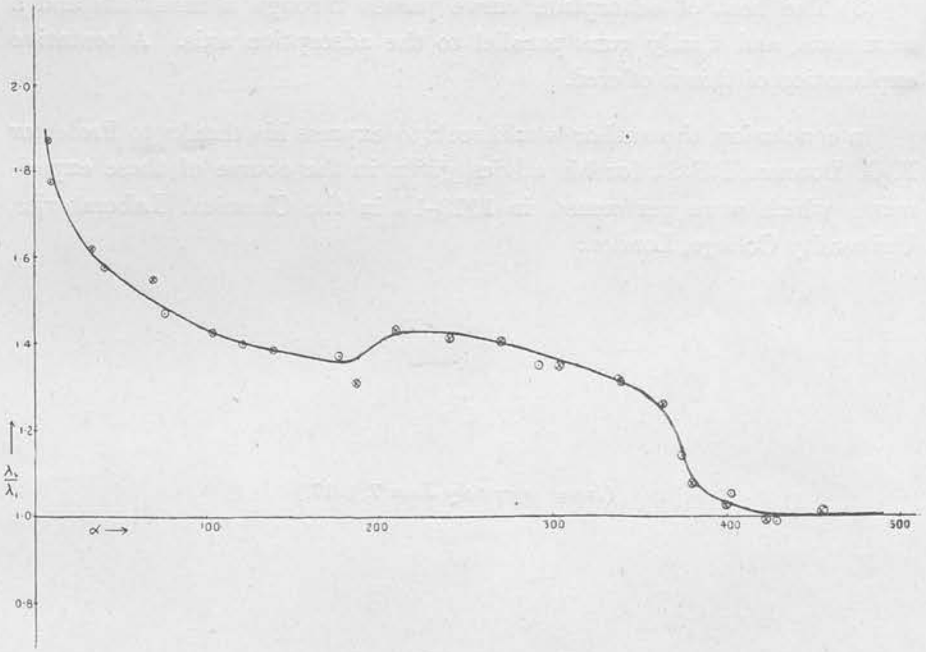

FIG. 4.

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* See Williams, *Trans. Far. Soc.*, x, p. 167 (1914).

† *Proc. Amer. Acad.*, xlix, 1 (1913).

‡ *Cf.* Donnan's negative surface tension of colloids.

SUMMARY.

(1) The adsorption of sulphur dioxide by blood charcoal at −10° C. was studied, and measurements were taken of the amount adsorbed, the pressure, and the isothermal heat of adsorption at constant volume.

(2) The adsorption isotherm is a typical vapour adsorption curve, and runs the same course as that found by Trouton for the adsorption of water vapour.

(3) The heat of adsorption curve passes through a minimum and a maximum, and finally runs parallel to the adsorption axis. A tentative explanation of this is offered.

In conclusion, the author would seek to express his thanks to Professor F. G. Donnan, F.R.S., for his advice given in the course of these experiments which were performed in 1913–14 in the Chemical Laboratories, University College, London.

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Thermodynamics of Adsorption.

By **A. M. Williams,** M.A., B.Sc.

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V.—Thermodynamics of Adsorption.

By **A. M. Williams, M.A., B.Sc.**,
1851 Exhibition Scholar of the University of Edinburgh, 1911–14.
Communicated by Professor JAMES WALKER, F.R.S.

(MS. received July 10, 1917. Read December 3, 1917.)

SOME calorimetric work on adsorption* led the author to a closer consideration of the thermodynamical aspects of the problem, and the ensuing paper is the result.

Let us consider an adsorbent whose surface of contact with a gas we can reversibly change.

Let v = volume of the system;
T = absolute temperature of the system;
p = equilibrium pressure of the gas;
n = number of mols. of gas in the system;
m = „ grms. adsorbent;
g = „ „ „ , adsorbing at p, T;
a = „ mols. of gas adsorbed per grm. adsorbent, adsorbing at p, T;
V = volume of one mol. gas at p, T;
V_a = „ „ adsorbed gas at p, T;
v_0 = „ one grm. adsorbent, not adsorbing;
v_a = „ „ „ adsorbing;
s = surface area adsorbing;
A = „ „ per grm. adsorbing;
σ = surface tension;
H = heat taken in by system from without;
W = work done by system;
E = change in energy of system;
ϕ = „ entropy of system.

We have the two following relations among the variables:—

$$s = Ag \qquad (1)$$

$$v = (n - ga)V + gaV_a + (m - g)v_0 + gv_a \qquad (2)$$

We will assume that we cannot arbitrarily alter the dispersivity of the system which is measured by A. When n and m are given p and T

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* *Proc. Roy. Soc. Edin.*, vol. xxxvii, p. 161 (1917). Before this, Professor F. G. Donnan, F.R.S., and the author projected a thermodynamical paper on somewhat different lines from the present. The author acknowledges with pleasure his indebtedness to Professor Donnan.

fix α, V, V_a, v_0, v_a, A and σ, but not g, v, s. The system will, in general, have its state completely defined by fixing any three of p, T, v, g, s. (It can, of course, be defined by other combinations of three variables.) Let us select as our controllable variables p, T, and s.

We have the thermodynamical relations

$$d\mathrm{E} = d\mathrm{H} - d\mathrm{W}$$

and

$$d\mathrm{H} = \mathrm{T}d\phi$$

for the reversible change considered, where $d\mathrm{E}$ and $d\phi$ are complete differentials.

$$d\mathrm{E} = \left(\frac{\partial \mathrm{E}}{\partial \mathrm{T}}\right)_{p,s} d\mathrm{T} + \left(\frac{\partial \mathrm{E}}{\partial p}\right)_{\mathrm{T},s} dp + \left(\frac{\partial \mathrm{E}}{\partial s}\right)_{p,\mathrm{T}} ds \qquad . \quad . \quad . \quad (3)$$

and

$$\left.\begin{aligned} d\phi &= (d\mathrm{E} + d\mathrm{W})/\mathrm{T} \\ &= (d\mathrm{E} + p\,dv - \sigma ds)/\mathrm{T} \\ &= \frac{1}{\mathrm{T}}\left(\frac{\partial \mathrm{E}}{\partial \mathrm{T}} + p\frac{\partial v}{\partial \mathrm{T}}\right)d\mathrm{T} + \frac{1}{\mathrm{T}}\left(\frac{\partial \mathrm{E}}{\partial p} + p\frac{\partial v}{\partial p}\right)dp + \frac{1}{\mathrm{T}}\left(\frac{\partial \mathrm{E}}{\partial s} + p\frac{\partial v}{\partial s} - \sigma\right)ds \end{aligned}\right\} \quad . \quad (4)$$

If we employ as variables p, T, and g, equation (4) takes a more symmetrical form, while if we use v, T, and s, it assumes a simpler form.

Evidently

$$\left(\frac{\partial \phi}{\partial \mathrm{T}}\right)_{p,s} = \frac{1}{\mathrm{T}}\left(\frac{\partial \mathrm{E}}{\partial \mathrm{T}} + p\frac{\partial v}{\partial \mathrm{T}}\right) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\left(\frac{\partial \phi}{\partial p}\right)_{\mathrm{T},s} = \frac{1}{\mathrm{T}}\left(\frac{\partial \mathrm{E}}{\partial p} + p\frac{\partial v}{\partial p}\right) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\left(\frac{\partial \phi}{\partial s}\right)_{p,\mathrm{T}} = \frac{1}{\mathrm{T}}\left(\frac{\partial \mathrm{E}}{\partial s} + p\frac{\partial v}{\partial s} - \sigma\right) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Since

$$\frac{\partial^2 u}{\partial y \partial x} = \frac{\partial^2 u}{\partial x \partial y},$$

we have from (6) and (7)

$$\left.\begin{aligned} \frac{1}{\mathrm{T}}\left(\frac{\partial^2 \mathrm{E}}{\partial p \partial s} + p\frac{\partial^2 v}{\partial p \partial s}\right) &= \frac{1}{\mathrm{T}}\left(\frac{\partial^2 \mathrm{E}}{\partial p \partial s} + \frac{\partial v}{\partial s} + p\frac{\partial^2 v}{\partial p \partial s} - \frac{\partial \sigma}{\partial p}\right) \\ \text{or} \qquad \left(\frac{\partial v}{\partial s}\right)_{p,\mathrm{T}} &= \left(\frac{\partial \sigma}{\partial p}\right)_{s}, \end{aligned}\right\} \quad . \quad . \quad (8)$$

Now

$$\left(\frac{\partial \sigma}{\partial p}\right)_{s,\mathrm{T}} = \left(\frac{\partial \sigma}{\partial p}\right)_{\mathrm{T}}$$

and

$$\begin{aligned} \left(\frac{\partial v}{\partial s}\right)_{p,\mathrm{T}} &= \left(\frac{\partial v}{\partial g}\right)_{p,\mathrm{T}} \cdot \left(\frac{\partial g}{\partial s}\right)_{p,\mathrm{T}} \\ &= \{-\alpha(\mathrm{V} - \mathrm{V}_a) - (v_0 - v_a)\} \cdot \frac{1}{\mathrm{A}}. \end{aligned}$$

$$\therefore \quad \alpha\left(1 - \frac{\mathrm{V}_a}{\mathrm{V}}\right) + \frac{v_0 - v_a}{\mathrm{V}} = -\frac{\mathrm{A}}{\mathrm{V}} \cdot \frac{\partial \sigma}{\partial p}.$$

If we denote by Γ the excess concentration on unit area of the surface over and above what it would be if occupied by the gas alone without alteration of the volume of the adsorbent,

$$\Gamma = -\frac{1}{\mathrm{V}}\frac{\partial\sigma}{\partial p} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$= -\frac{p}{\mathrm{RT}}\frac{\partial\sigma}{\partial p}, \text{ when } p\mathrm{V} = \mathrm{RT} \quad . \quad . \quad . \quad (9')$$

which is the well-known equation due to Gibbs.*

It is interesting to notice that since the amount adsorbed per grm. adsorbent is usually calculated without correcting for the volume of the adsorbed gas, etc., what is measured is not α, but $\Gamma\mathrm{A}$. Thus, let

v_1 = volume of reservoir containing gas,
v_2 = " adsorption chamber less volume of adsorbent.

Then with the above notation we have

$$n = \frac{v_1}{\mathrm{V}} + \frac{v_2 - g\alpha\mathrm{V}_\alpha + gv_0 - gv_\alpha}{\mathrm{V}} + g\alpha.$$

But if a denote the calculated value of α, neglecting the volume of the adsorbed gas, etc.,

$$n = \frac{v_1}{\mathrm{V}} + \frac{v_2}{\mathrm{V}} + ga,$$

$$\therefore \quad ga = g\alpha - \frac{g\alpha\mathrm{V}_\alpha - g(v_0 - v_\alpha)}{\mathrm{V}}$$

or

$$a = \alpha\left(1 - \frac{\mathrm{V}_\alpha}{\mathrm{V}}\right) + \frac{v_0 - v_\alpha}{\mathrm{V}}$$

$$= \Gamma\mathrm{A}.$$

On the analogy between the specific volumes of a liquid and its saturated vapour the difference between α and a will, in ordinary cases of adsorption, be less than 1 in 1000.

From equations (5) and (7) we have by differentiation as before

$$\left.\begin{aligned} \frac{1}{\mathrm{T}}\left(\frac{\partial^2\mathrm{E}}{\partial s\partial\mathrm{T}} + p\frac{\partial^2 v}{\partial s\partial\mathrm{T}}\right) &= \frac{1}{\mathrm{T}}\left(\frac{\partial^2\mathrm{E}}{\partial s\partial\mathrm{T}} + p\frac{\partial^2 v}{\partial s\partial\mathrm{T}} - \frac{\partial\sigma}{\partial\mathrm{T}}\right) - \frac{1}{\mathrm{T}^2}\left(\frac{\partial\mathrm{E}}{\partial s} + p\frac{\partial v}{\partial s} - \sigma\right) \\ \text{or} \qquad \left(\frac{\partial\mathrm{E}}{\partial s}\right)_{p,\mathrm{T}} &= \sigma - \mathrm{T}\left(\frac{\partial\sigma}{\partial\mathrm{T}}\right)_p - p\left(\frac{\partial v}{\partial s}\right)_{p,\mathrm{T}} \\ &= \sigma - \mathrm{T}\left(\frac{\partial\sigma}{\partial\mathrm{T}}\right)_p + p\mathrm{V}\Gamma \end{aligned}\right\} \quad . \quad (10)$$

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* *Papers*, vol. i, p. 235. For other methods of deriving the equation, see, among others, Milner, *Phil. Mag.* (1907) (vi), 13, p. 96; Ostwald, *General Chemistry* (1912), p. 499; and, more recently, Porter, *Trans. Far. Soc.* (1915), vol. xi, p. 51, and Harlow and Willows, *ibid.*, p. 53.

If we are dealing with a gas below its critical temperature, we may regard σ as a function not of p and T but of p/P and T, where P is the saturated vapour pressure at T.

Then

$$\left.\begin{aligned}\left(\frac{\partial\sigma}{\partial \mathrm{T}}\right)_p &= \left(\frac{\partial\sigma}{\partial \mathrm{T}}\right)_{p/\mathrm{P}} + \left(\frac{\partial\sigma}{\partial p/\mathrm{P}}\right)_\mathrm{T} \cdot \left(\frac{\partial p/\mathrm{P}}{\partial \mathrm{T}}\right)_p \\ &= \left(\frac{\partial\sigma}{\partial \mathrm{T}}\right)_{p/\mathrm{P}} + \mathrm{P}\left(\frac{\partial\sigma}{\partial p}\right)_\mathrm{T} \cdot -\frac{p}{\mathrm{P}^2} \cdot \frac{d\mathrm{P}}{d\mathrm{T}} \\ &= \left(\frac{\partial\sigma}{\partial \mathrm{T}}\right)_{p/\mathrm{P}} + \Gamma \mathrm{V}\frac{p}{\mathrm{P}} \cdot \frac{d\mathrm{P}}{d\mathrm{T}} . \\ \therefore \quad \left(\frac{\partial \mathrm{E}}{\partial s}\right)_{p,\mathrm{T}} &= \left\{\sigma - \mathrm{T}\left(\frac{\partial\sigma}{\partial \mathrm{T}}\right)_{p/\mathrm{P}}\right\} - \left\{\mathrm{T}\frac{d\mathrm{P}}{d\mathrm{T}} - \mathrm{P}\right\} \cdot \frac{p\mathrm{V}}{\mathrm{P}} \cdot \Gamma\end{aligned}\right\} \quad . \quad . \quad (10')$$

Let us consider the case when $p = \mathrm{P}$, and denote $\sigma(\mathrm{P}, \mathrm{T})$ by σ_P. Then

$$\left(\frac{\partial \mathrm{E}}{\partial s}\right)_{\mathrm{P},\mathrm{T}} = \left\{\sigma_p - \mathrm{T}\frac{\partial\sigma_p}{\partial \mathrm{T}}\right\} - \left\{\mathrm{T}\frac{d\mathrm{P}}{d\mathrm{T}} - \mathrm{P}\right\}\mathrm{V} . \Gamma \quad . \quad . \quad . \quad (10'')$$

Now the change in energy when one mol. vapour condenses into liquid is given by

$$\Delta \mathrm{E} = -\left(\mathrm{V}_\mathrm{G} - \mathrm{V}_\mathrm{L}\right)\left(\mathrm{T}\frac{d\mathrm{P}}{d\mathrm{T}} - \mathrm{P}\right).$$

Hence, since

$$\begin{aligned}\Gamma \mathrm{V} &= \alpha(\mathrm{V}_\mathrm{G} - \mathrm{V}_\alpha) \text{ approximately,} \\ &= \alpha(\mathrm{V}_\mathrm{G} - \mathrm{V}_\mathrm{L}) \qquad \text{,,}\end{aligned}$$

the energy change when the adsorbent is exposed to liquid instead of vapour is given by

$$\left(\frac{\partial \mathrm{E}'}{\partial s}\right)_{\mathrm{P},\mathrm{T}} = \sigma_\mathrm{P} - \mathrm{T}\frac{d\sigma_\mathrm{P}}{d\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

an equation similar to that originally given by Kelvin for the stretching of a film. σ_P evidently corresponds to the surface tension between two liquids.

When a powder is immersed in a liquid no external work is done, hence the heat of immersion *emitted* per grm. adsorbent is given by

$$\begin{aligned}\lambda_\mathrm{P}' &= -\left(\frac{\partial \mathrm{E}'}{\partial g}\right)_{\mathrm{P},\mathrm{T}} \\ &= -\left(\frac{\partial \mathrm{E}'}{\partial s}\right)_{\mathrm{P},\mathrm{T}} \cdot \mathrm{A} \\ &= -\left(\sigma_\mathrm{P} - \mathrm{T}\frac{d\sigma_\mathrm{P}}{d\mathrm{T}}\right) \cdot \mathrm{A}\end{aligned}$$

when the powder is free from any adsorbate before immersion. It must, however, be noticed that in the equations above we have considered the development of the surface to proceed from the interior of the adsorbent amidst the gas. In the case of immersion a surface has already been formed out of contact with the gas. For this surface let $\sigma=\sigma_0$ and $A=A_0$. Let the surface contract so that it has minimum surface negligible, we will suppose, compared with A_0. Let it now be introduced to the gas and expanded to A at P, T. The total change of energy is given by

$$\left(\frac{\partial E''}{\partial g}\right)_{P,T}=-A_0\left(\sigma_0-T\frac{d\sigma_0}{dT}\right)+A\left(\sigma_P-T\frac{d\sigma_P}{dT}\right) \quad . \quad . \quad . \quad (11')$$

and the heat of immersion will therefore be

$$\lambda_P''=A_0\left(\sigma_0-T\frac{d\sigma_0}{dT}\right)-A\left(\sigma_P-T\frac{d\sigma_P}{dT}\right).$$

If we use equation (9) to define σ, we can replace σ in the above expressions. Thus

$$\Gamma=-\frac{1}{V}\frac{\partial\sigma}{\partial p}. \qquad (9)$$

$$\begin{aligned}\therefore\quad \sigma_P-\sigma_0&=-\int_0^P\Gamma V dp\\&=-\int_0^P\frac{aV}{A}dp\\&=-\frac{RT}{A}\int^P\frac{adp}{p},\end{aligned}$$

assuming A constant and $pV=RT$.

Again, since

$$\begin{aligned}\sigma_P-\sigma_0&=-\frac{RT}{A}\int_0^p\frac{adp}{p}=-\frac{RT}{A}\int_0^{p/P}\frac{a}{p/P}dp/P\\ \left(\frac{\partial\sigma_P-\sigma_0}{\partial T}\right)_{p/P}&=-\frac{R}{A}\int_0^{p/P}\frac{a}{p/P}dp/P-\frac{RT}{A}\int_0^{p/P}\left(\frac{\partial a}{\partial T}\right)_{p/P}\frac{dp/P}{p/P}\\&=-\frac{R}{A}\int_0^p\frac{a}{p}dp-\frac{RT}{A}\int_0^p\left(\frac{\partial a}{\partial T}\right)_{p/P}\frac{dp}{p}.\end{aligned}$$

Now

$$\left.\begin{aligned}\left(\frac{\partial a}{\partial T}\right)_{p/P}&=\left(\frac{\partial a}{\partial T}\right)_p+\left(\frac{\partial a}{\partial p}\right)_T\cdot\left(\frac{\partial p}{\partial T}\right)_{p/P}\\&=-\left(\frac{\partial a}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_a+\left(\frac{\partial a}{\partial p}\right)_T\cdot\frac{p}{P}\cdot\frac{dP}{dT}.\\ \therefore\quad A(\sigma_P-\sigma_0)-AT\frac{d\sigma_P-\sigma_0}{dT}&=RT^2\int_0^{a_P}\left(-\frac{1}{p}\frac{\partial p}{\partial T}+\frac{1}{P}\frac{dP}{dT}\right)da\\ \text{or}\qquad \lambda_P''&=RT^2\int_0^{a_P}\left(\frac{\partial\log p/P}{\partial T}\right)_a da\\&=RT^2\int_0^{a_P}\frac{\partial\log p}{\partial T}da-RT^2\frac{d\log P}{dT}\,.\,a_P\end{aligned}\right\} \quad . \quad (12)$$

This equation for the heat of immersion is derived on the assumption that $pV=RT$ and A does not vary, and might have been expected from the analogy with solution. Expressions for the heat of immersion when the adsorbent is already partially saturated may be derived in a similar manner. It is, however, desirable to take into account the variation of A, and this we now proceed to do in the differentiation of equations (5) and (6). We have

$$\left.\begin{aligned} &\frac{1}{\mathrm{T}}\left\{\frac{\partial^2 \mathrm{E}}{\partial p \partial \mathrm{T}}+p\frac{\partial^2 v}{\partial p \partial \mathrm{T}}\right\}-\frac{1}{\mathrm{T}^2}\left\{\frac{\partial \mathrm{E}}{\partial p}+p\frac{\partial v}{\partial p}\right\}=\frac{1}{\mathrm{T}}\left\{\frac{\partial^2 \mathrm{E}}{\partial p \partial \mathrm{T}}+\frac{\partial v}{\partial \mathrm{T}}+p\frac{\partial^2 v}{\partial p \partial \mathrm{T}}\right\} \\ \text{or}\qquad & \left(\frac{\partial \mathrm{E}}{\partial p}\right)_{s,\mathrm{T}}=-p\left(\frac{\partial v}{\partial p}\right)_{s,\mathrm{T}}-\mathrm{T}\left(\frac{\partial v}{\partial \mathrm{T}}\right)_{s,p} \end{aligned}\right\} \quad . \quad (13)$$

Now

$$v=(n-\Gamma s)\mathrm{V}.$$

$$\therefore \quad \left(\frac{\partial v}{\partial p}\right)_{s,\mathrm{T}}=-s\mathrm{V}\left(\frac{\partial \Gamma}{\partial p}\right)_{\mathrm{T}}+(n-\Gamma s)\left(\frac{\partial \mathrm{V}}{\partial p}\right)_{\mathrm{T}}$$

$$\left(\frac{\partial v}{\partial \mathrm{T}}\right)_{s,p}=-s\mathrm{V}\left(\frac{\partial \Gamma}{\partial \mathrm{T}}\right)_{p}+(n-\Gamma s)\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{p}.$$

$$\begin{aligned} \therefore \quad \left(\frac{\partial \mathrm{E}}{\partial p}\right)_{s,\mathrm{T}} &= s\mathrm{V}\left(p\frac{\partial \Gamma}{\partial p}+\mathrm{T}\frac{\partial \Gamma}{\partial \mathrm{T}}\right)-\left(n-\Gamma s\right)\left(p\frac{\partial \mathrm{V}}{\partial p}+\mathrm{T}\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right) \\ &= -s\mathrm{V}\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\Gamma}-p\right\}\frac{\partial \Gamma}{\partial p}+\left(n-\Gamma s\right)\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{V}}-p\right\}\frac{\partial \mathrm{V}}{\partial p}. \end{aligned}$$

$$\therefore \quad \left(\frac{\partial \mathrm{E}}{\partial \Gamma}\right)_{s,\mathrm{T}}=-s\mathrm{V}\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\Gamma}-p\right\}+\left(n-\Gamma s\right)\left(\frac{\partial \mathrm{E}}{\partial \mathrm{V}}\right)_{\mathrm{T}}\cdot\frac{\partial \mathrm{V}}{\partial \Gamma}.$$

The second term on the right represents the change in energy of the unadsorbed gas. Since $\left(\frac{\partial \mathrm{E}}{\partial \mathrm{V}}\right)_{\mathrm{T}}=0$ approximately for a gas, this second term may in general be neglected, and we may write

$$\frac{1}{s}\cdot\left(\frac{\partial \mathrm{E}}{\partial \Gamma}\right)_{s,\mathrm{T}}=-\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\Gamma}-p\right\}\mathrm{V} \quad . \quad . \quad . \quad . \quad (14)$$

In ordinary adsorption observations s and Γ are not directly measured, but rather g and a. It will therefore be of interest to convert the equation into terms of g and a. We have

$$\left(\frac{\partial \mathrm{E}}{\partial p}\right)_{g,\mathrm{T}}=\left(\frac{\partial \mathrm{E}}{\partial p}\right)_{s,\mathrm{T}}+\left(\frac{\partial \mathrm{E}}{\partial s}\right)_{p,\mathrm{T}}\cdot\left(\frac{\partial s}{\partial p}\right)_{g,\mathrm{T}}.$$

But

$$\left(\frac{\partial \mathrm{E}}{\partial p}\right)_{s,\mathrm{T}}=-p\left(\frac{\partial v}{\partial p}\right)_{s,\mathrm{T}}-\mathrm{T}\left(\frac{\partial v}{\partial \mathrm{T}}\right)_{s,p} \quad (13)$$

and

$$v=(n-ag)\mathrm{V}, \quad g=s/\mathrm{A}$$

$$\left(\frac{\partial v}{\partial p}\right)_{s,\mathrm{T}}=\left(\frac{\partial v}{\partial p}\right)_{\mathrm{T}}+\left(\frac{\partial v}{\partial g}\right)_{p,\mathrm{T}}\cdot\left(\frac{\partial g}{\partial p}\right)_{s,\mathrm{T}}$$

$$\left(\frac{\partial v}{\partial p}\right)_{g,\mathrm{T}}=-g\mathrm{V}\left(\frac{\partial a}{\partial p}\right)_{\mathrm{T}}+\left(n-ag\right)\left(\frac{\partial \mathrm{V}}{\partial p}\right)_{\mathrm{T}}$$

$$\left(\frac{\partial v}{\partial g}\right)_{p,\mathrm{T}}\cdot\left(\frac{\partial g}{\partial p}\right)_{s,\mathrm{T}}=-a\mathrm{V}\cdot-\frac{s}{\mathrm{A}^2}\left(\frac{\partial \mathrm{A}}{\partial p}\right)_{\mathrm{T}}.$$

$$\therefore \quad \left(\frac{\partial v}{\partial p}\right)_{s,\mathrm{T}} = -g\mathrm{V}\left(\frac{\partial a}{\partial p}\right)_{\mathrm{T}} + \left(n - ag\right)\left(\frac{\partial \mathrm{V}}{\partial p}\right)_{\mathrm{T}} + a\mathrm{V}\frac{s}{\mathrm{A}^2}\left(\frac{\partial \mathrm{A}}{\partial p}\right)_{\mathrm{T}}.$$

Similarly,

$$\left(\frac{\partial v}{\partial \mathrm{T}}\right)_{s,p} = -g\mathrm{V}\left(\frac{\partial a}{\partial \mathrm{T}}\right)_{p} + \left(n - ag\right)\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{p} + a\mathrm{V}\frac{s}{\mathrm{A}^2}\left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{p}.$$

Neglecting as before the change in energy of the unadsorbed gas, we get

$$\left(\frac{\partial \mathrm{E}}{\partial p}\right)_{s,\mathrm{T}} = g\mathrm{V}\left(p\frac{\partial a}{\partial p} + \mathrm{T}\frac{\partial a}{\partial \mathrm{T}}\right) - \frac{as}{\mathrm{A}^2}\mathrm{V}\left(p\frac{\partial \mathrm{A}}{\partial p} + \mathrm{T}\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right).$$

$$\therefore \quad \left(\frac{\partial \mathrm{E}}{\partial p}\right)_{g,\mathrm{T}} = g\mathrm{V}\left(p\frac{\partial a}{\partial p} + \mathrm{T}\frac{\partial a}{\partial \mathrm{T}}\right) - \frac{as}{\mathrm{A}^2}\mathrm{V}\left(p\frac{\partial \mathrm{A}}{\partial p} + \mathrm{T}\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right) + \frac{\partial \mathrm{E}}{\partial s}\cdot g\cdot\frac{\partial \mathrm{A}}{\partial p}.$$

$$\therefore \quad \left(\frac{\partial \mathrm{E}}{\partial a}\right)_{g,\mathrm{T}} = -g\mathrm{V}\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{a} - p\right\} + \frac{ag\mathrm{V}}{\mathrm{A}}\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} - p\right\}\left(\frac{\partial \mathrm{A}}{\partial a}\right)_{\mathrm{T}} + \frac{1}{\mathrm{A}}\cdot\left(\frac{\partial \mathrm{E}}{\partial g}\right)_{p,\mathrm{T}}\cdot g\left(\frac{\partial \mathrm{A}}{\partial a}\right)_{\mathrm{T}}.$$

Taking for simplicity $g = 1$, we have

$$\left(\frac{\partial \mathrm{E}}{\partial a}\right)_{g,\mathrm{T}} = -\mathrm{V}\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{a} - p\right\} + \left\{\left(\frac{\partial \mathrm{E}}{\partial g}\right)_{p,\mathrm{T}} + a\mathrm{V}\left(\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} - p\right)\right\}\frac{1}{\mathrm{A}}\left(\frac{\partial \mathrm{A}}{\partial a}\right)_{\mathrm{T}}. \quad (15)$$

The effect of a possible variation of A is represented by the second term on the right-hand side. We cannot easily directly estimate its value, since we cannot measure A. It is therefore necessary to compare the two sides of the equation (15) by means of other observed quantities.

We may define the *heat of adsorption* as the ratio of the heat *evolved* to the gas adsorbed when only a very small quantity of gas is adsorbed. For our present purposes we will consider a and not α as the gas adsorbed per grm. As has been noted before, a and α differ in ordinary cases by a small quantity only. We will consider the following three cases* of adsorption at constant temperature:—

(1) The gas is adsorbed very slowly, so that the vapour phase is constantly in equilibrium with the adsorbed phase. Work is done by pressure and surface forces. Let us denote this, the *isothermal equilibrium heat of adsorption*, by λ_{T}. Then

$$\left.\begin{aligned} d\mathrm{E} &= -\lambda_{\mathrm{T}}da - pdv + \sigma d\mathrm{A}. \\ \therefore \quad \lambda_{\mathrm{T}} &= -\left(\frac{\partial \mathrm{E}}{\partial a}\right)_{g,\mathrm{T}} - p\left(\frac{\partial v}{\partial a}\right)_{g,\mathrm{T}} + \sigma\left(\frac{\partial \mathrm{A}}{\partial a}\right)_{\mathrm{T}} \\ &= -\left(\frac{\partial \mathrm{E}}{\partial a}\right)_{g,\mathrm{T}} + p\mathrm{V} - (n-\alpha)p\left(\frac{\partial \mathrm{V}}{\partial p}\right)_{\mathrm{T}}\left(\frac{\partial p}{\partial a}\right)_{\mathrm{T}} + \sigma\left(\frac{\partial \mathrm{A}}{\partial a}\right)_{\mathrm{T}} \end{aligned}\right\} \quad . \quad . \quad (16)$$

The third term represents the work done by the gaseous phase in expanding, and may in general be ignored.

(2) The gas is adsorbed at constant pressure. Consider first an equilibrium arrangement whereby a small portion da' of the gas at pressure p'

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* Following Donnan in an unpublished paper.

is isothermally expanded to the equilibrium pressure p of the adsorption chamber, which is isolated from the gas to be adsorbed. The change of energy on expansion will be

$$da'\int_{V'}^{V}\left(\frac{\partial E}{\partial V}\right)_T dV.$$

The change of energy on equilibrium adsorption of da, the adsorption chamber being brought back to its original volume, will be

$$\left(\frac{\partial E}{\partial a}\right)_{g,T} da.$$

Hence the total change in energy of the system will be

$$\left(\frac{\partial E}{\partial a}\right)_{g,T} da + da'\int_{V'}^{V}\left(\frac{\partial E}{\partial V}\right)_T dV$$

where the second term is in general negligible.

In the non-equilibrium adsorption of da, the work done by the gas will be $-p'V'da'$. The change of energy will be the same as in the equilibrium adsorption. Hence, if $\lambda_{p,T}$ denote the *isothermal heat of adsorption at constant pressure,*

$$\left.\begin{aligned} \left(\frac{\partial E}{\partial a}\right)_{g,T} da &= -\lambda_{p,T}da + p'V'da' \\ \text{or}\qquad \lambda_{p,T} &= -\left(\frac{\partial E}{\partial a}\right)_{g,T} + p'V'\left(\frac{da'}{da}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad (17)$$

$\frac{da'}{da}$ is the ratio of the gas entering the adsorption chamber to the gas actually absorbed, and will in general (*i.e.* at low pressure, etc.) be approximately unity. Thus we have, equating volumes,

$$(n-a)V = (n + da' - a - da)\left\{V + \left(\frac{\partial V}{\partial a}\right)_T da\right\}.$$

$$\therefore \quad \frac{da'}{da} = 1 - (n-a)\frac{1}{V}\cdot\left(\frac{\partial V}{\partial p}\right)_T\cdot\left(\frac{\partial p}{\partial a}\right)_T.$$

The second term is usually negligible. For example, taking $pV = RT$, we have

$$\begin{aligned} -(n-a)\frac{1}{V}\cdot\frac{\partial V}{\partial p}\cdot\frac{\partial p}{\partial a} &= (n-a)\frac{1}{p}\cdot\frac{\partial p}{\partial a} \\ &= \frac{n-a}{a}\cdot\frac{\partial \log p}{\partial \log a}. \end{aligned}$$

By taking the gaseous phase in the adsorption chamber $n-a$ sufficiently small relative to a, we can make the expression as small as we please, since $\frac{\partial \log p}{\partial \log a}$, although never less than unity, is finite. $\left(\frac{\partial \log p}{\partial \log a} = n\right.$ when $a = a_0 p^{\frac{1}{n}}$ and n is usually greater than unity.) The third term in case (1) may be similarly treated.

(3) The gas is adsorbed at constant volume. Consider first an equilibrium arrangement as before, whereby a small portion da' is isothermally expanded to the equilibrium pressure p of the isolated adsorption chamber. The remaining gas is expanded to occupy the initial volume, while da is adsorbed. The total change in energy is, as before,

$$\left(\frac{\partial \mathrm{E}}{\partial a}\right)_{g,\,\mathrm{T}} da + da' \int_{\mathrm{V}'}^{\mathrm{V}} \left(\frac{\partial \mathrm{E}}{\partial \mathrm{V}}\right)_{\mathrm{T}} d\mathrm{V} + \left(n_0 - da'\right)\left(\frac{\partial \mathrm{E}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \mathrm{V}'da' = \left(\frac{\partial \mathrm{E}}{\partial a}\right)_{g,\,\mathrm{T}} da \text{ approx.}$$

In the non-equilibrium adsorption the work done is nil. The energy change is the same as in the equilibrium adsorption. (We are again assuming the gas phase in the adsorption chamber negligibly small.) Hence, if $\lambda_{v,\,\mathrm{T}}$ denote the *isothermal heat of adsorption at constant volume,*

$$\lambda_{v,\,\mathrm{T}} = -\left(\frac{\partial \mathrm{E}}{\partial a}\right)_{g,\,\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

In practice the heat effect measured in any case will not be λ, but $\int_{a_1}^{a_2} \lambda da$.

Freundlich, who has dealt with heats of adsorption in his *Kapillarchemie*,* considers an "isosteric" heat of adsorption *where a is constant*, p and T variables, and gives the heat of adsorption per mol. under these conditions in terms of the Clapeyron equation $\lambda = \mathrm{RT}^2 \frac{\partial \log p}{\partial \mathrm{T}}$. The *formula* corresponds to the value for $\lambda_{p,\,\mathrm{T}}$ above. But it is difficult to see how we can have an *isosteric heat of adsorption per mol. adsorbed*, for under the defined conditions *nothing* is adsorbed. We have merely a readjustment of p and T. The energy change is, in fact, $\left(\frac{\partial \mathrm{E}}{\partial \mathrm{T}}\right)_{g,\,a} d\mathrm{T}$, and the work done $p\left(\frac{\partial v}{\partial \mathrm{T}}\right)_{g,\,a} d\mathrm{T}$. Hence the heat change is

$$\left\{\left(\frac{\partial \mathrm{E}}{\partial \mathrm{T}}\right)_{g,\,a} + p\left(\frac{\partial v}{\partial \mathrm{T}}\right)_{g,\,a}\right\} d\mathrm{T}$$

where the quantity in brackets is evidently the specific heat of the system at constant a.

The only published measurements connecting the heat of adsorption with p, a, T are those of Titoff.† He compares his measured heat of adsorption with that calculated from Freundlich's empirical formula, which is based on the substitution of $a = a_0 p^{\frac{1}{n}}$ in the Clapeyron equation. It seems more desirable to compare the observed heat with that calculated directly from the thermodynamical formula. As Titoff carried out his observations under none of the arrangements (1), (2), (3) studied above,

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* P. 108 *et sequitur*. See also Partington, *Thermodynamics*, p. 444.

† *Zeits. f. physik. Chem.*, lxxiv, p. 641 (1910).

but allowed the adsorption to proceed with a fall in pressure and a decrease in volume of the system, we cannot apply any of the formulæ (16), (17), (18). The observed value will presumably fall between the values for the heat of adsorption at constant volume and the heat of adsorption at constant pressure. It will be noted that approximately

$$\lambda_{p, \mathrm{T}} = \lambda_{v, \mathrm{T}} + \mathrm{RT},$$

and hence it will be assumed that Titoff measured

$$\lambda_{p, \mathrm{T}} - \tfrac{1}{2}\mathrm{RT} = \lambda_{v, \mathrm{T}} + \tfrac{1}{2}\mathrm{RT}.$$

We have

$$\left.\begin{aligned} \lambda_{p, \mathrm{T}} &= -\left(\frac{\partial \mathrm{E}}{da}\right)_{g, \mathrm{T}} + \mathrm{RT} \text{ approx.} \\ &= \mathrm{V} \,.\, \mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_a - \left\{\frac{\partial \mathrm{E}}{\partial g} + a\mathrm{V}\left(\mathrm{T}\frac{\partial p}{\partial \mathrm{T}} - p\right)\right\}\frac{1}{\mathrm{A}}\,\frac{\partial \mathrm{A}}{\partial a} \end{aligned}\right\} \quad . \quad . \quad . \quad (19)$$

Hence if A were constant

$$\begin{aligned} \lambda_{p, \mathrm{T}} &= \mathrm{V} \,.\, \mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_a \\ &= \mathrm{RT}^2\left(\frac{\partial \log p}{\partial \mathrm{T}}\right)_a, \end{aligned}$$

which corresponds to the Clapeyron equation.

In the tables below, $\mathrm{RT}^2\left(\frac{\partial \log p}{\partial \mathrm{T}}\right)_a\Big/22400$ is given as calculated by the author from Titoff's observations. Brackets round a value indicate that it is doubtful. From these values is calculated the heat of adsorption at 0° C., and compared with the observed heat at the same temperature. a is measured in c.cm. gas per grm. at N.T.P., λ in calories per c.cm. adsorbed.

TABLE I.—AMMONIA.

	$\mathrm{RT}^2 \frac{\partial \log p}{\partial \mathrm{T}}\Big/22400.$					$\lambda.$		
$\log_{10} a.$	116° C.	55°.	15°.	−12°.	0° calc.	λ calc.	λ obs.	λ obs. − λ calc.
2·10	...	...	...	·298	(·277)	(·265)	·386	(·121)
2·00	...	...	·284	·315	·302	·290	·355	·065
1·80	...	...	·306	·351	·331	·319	·360	·041
1·60	...	·328	·306	·369	·341	·329	·370	·041
1·40	...	·328	·323	·375	·352	·340	·375	·035
1·20	...	·328	·323	·375	·352	·340	·388	·048
1·00	·30	·328	(·38)	...	(·41)	(·40)	·41	(·01)
0·80	·31	·373	...	...	...	...	·43	...
0·50	·41	(·44)	...	...	...	...	·45	...
0·00	·42	...	...	...	...	...	...	...

The variation from $p\mathrm{V} = \mathrm{RT}$ would not affect any of the calculated values more than 1·3 per cent., *i.e.* ·005.

TABLE II.—CARBON DIOXIDE.

$RT^2\frac{\partial \log p}{\partial T}\Big/22400.$						λ.		
$\log_{10} a$.	116° C.	55°.	15°.	− 38°.	0° calc.	λ calc.	λ obs.	λ obs. − λ calc.
1·80	...	...	(·293)	(·269)	(·285)	(·273)	·284	(·011)
1·70	...	...	(·300)	(·269)	(·290)	(·278)	·280	(·002)
1·60	...	...	·288	(·273)	·289	·277	·294	·017
1·40	...	·295	·283	(·287)	·284	·272	·301	·029
1·20	...	·299	·300	(·286)	·296	·284	·307	·023
1·00	·29	·308	·317	(·287)	·307	·295	·315	·020
0·80	·28	·317	·305	...	(·31)	(·30)	·324	(·024)
0·40	·33	·327	·328	...	(·33)	(·32)	·337	(·015)
0·00	·33	·348	·367	...	...	...	·346	...
$\bar{1}$·80	·34	·348	...	...	...	...	...	...
$\bar{1}$·80	·35	...	...	...	...	...	...	...

The variation from $pV = RT$ would not affect any of the calculated values more than 0·6 per cent., *i.e.* ·002.

TABLE III.—NITROGEN.

$RT^2\frac{\partial \log p}{\partial T}\Big/22400.$						λ.		
$\log_{10} a$.	116° C.	55°.	15°.	− 40°.*	0° calc.	λ calc.	λ obs.	λ obs. − λ calc.
1·10	...	...	...	·002	...	...	·21	...
1·00	...	...	...	·003	...	...	·21	...
0·80	...	...	·176	·004	(·17)	(·16)	·21	(·05)
0·50	...	·195	·176	·010	(·17)	(·16)	·22	(·06)
0·00	·202	·193	·178	(− *ve*)	(·17)	(·16)	·22	(·06)
$\bar{1}$·80	·227	·154	·186	(− *ve*)	(·18)	(·17)	·22	(·05)
$\bar{1}$·50	·202	·167	·189	...	(·18)	(·17)	·24	(·07)
$\bar{1}$·00	·214	·112	(·237)	...	...	...	·29	...
$\bar{2}$·80	·277	...	...	...	...	...	...	...

The tabulated values evidently indicate either (1) some systematic error in the calorimetric observations, or (2) some systematic error in the thermodynamical formula. Even if we assume that Titoff observed the heat of adsorption at constant pressure, only in three doubtful cases out of twenty tabulated would the reduction by ·012 account for the discrepancy between calculated and observed values. Assuming the calorimetric observations to be sound, we may perhaps lead back the divergence to ignored terms in equation (19). We have

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* Apparently at the lowest ~~temperature of observation, − 80° C., the charcoal was not~~ allowed time to saturate itself.

$$\lambda_{p,\mathrm{T}} = -\left(\frac{\partial \mathrm{E}}{\partial a}\right)_{g,\mathrm{T}} + p'\mathrm{V}'\frac{da'}{da} \qquad (17)$$

$$= \mathrm{V}\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_a - p\right\} - \left\{\frac{\partial \mathrm{E}}{\partial g} + a\mathrm{V}\left(\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} - p\right)\right\}\frac{1}{\mathrm{A}}\frac{\partial \mathrm{A}}{\partial a}$$

$$+ p'\mathrm{V}'\left\{1 - (n-a)\frac{1}{\mathrm{V}} \cdot \frac{\partial \mathrm{V}}{\partial p} \cdot \frac{\partial p}{\partial a}\right\}$$

$$= \mathrm{RT}^2\left(\frac{\partial \log p}{\partial \mathrm{T}}\right)_a + \frac{n-a}{a} \cdot \frac{\partial \log p}{\partial \log a} \cdot \mathrm{RT} + \left\{-\frac{\partial \mathrm{E}}{\partial g} - a\mathrm{V}\left(\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} - p\right)\right\}\frac{1}{\mathrm{A}}\frac{\partial \mathrm{A}}{\partial a}$$

assuming $p\mathrm{V} = \mathrm{RT}$.

The value of the second term is shown in Table IV. below. It evidently tends to reduce the discrepancy, but does not remove it. The value of the term was calculated assuming the volume of the gas in the adsorption chamber to be 20 c.c. Titoff gives the volume of the smaller bulb employed as *circa* 25 c.c., containing 4–10 grm. charcoal, density 1·8. Hence

$$\frac{n-ga}{ga} \cdot \frac{\partial \log p}{\partial \log a} \cdot \frac{\mathrm{RT}}{22{,}400} = \frac{20}{ga} \cdot \frac{p}{76} \cdot \frac{\partial \log p}{\partial \log a} \cdot {}·024.$$

TABLE IV.

	p.	ga.	$\frac{\partial \log p}{\partial \log a}$.	a.	λ.	Correction.
NH_3	0·3 cm.	20 c.c.	1·4	5·5	0·44	0·0001
	76	510	7	135	·38	·007
CO_2	0·2	25	1·3	2·3	0·35	·0001
	73	690	3	65	·28	·002
N_2	1·0	27	1	0·26	0·29	·002
	76	140	1·3	13	·31	·004

Since the second term does not remove the discrepancy, we must consider it mainly due to the third term, which represents the change in energy due to *an alteration in the extent of the adsorbing area per grm.* The third term is

$$\left[-\frac{\partial \mathrm{E}}{\partial g} - a\mathrm{V}\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} - p\right\}\right]\frac{1}{\mathrm{A}}\frac{\partial \mathrm{A}}{\partial a}$$

$$= \left[-\mathrm{A}\left\{\sigma - \mathrm{T}\left(\frac{\partial \sigma}{\partial \mathrm{T}}\right)_p\right\} - p\mathrm{V}a - a\mathrm{VT}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} + ap\mathrm{V}\right]\frac{1}{\mathrm{A}}\frac{\partial \mathrm{A}}{\partial a} \qquad \text{from (10)}$$

$$= \left\{-\sigma + \mathrm{T}\frac{\partial \sigma}{\partial \mathrm{T}} - \frac{a}{\mathrm{A}} \cdot \mathrm{V} \,.\, \mathrm{T} \,.\, \left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}}\right\} \cdot \frac{\partial \mathrm{A}}{\partial a}\,.$$

We may derive an estimate for the value of $-\frac{a}{\mathrm{A}} \,.\, \mathrm{V} \,.\, \mathrm{T} \,.\, \left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} \cdot \frac{\partial \mathrm{A}}{\partial a}$ as follows:—

$$-\frac{a}{\mathrm{A}} \cdot \mathrm{VT} \cdot \left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} \cdot \left(\frac{\partial \mathrm{A}}{\partial a}\right)_{\mathrm{T}} = -\frac{a}{\mathrm{A}} \cdot \mathrm{V} \cdot \mathrm{T} \cdot \left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} \cdot \left(\frac{\partial \mathrm{A}}{\partial \mathrm{P}}\right)_{\mathrm{T}} \cdot \left(\frac{\partial p}{\partial a}\right)_{\mathrm{T}}$$

$$= +\frac{a}{\mathrm{A}} \cdot \mathrm{V} \cdot \mathrm{T} \cdot \left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\mathrm{P}} \cdot \left(\frac{\partial p}{\partial a}\right)$$

$$= \mathrm{RT}^2 \cdot \frac{1}{\mathrm{A}}\left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\mathrm{P}} \cdot \left(\frac{\partial \log p}{\partial \log a}\right)_{\mathrm{T}}.$$

Now

$$\mathrm{A} \propto v_{a}^{\frac{2}{3}} \quad \propto v_0^{\frac{2}{3}} \text{ approx.}$$

$$\therefore \quad \frac{1}{\mathrm{A}}\frac{\partial \mathrm{A}}{\partial \mathrm{T}} = \frac{2}{3}\alpha$$

where α is the coefficient of volume expansion of the adsorbent,

$$\frac{\partial \log p}{\partial \log a} = n$$

where n is usually greater than unity, but finite.

Hence, assuming the adsorbing carbon to have the coefficient of expansion of graphite (and not of a liquid),

$$-\frac{a}{\mathrm{A}} \cdot \mathrm{VT} \cdot \left(\frac{\partial p}{\partial \mathrm{T}}\right)_{\mathrm{A}} \cdot \left(\frac{\partial \mathrm{A}}{\partial a}\right)_{\mathrm{T}} = \frac{2}{3} \times {\cdot}000024 \times n\mathrm{RT}^2$$

$$= {\cdot}005\mathrm{RT}n$$

$$= {\cdot}00012n \text{ per c.cm.,}$$

which is negligible compared with the terms to be corrected.

Again, we have

$$\sigma - \sigma_0 = -\int_0^p \frac{a\mathrm{V}}{\mathrm{A}} dp$$

$$= -\mathrm{RT}\int_0^p \frac{a}{\mathrm{A}}\frac{dp}{p} \text{ approx.}$$

$$\therefore \quad \left(\frac{\partial\sigma - \sigma_0}{\partial \mathrm{T}}\right)_p = -\mathrm{R}\int_0^p \frac{a}{\mathrm{A}}\frac{dp}{p} - \mathrm{RT}\int_0^p \left(\frac{1}{\mathrm{A}}\frac{\partial a}{\partial \mathrm{T}} - \frac{a}{\mathrm{A}^2}\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)\frac{dp}{p}.$$

$$\therefore \quad \sigma - \sigma_0 - \mathrm{T}\frac{\partial\sigma - \sigma_0}{\partial \mathrm{T}} = \mathrm{RT}^2\int_0^p \left(\frac{1}{\mathrm{A}}\frac{\partial a}{\partial \mathrm{T}} - \frac{a}{\mathrm{A}^2}\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)\frac{dp}{p}.$$

Now

$$\mathrm{RT}^2\int_0^p - \frac{a}{\mathrm{A}^2}\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\frac{dp}{p} = \mathrm{RT}^2\int_0^p -\frac{2}{3}\alpha \cdot \frac{a}{\mathrm{A}} \cdot \frac{dp}{p} \text{ approx.}$$

where α is the coefficient of volume expansion

$$= -\frac{2}{3}\alpha\mathrm{RT}^2\int_0^p \frac{a}{\mathrm{A}}\frac{dp}{p}$$

$$= -\frac{2}{3}\alpha\mathrm{T}(\sigma - \sigma_0)$$

$$= {\cdot}0044(\sigma - \sigma_0),$$

which is negligible compared with $(\sigma - \sigma_0)$.

$$\therefore \quad \sigma - \sigma_0 - \mathrm{T}\frac{\partial\sigma - \sigma_0}{\partial\mathrm{T}} = \mathrm{RT}^2\int_0^p \frac{1}{\mathrm{A}}\left(\frac{\partial a}{\partial\mathrm{T}}\right)_p \frac{dp}{p}$$

$$= -\mathrm{RT}^2\int_0^a \frac{1}{\mathrm{A}} \cdot \left(\frac{\partial \log p}{\partial\mathrm{T}}\right)_a \cdot da.$$

If we denote by Δ the divergence between observed and calculated values of the heat of adsorption, and by Σ the expression $\sigma_0 - \mathrm{T}\frac{d\sigma_0}{\partial\mathrm{T}}$, we have

$$\left.\begin{aligned} \Delta &= -\mathrm{A}\left(\sigma - \mathrm{T}\frac{\partial\sigma}{\partial\mathrm{T}}\right) \cdot \frac{1}{\mathrm{A}} \cdot \frac{\partial\mathrm{A}}{\partial a} \text{ approx.} \\ &= \left\{\mathrm{ART}^2\int_0^a \frac{1}{\mathrm{A}} \cdot \frac{\partial \log p}{\partial\mathrm{T}} da - \mathrm{A}\Sigma\right\}\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a} \end{aligned}\right\} \quad . \quad . \quad . \quad (20)$$

$$= \left\{\mathrm{RT}^2\int_0^a \frac{\partial \log p}{\partial\mathrm{T}} da - \mathrm{A}\Sigma\right\}\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a} \text{ approx.} \quad . \quad . \quad . \quad (20')$$

Since $\mathrm{A}\Sigma$ is unknown, we cannot evaluate $\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a}$. We may, however, proceed by another step. From (20)

$$\left.\begin{aligned} \left(\frac{\partial\Delta}{\partial a}\right)_{\mathrm{T}} &= \frac{\mathrm{RT}^2}{\mathrm{A}} \cdot \frac{\partial \log p}{\partial\mathrm{T}} \cdot \frac{\partial\mathrm{A}}{\partial a} + \left\{\mathrm{RT}^2\int_0^a \frac{1}{\mathrm{A}}\frac{\partial \log p}{\partial\mathrm{T}} da - \Sigma\right\} \cdot \frac{\partial^2\mathrm{A}}{\partial a^2} \\ &= \mathrm{RT}^2 \cdot \frac{\partial \log p}{\partial\mathrm{T}} \cdot \frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a} + \Delta\frac{\partial^2\mathrm{A}}{\partial a^2}\Big/\frac{\partial\mathrm{A}}{\partial a} \\ &= \mathrm{RT}^2\frac{\partial \log p}{\partial\mathrm{T}} \cdot \frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a} + \Delta\left\{\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a} + \frac{\frac{\partial}{\partial a}\left(\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a}\right)}{\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a}}\right\} \\ &= \lambda \cdot \frac{1}{\mathrm{A}} \cdot \frac{\partial\mathrm{A}}{\partial a} + \Delta\frac{\partial}{\partial a}\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a}\Big/\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\delta a} \end{aligned}\right\} \quad . \quad (21)$$

If the second term in (21) is negligible compared with $\frac{\partial\Delta}{\partial a}$, we may evaluate $\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a}$. Assuming the term negligible for the moment, we may apply (21) to the first three observations in Table I, the only place where the tendency to increase or decrease of the differences Δ is clearly indicated. Here it is presumably due to the upward bend in the heat curve shown in the figure.

Neglecting the doubtful value of Δ, we have from the second and third values, when $a = 82$,

$$\cdot 022/37 = \cdot 355\frac{1}{\mathrm{A}} \cdot \frac{\partial\mathrm{A}}{\partial a}$$

$$\frac{1}{\mathrm{A}}\frac{\partial\mathrm{A}}{\partial a} = \cdot 0017-.$$

From (20′),

$$\cdot 051 = (28 - \mathrm{A}\Sigma) \cdot 0017.$$

$$\mathrm{A}\Sigma = -3 \text{ approx.}$$

Hence, when $a=100$, from (20′),

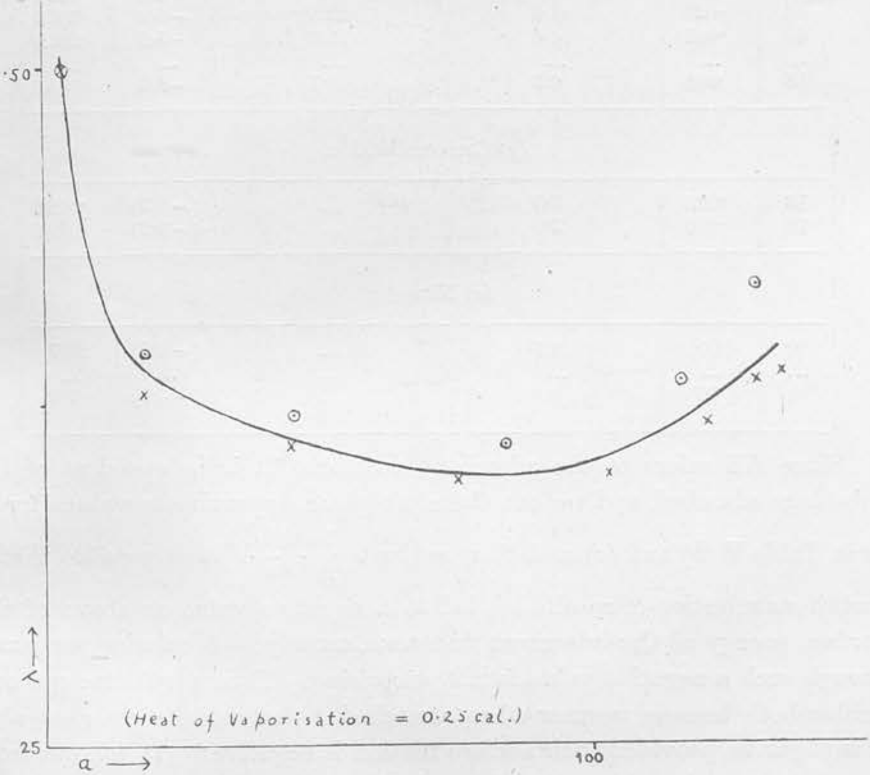
$$\frac{1}{A}\frac{\partial A}{\partial a} = \cdot 062/36$$

$$= \cdot 0017-,$$

and when $a=63$,

$$\frac{1}{A}\frac{\partial A}{\partial a} = \cdot 041/25$$

$$= \cdot 0016-.$$



∴ when $a=82$,

$$\Delta \cdot \frac{\partial}{\partial a} \cdot \left(\frac{1}{A} \cdot \frac{\partial A}{\partial a}\right) \Big/ \frac{1}{A} \cdot \frac{\partial A}{\partial a} = \cdot 051 \times \cdot 0001/37 \times \cdot 0017$$

$$= \cdot 0008,$$

whence, from (21),

$$\frac{1}{A}\frac{\partial A}{\partial a} = \cdot 0014 \text{ more nearly.}$$

This leads to $A\Sigma = -8$ from (20′), but if we calculate a series of values of $A\Sigma$ and hence evaluate the integral in (20), we get $A\Sigma = -6$. The results of such an evaluation are shown in Table IV, where it is assumed that $A\Sigma = -6{\cdot}0$ when $a=82$.

TABLE V.

a.	Δ.	$RT^2\int_0^a \frac{\partial \log p}{\partial T} da$.	$ART^2\int_0^a \frac{1}{A}\frac{\partial \log p}{\partial T} da$.	AΣ.	$\frac{1}{A}\frac{\partial A}{\partial a}$.
(*a*) Ammonia.					
126	(0·113)	40·4	44·3	−6·4	0·0022
100	·062	33·1	36·0	−6·2	·0015
82	...	...	...	−6·0	·0014
63	·040	21·9	23·5	−5·8	·0013
40	·041	14·4	15·6	−5·6	·0019
...	...	...	...	...	...
16	·048	6·3	6·7	−5·3	·004
(*b*) Carbon Dioxide.					
16	·023	5·0	...	(−5·3)	·0022
10	·020	3·0	...	(−5·2)	·0024
(*c*) Nitrogen.					
10	(·05)	2·1	...	(−5·2)	·007
...	...	...	...	...	...
1	(·06)	0·2	...	(−4·8)	·012

Since AΣ refers to the adsorbent *in vacuo*, it is independent of the substance adsorbed, and we can therefore place approximate values for it as in Table V (*b*) and (*c*), and thus evaluate $\frac{1}{A}\cdot\frac{\partial A}{\partial a}$. It is possible that a fortuitous selection of results has led to a negative value as above of the surface energy of the adsorbent *in vacuo*, namely, −5 calories per grm.; though such a negative value is not surprising. Thus a gelatine gel and rubber both become warmer when stretched;* that is, in these cases also, Σ is negative, provided their surface tension is negative.† It follows from the above negative value that adsorption is accompanied by an increase in surface, which is apparently most marked initially and presumably vanishes finally. This is analogous with the expansion of a gel on picking up water * and the swelling of rubber on adsorbing organic vapours. In both cases there is very probably an expansion of "surface."

SUMMARY.

1. The adsorption of a gas has been investigated thermodynamically with special reference to the heat effects accompanying adsorption.

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* Taylor, *Chemistry of Colloids*, p. 142.

† *Cf.* Donnan's negative surface tension of colloids.

2. Expressions are developed for three isothermal heats of adsorption of a gas and for the heat of immersion of a powder in a liquid.

3. The effect of the variation of the surface of an adsorbent when adsorbing is examined, and it is shown from Titoff's observations (assuming, of course, the adsorption to be reversible) that the divergence between calculated and observed values of the heat of adsorption can be explained on the assumption of a change of surface area. The fractional change of surface per c.cm. adsorbed can be calculated, and also the surface energy per grm. adsorbent *in vacuo.*

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ON ADSORPTION.

A Thesis

presented for the Degree of Doctor of Science

by

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NOTE:- The following thesis is to be regarded as a resume and brief extension of some of the Author's work contained in the five accompanying papers. These will be referred to as Paper I, II, -- V as follows:-

Paper I. On Adsorption from Solutions.
II. On "Negative" Adsorption.
III. The Adsorption of Vapours.
IV. The Adsorption of Sulphur Dioxide by Charcoal at - 10° C.
V. Thermodynamics of Adsorption.

Papers I and II.

1. At the surface of separation of two phases there is assumed to exist a transition layer where the concentration of the constituents of the phases is in general different from their concentrations in bulk. We may, following Gibbs, consider this layer as that included between two imaginary surfaces selected one in each phase so that just outside the properties found are those of the phase in bulk while inside the properties vary from those outside.

If we sufficiently increase the interface and thus the extent of the transition layer we may expect to find a difference in the bulk concentration. This is shown by selecting a substance which has already a large specific surface and introducing it into a gas or a solution. Thus if charcoal is shaken up with a solution of A in a solvent B a change in the concentration of the solution is usually observed. When the concentration of A decreases A is said to be positively adsorbed by the charcoal, while if A's concentration increases A is said to be negatively adsorbed. A is positively adsorbed when the concentration in the surface layer (relative to B) is greater than its concentration in the solution. Positive adsorption of A is negative adsorption of B and vice versa.

2. Let us denote the mass of A and B occurring in the transition layer per gram adsorbent by u and w respectively. Let there be G grams adsorbent introduced into M grams of solution of concentration C_o grams A per gram solution initially and C grams when adsorption has taken place. The quantity of B present in the surface layer is W grams per gram adsorbent. If the concentration of A relative to B were the same in the transition layer as in the solution the amount of A present for W grams B would be/

be W.C/1 - C grams. Since the amount of A actually present is U, the excess of A per gram adsorbent is U - W.C/1 - C. Now the total amount of A in the system is unchanged.

$$\therefore\ M\,C_o = U + (M - \overline{U+W}.\,G)C$$

$$\text{or}\quad \frac{M}{G}\,\frac{Co - C}{1 - C} = U - W\,\frac{C}{1 - C}\,.$$

Hence if we denote the excess of A by U_o

$$U_o = \frac{M}{G}.\ \frac{Co - C}{1 - C}$$

and is obviously measurable. In the same way the excess of B is

$$W_o = \frac{M}{G}.\ \frac{(1 - Co) - (1 - C)}{1 - (1 - C)}$$

$$= \frac{M}{G}.\ \frac{C - Co}{C}$$

$$= -\frac{M}{G}.\ \frac{Co - C}{1 - C}\,.\,\frac{1 - C}{C}$$

$$= -\,Uo.(1 - C)/C\,.$$

A positive excess of A denotes a negative excess of B as is indicated by the formula. U_o or an approximation to U_o is usually called the amount adsorbed and denoted by α . When α is positive A is simply said to be adsorbed, "positively" being omitted. If the initial volume of the solution is V and the initial

and/

and final volume concentrations Co and C then $\alpha = \underline{V} .(C_o - C)$, when the volume change on adsorption is negligible.

3. In practise it has been generally found that in dilute solutions of A in B, A is adsorbed. Hence it might be expected that in dilute solutions of B in A, B would be adsorbed. Thus U_o would be positive initially and negative finally as in Figure I. Suppose the relation between α and C when C is small to be given by a formula of the type

$$\alpha = k\,C^m$$

where **k** and **m** are constants and **m** positive and not greater than unity. Then when C is small

$$U_o = k\,C^m$$

and when (1 - C) is small

$$W_o = k'(1 - C)^n$$

$\therefore$ when C is nearly 1

$$U_o = -\frac{C}{1-C} . W_o$$

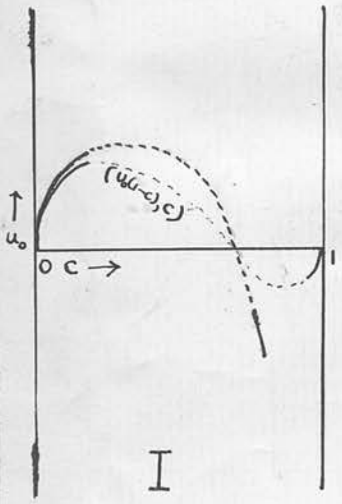
$$= -\frac{C(1-C)^n}{1 - C} . \frac{W}{(1-C)^n}$$

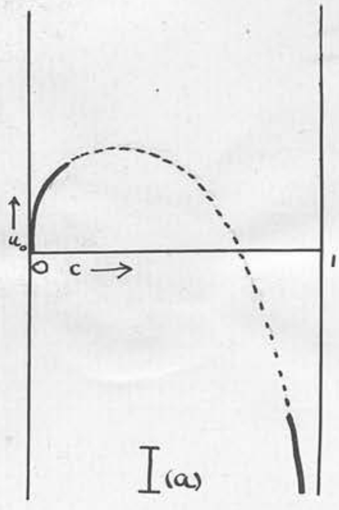
$$= -k' C / (1-C)^{1-n}$$

$$\therefore U_o \left.\begin{aligned} &= -\infty \text{ if } n < 1 \\ &= -k' \text{ if } n = 1 \end{aligned}\right) \text{ when } C = 1$$

We/

We may therefore expect to find the complete (Uo,C) curve to be either of type I(a) or I(b). Curves of





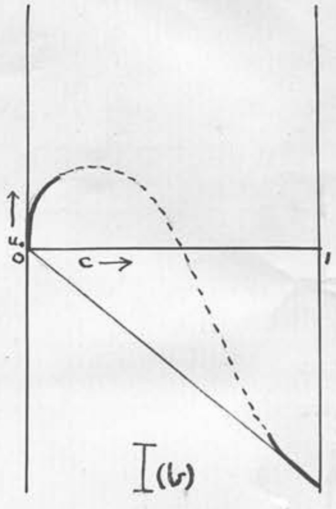
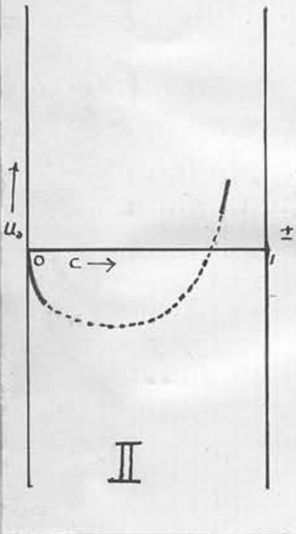
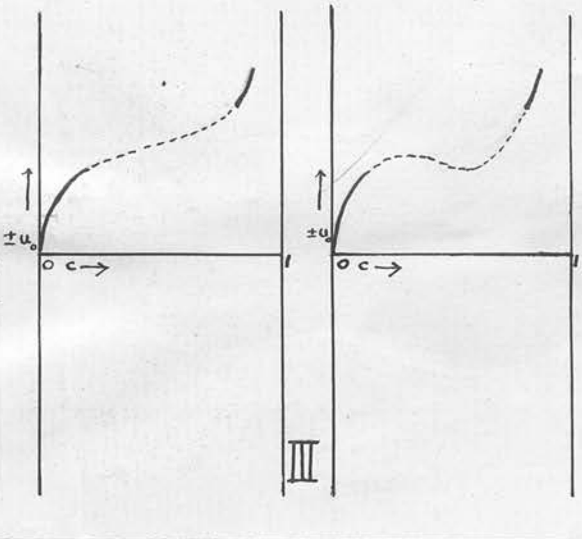


Fig. I.   Fig. I(a)   Fig. I(b)

type I have been obtained by the author and others as will be mentioned later. If k and k' were negative we would obtain a curve of type II. Such a curve, it may be pointed out, has been obtained by Trouton (B.A. Reports, 1911, p.328) for the adsorption of certain inorganic salts in aqueous solution by silica. When one of K and k' is negative curves of type III may be expected. These appear to have been obtained by Trouton (loc. cit.) though as with II his interpretation of the curves is not on the lines here indicated.





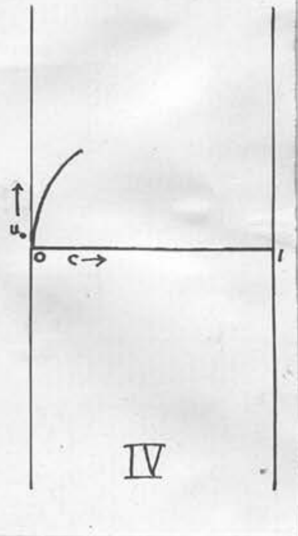


Fig. II. Fig. III. Fig. IV.

4. Several formulae have been proposed to express the adsorption equilibrium between α and C. That most extensively employed is due to Ostwald (Lehrbuch der Allgemeinen Chemie (1906) II, 3, p.232) and is based on the increasing positive adsorption of the first portion of the (U_0, C) curve as indicated in Fig IV. The graph of $(\log\alpha, \log C)$ is found to be approximately a straight line with a gradient less than unity and hence

$$\log\alpha = \log K + m \log C$$

$$\text{or} \qquad \alpha = K C^m.$$

This formula evidently takes no account of the subsequent course of the curve which was not established until later.

5./

5. Schmidt (Zeits. f. physik. Chem. (1910) 74, p.689) examined the adsorption by charcoal of acetic acid in fairly concentrated aqueous solutions. In his calculations he made the assumption that the mass of the solution remained constant even when several per cent as acetic acid was being (positively) adsorbed - apparently on analogy with the usual constant volume assumption implied in the formula $\alpha = \frac{V}{G}.(Co - C)$. He thus obtained neither U_o nor, as he believed, U but the value

$$(M\ Co - M\ C)/G = M(Co - C)\ /G = Uo(1 - C)$$

and the (Uo(1-C), C) curve shewed a maximum of Uo(1-C) which Schmidt assumed to indicate a saturation of the adsorbing surface for C = 1. Schmidt has now abandoned (Zeits. f. physik. Chem. (1916) 91, p.103) the formula he proposed to express his supposed results.

The Author (Paper I) shewed that in the case in question Uo (1-C) passed through a maximum to decrease rapidly near C = 1, but Uo steadily increased. He was unable to prove definitely the existence of negative adsorption even in very concentrated solutions (C = 0.96) with acetic acid and blood charcoal. He however obtained it easily with acetic acid and silica and subsequently with blood charcoal and aqueous solutions of KCl and $Mg\ SO_4$ (Paper II). These results are/

are shown in the tables I - IV below (which are taken from Paper I, p. 8, 15 and II, p.3) .

Table I.
(Acetic Acid and Charcoal)

C	U	$U_o(1-C)$
0.0253	0.113	0.108
.0391	.129	.124
.0801	.153	.141
.0858	.156	.143
.170	.178	.148
.179	.178	.146
.313	.189	.130
.373	.196	.123
.50	.21	.105
.92	.41	.035

Table II.
(Acetic Acid and Silica)

C	U_o
0.00007	0.0010
.0012	.0015
.0038	.0009
.0061	.0010
.014	.0007
.056	-0.0016
.35	-0.0022

Table III.
(KCl and Charcoal)

C	U_o
0.00044	0.00032
.00266	.00128
.00616	.0023
.0205	.0025
.0398	.0011
.0563	.0017
.0680	-0.0017
.0721	- .0018
.101	- .0012
.128	- .0026
.170	- .0077

Table IV.
($MgSO_4$ and Charcoal)

C	U_o
0.00043	0.00089
.00123	.0024
.0257	-0.0044
.0516	- .014
.0528	- .016
.100	- .034
.154	- .039

Table I is represented graphically in Figure V. The maximum of Uo (1 - C) is very obvious but it is evident that the (Uo,C) curve is rather of type III than of type I. The (Uo, C) curves in the other three cases appear to be all of type I.

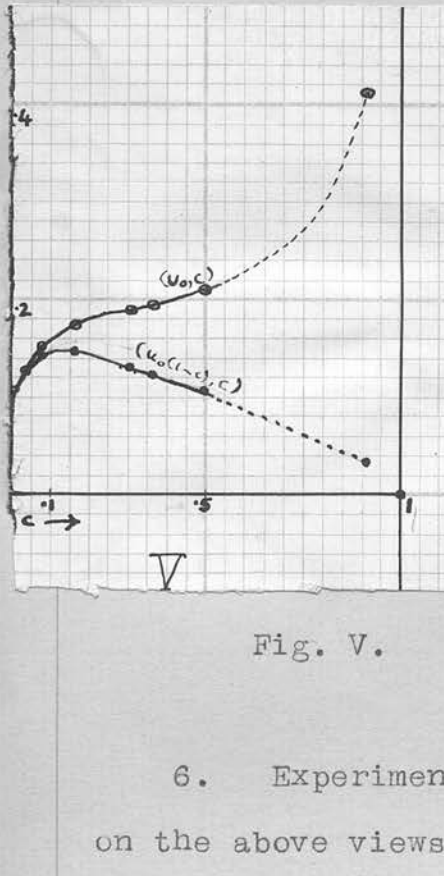


Fig. V.

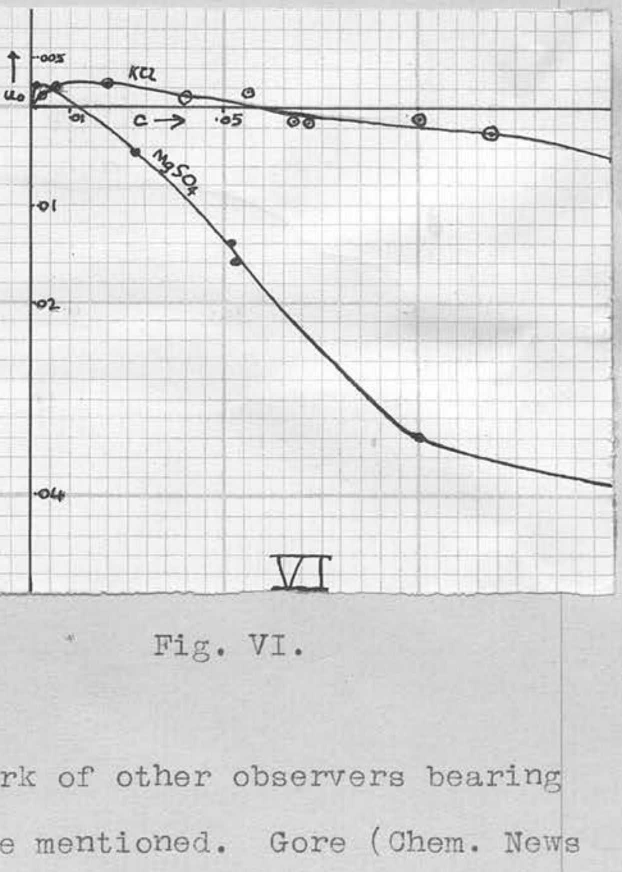


Fig. VI.

6. Experimental work of other observers bearing on the above views may be mentioned. Gore (Chem. News (1894) 69, p.23) studied the adsorption of inorganic salts by silica and obtained cases of both positive and negative adsorption. In only one case - pyrophosphoric acid - does he record initial positive adsorption followed by negative adsorption, but with zinc chloride and magnesium chloride he gives maxima of/

of negative adsorption. The results of his observations in these cases are as follows in Table V.

Table V.

	C	$5 0\alpha$
$H_4 P_2 O_7$	0.0097	+ 0.05
	.107	- 2.63
$Zn Cl_2$	.0107	- 0.25
	.054	- 1.45
	.102	- 0.89
$Mg Cl_2$	.0102	- 0.08
	.0535	- 1.33
	.103	- 1.00

Lagergren (Bihang till K. Svenska Vet.-Akad. Handlingar (1898) 24, II, 4) observed isolated cases of positive and negative adsorption but like Gore made no attempt to construct a curve connecting α and C. Evans (Journ. Phys. Chem. 10 p.290) using filter paper as adsorbent found an adsorption maximum passing to zero but not negative adsorption. Reference has already been made to Trouton but as none of his experimental data are accessible (save as curves) his work will not be further noticed. Other cases are cited on p.1 Paper II. Dora Schmidt-Walter (Koll. Zeits. (1914) 14 p.242) as a result of the author's criticism of Schmidt's papers tried "to find the/

the influence of the solvent on adsorption". She used solutions of acetic acid in various solvents and investigated the adsorption by charcoal up to great concentrations. Following Schmidt, she calculates first Uo (1 - C) — C_2 in the tables below — and then by making successive allowances for the amount adsorbed from the mass of solution works back to Uo — C_3 below. The observations with water, benzene and toluene may justifiably be regarded as confirming the author's views. Her calculations are given in tables VI - VIII. C_1 is % acetic acid present in equilibrium. In Tables VII and VIII C_3 has been calculated by the author.

Table VI. (Water.)

C_1	C_2	C_3
1.26	1.37	1.47
3.99	2.10	2.19
8.51	2.51	2.78
14.0	2.77	3.23
23.8	2.66	3.52
35.2	2.53	3.90
57.2	1.80	4.17
73.7	1.51	5.70

Table VII (Benzene)

C_1	C_2	C_3
2.07	0.409	0.42
4.47	.540	.56
10.5	.861	.96
17.2	.574	.79
17.8	.783	.95
29.8	.407	.58
43.5	.235	.42
68.0	-0.414	-1.3
82.0	-0.195	-1.1

Table VIII (Toluene)

C_1	C_2	C_3
1.55	0.439	0.45
3.68	.620	.64
9.09	.900	.99
18.1	1.08	1.20
39.6	-0.225	-0.37
58.0	-0.522	-1.24
68.4	-0.497	-1.6
85.4	-0.633	-4.3

It may be noted that in her curves she assumes the last point to be $C_2 = 0$ when $C_1 = 100$. This is shewn in Fig. VII.

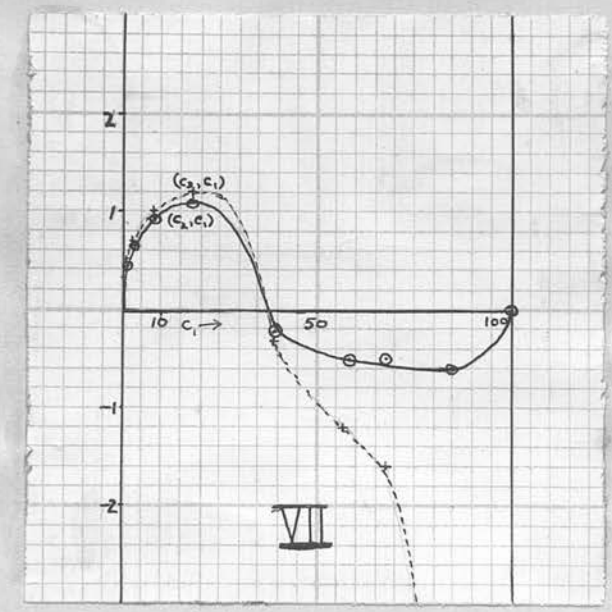


Fig. VII.

for acetic acid adsorbed from toluene by blood charcoal.

The/

The assumption is correct for

$$C_2 = U_0\ (1 - C) = -\ W_0 C \ = -W_0 \text{ When } C = 1$$
$$= 0$$

She is not graphing (U_0, C) as in the curve I above (Fig.I in the author's Paper I). By deliberately confusing the author's U_0 with U she attempts to defend Schmidt and incidentally annexes without acknowledgment certain of the author's views. This is pointed out by Gustafson (Zeits. f. Physik. Chem. (1916) 91, p.385) who states: "It is clear that the U_0 curve (from D. S-W's observations) runs in the manner indicated by Williams". Gustafson finds that the U_0 and U_0 (1 - C) curves run as indicated by the author and further claims to have obtained negative adsorption with phenol in alcoholic solution. These observations are given below in Table IX.

Table IX.

Co	C	Uo	Uo(1 - C)
	0.016	0.069	0.068
	.11	.143	.128
	.19	.190	.154
	.26	.204	.152
	.38	.207	.129
	.49	.205	.105
	.58	.195	.081
	.66	.146	.050
	.70	.109	.034
0.862	.864	-ve	-ve

7. We may now return to a consideration of the adsorption curve when C is small and the formula

$$\alpha = K C^{M}$$

$$\text{or } \log \alpha = \log K + M \log C$$

is applicable.

Careful examination of the ($\log U_0$, $\log C$) curve indicates that the curve is not a straight line but decidedly concave to the log C axis. This is shown in Fig. VIII below (Fig. 3 of the author's Paper I.) It is also indicated by the following unpublished observations of the author (1912-13) on the adsorption at 25° C. of hydrochloric acid by blood charcoal.

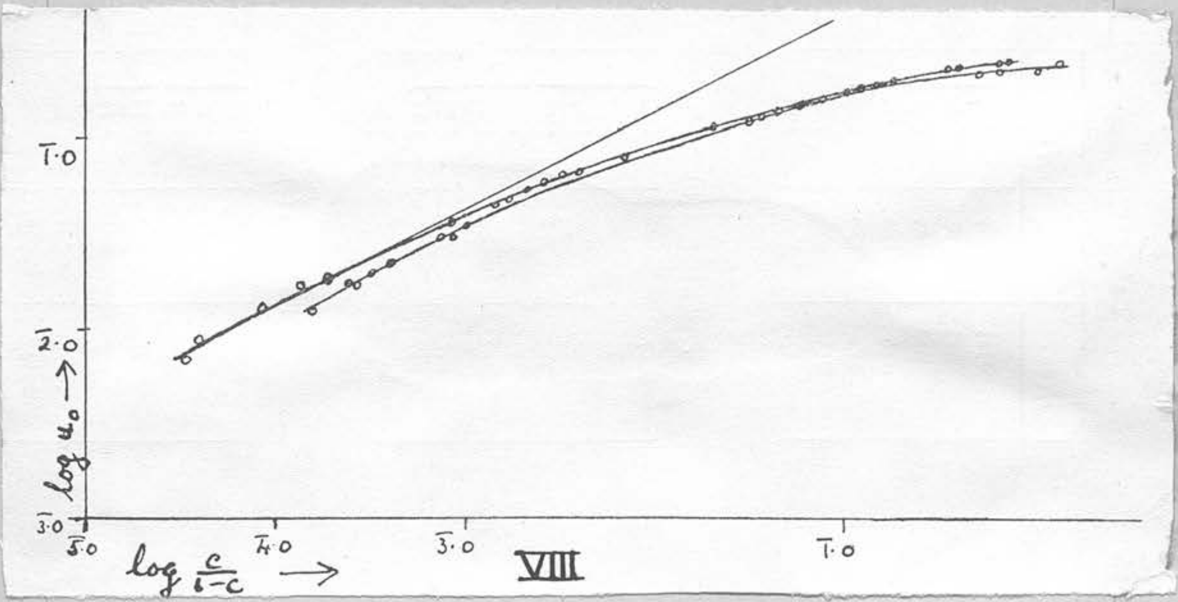


Fig. VIII.

Table X.

C	U_o	$\log C$	$\log U_o$	$\Delta \log U_o / \Delta \log C$
0.0000122	0.0042	$\bar{5}.086$	$\bar{3}.623$	0.52
347	73	.540	.860	.31
704	90	.848	.954	.28
.000128	.0108	$\bar{4}.127$	$\bar{2}.033$	.23
305	130	.484	.114	.18
490	142	.690	.152	.14
916	155	.862	.190	.21
.00124	165	$\bar{3}.095$	.218	.14
159	171	.200	.233	

Hence if we use the formula in question M is only a mean value of the logarithmic curve gradient which steadily increases as C diminishes. It is of interest to consider the final value of the gradient.

8. An examination of the values of the exponent m tabulated for different substances by Freundlich (Kapillarchemie p.150) shows that of 44 values only in one case is the value 0.50 exceeded - viz. 0.52 with Mercuric chloride and blood charcoal in water. Numerous other cases in recent work indicate that the value 0.50 is not exceeded and this suggests that $\frac{1}{2}$ is the limiting value of the exponent when $C = 0$. Fig. VIII and table X above also yield favourable evidence. It is however conceivable that at still greater dilutions the value of M approaches unity. It is further to be noted that while in the cases mentioned/

mentioned C may be small the concentration in the transition layer is still not small. Thus using the fact that W = 0.69 we have from Table X

C	U_0	U/W
0.0000122	0.0042	0.006
347	73	.011

We may expect to obtain smaller values of U_0 for a given C when we increase the temperature (on analogy with gaseous adsorption) and Freundlich (Kapillarchemie p.171) gives ($\log \alpha$, $\log C$) curves for acetic acid and charcoal where the gradient is 0.45 at 0°C, 0.6 at 50°C, and 0.8 at 94°C. Again Georgievics and Dietl (Zeits. f. physik. Chem. (1914) 87, p.669) in studying the time rate of adsorption from aqueous solution of various acids by wool at 20°C give figures which indicate a gradient of 0.7 with acetic acid and 0.75 with propionic acid. Ritzel (Zeits. f. physik. Chem. (1909) 67, p.732) shows that the adsorption of U X by charcoal appears to obey Henry's Law and this is confirmed by Freundlich and Kaempfer (Zeits. f. physik. Chem. (1915) 90, p.681).

In the case of adsorption of metallic salts by silica Schmidt (Zeits. f. physik. Chem. (1895) 15, p.56) showed from van Bemelen's results (Jour. f. prakt. Chem.(1881) 23, p.324) that Henry's Law held. The/

The following figures in Table XI show this in the case of sodium chloride where W and R are proportional to C and α respectively. (Table XI is from Ostwald, Lehrbuch, p.258).

Table XI.

W	R	W/R
0.157	0.286	1.82
.190	.335	1.77
.227	.376	1.65
.278	.465	1.68
.350	.546	1.56
.447	.746	1.67
.601	.983	1.63

The author's own figures given in tables III and IV above may be examined at low concentrations.

Table XII.

	C	U_o	log C	log U_o	Δ log U_o/Δ log C.
KCl	0.00044	0.00032	$\bar{3}.64$	$\bar{4}.51$	0.77
	.00266	.00128	$\bar{2}.43$	$\bar{3}.11$	0.70
	.00616	.00230	$\bar{2}.79$	$\bar{3}$ 36	
Mg.SO$_4$	0.00043	0.00089	$\bar{3}.63$	$\bar{4}.95$	0.95
	.00123	.0024	$\bar{2}.09$	$\bar{3}.38$	

These figures would seem to indicate that if different substances behave the same at low concentrations the limiting value of the exponent M is unity i.e at low concentrations/

concentrations Henry's Law holds. It will be shown later that there is strong evidence that this law holds in the cases of gases at low concentrations.

9. In the case of the adsorption from aqueous solution of a substance which is ionised we are not dealing with the partition of one substance between two phases (neglecting the influence of the adsorbent itself in very dilute solution and attending only to the solvent in the transition layer.) but of three, namely undissociated molecules and ions.(cf Ostwald, Lehrbuch p.254). In the case of KCl and $MgSO_4$ above C and U/W are of the same order of magnitude (e.g. C = 0.00044, U/W = .00044 + .00032/.69 = .00090) and hence the dissociation is nearly the same and since there is thus the same ratio between ions and molecules in the two phases U_0/C is more likely to be a constant if Henry's Law holds. In the other case the difference in order of magnitude between C and U/W may forbid this simple relation being found at the concentrations considered. If we apply the dilution law $M^2/(1 - M)V = K$ and find the ratio between the concentrations of the ions Henry's Law does not appear to be obeyed. This is shown in the table below (calculated from table 2(b) p.8, Paper I), assuming W = 0.5. I denotes the ionic concentration/

Table XIII.

(Acetic acid and charcoal)

C	U/W	I_c	I_u	I_u/I_c
0.00016	0.026	0.0000126	0.000169	13
34	41	187	21	11
74	59	274	25	9
92	68	304	27	9

concentration in grams per gram solvent. We may conclude therefore that if Henry's Law does hold at the concentrations considered the adsorbent influences the dissociation inside the transition layer or is involved in the calculation of the concentration which is not simply U/W.

10. The equation $U_o = U - WC/1-C$ does not enable us to evaluate U and W. If we expose the adsorbent to the vapour phase of the solution and there reach the same equilibrium as in the solution itself, we can obtain a second equation connecting U and W. Thus if i is the increase in mass (ascertained by direct weighing)

$$i = u + w$$

This the author was able to do with acetic acid - water mixtures as described in Paper I, p.16. The value of u found by solving these two equations was checked by dropping part of the charcoal in equilibrium into pure water and after heating, shaking up, and/

and allowing equilibrium to set in, finding the concentration C'. As the dilution was great U_0' (read from the curve already obtained) should be equal to U', for $U_0' = U' - W'C' / 1 - C'$

$= U'$ at great dilutions

Hence the amount of acid present in the system is given by

$$\begin{aligned} U &= U' + MC' \\ &= U_0' + MC' \end{aligned}$$

where M is the mass of water into which the charcoal is dropped. The results thus found were in excellent agreement with those calculated from the equations, thus proving that no decomposition had taken place at the surface of the charcoal. (Through an oversight these confirmatory observations were omitted from Paper I)

Gustafson (loc. cit.) endeavouring to repeat the author's method with phenol-alcohol solutions was unable to obtain equilibrium even after a year had elapsed. This may have been due to non-evacuation of the desiccators. As the author subsequently found (1912-14) presence of air greatly retards the attainment of equilibrium, presumably because the air adsorbed is not easily disengaged from the surface of the charcoal in presence of the surrounding air. The author set up a row of desiccators containing different/

different solutions of acetic, propionic, and butyric acids and weighing bottles with charcoal. He was unable to evacuate the desiccators and even after a year equilibrium had not been attained. The curves obtained would however confirm that the relation suggested by the author (Paper I, p.22) $U/U_\infty + W/W_\infty = 1$ is only an approximate one. We have

$$
\begin{aligned}
i &= u + w \\
&= U_\infty - \frac{u_\infty}{W_\infty} w + w, \text{ if the relation holds,} \\
&= U_\infty + \left(1 - \frac{u_\infty}{W_\infty}\right) w
\end{aligned}
$$

Hence if we assume that W decreases continuously from C = 0 to C = 1, i must also increase or decrease continuously according as $W_\infty \gtrless U_\infty$. But the curves obtained connecting i and C were as shown in Fig. IX.

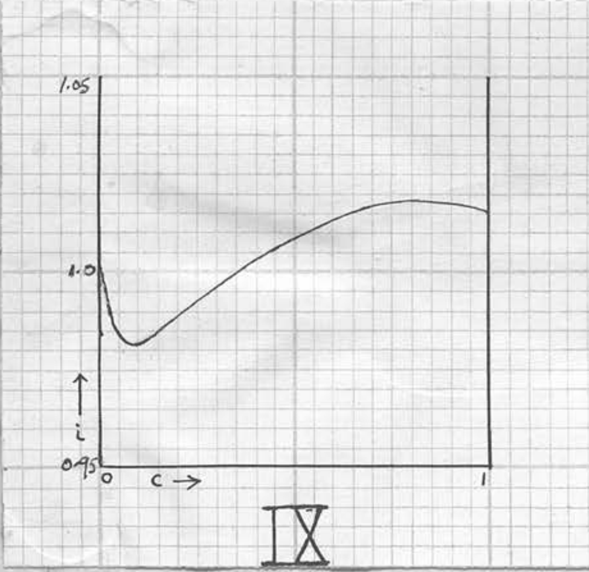


Fig. IX.

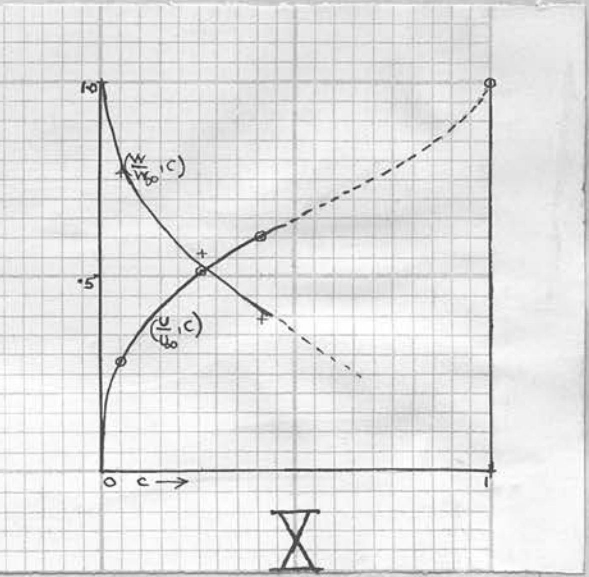


Fig. X.

The/

The initial fall in i with low concentrations was characteristic of the three acids examined. (It is of course conceivable that the presence of air entirely destroys the shape of the curve but this seems unlikely.)

The $(U/U_{\infty}, C)$ and $(W/W_{\infty}, C)$ curves as found for acetic acid at 18°C are shown in Fig X. It will be noticed that the $(U/U_{\infty}, C)$ curve almost seems to be a typical vapour adsorption curve. Gustafson (loc. cit.) appears to be of this opinion.

Paper III.

11. When we examine the adsorption of vapours and gases what we measure is again a surface excess and not the total amount in the transition layer (see Paper I, footnote p.2; Paper V, p.25). But here the correction to be applied is in general negligible. The formula most usually employed is similar to the one already discussed, namely,

$$\alpha = K p^{m}$$

where P is the pressure. Here again a careful examination reveals that m is only a mean value and the gradient of the $(\log\alpha, \log p)$ curve steadily increases as α decreases.

With gases like hydrogen at ordinary temperatures the value of the exponent appears to be unity for moderate/

moderate pressures. With other gases the mean value of M over the ordinary range of pressures rises with the temperature as is shown for example by Travers (Proc. Roy. Soc. (1906) 78 A, p.9) for the adsorption of carbon dioxide by charcoal.

Table XIV.

t	m
-78° C.	0.133
0°	.296
35°	.461
61°	.479
100°	.518

If, however, the ($\log\alpha$, $\log p$) curve for any individual temperature be examined the increase of M as α decreases is distinct. This may be shown by the author's figures for the adsorption of SO_2 by charcoal at -10° C (Paper IV, p.168)

Table XV.

p.	α	log p	log α	$\Delta \log\alpha / \Delta \log p$
0.10	21.4	1.000	1.330	.71
.36	54.2	.556	.734	.52
.92	87.6	.964	.943	.59
1.64	123.5	0.215	2.092	.46
4.48	193.	.651	.286	

p is pressure in cms. of mercury, α is ccm. at N.T.P. The limiting value of m would in all cases appear to be/

be unity, i.e. at low concentrations Henry's Law holds.

(In two of Miss Homfray's tables (Zeits. f. physik. Chem. (1910) 74, p.129) the exponent distinctly rises above unity. If this is not due to errors of observation the author's conclusion above is vitiated.)

12. In comparing the adsorption isotherms of vapours the author was led to use the fractional vapour pressure p/P instead of the vapour pressure P and it was then found that the curves became more obviously of the same type. This is well shown in Figs. XI and XII (Figs. 1 and 2 in Paper III.)

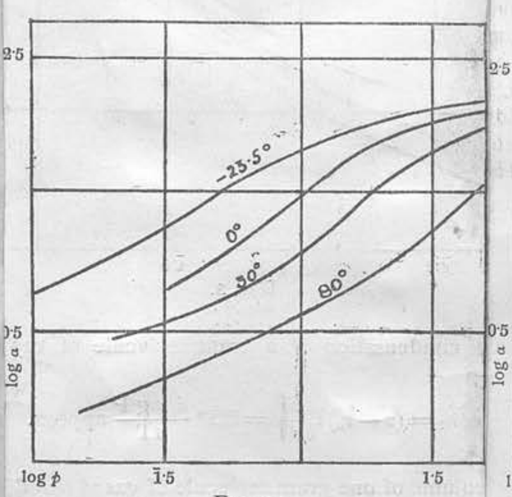


FIG. 1.

XI

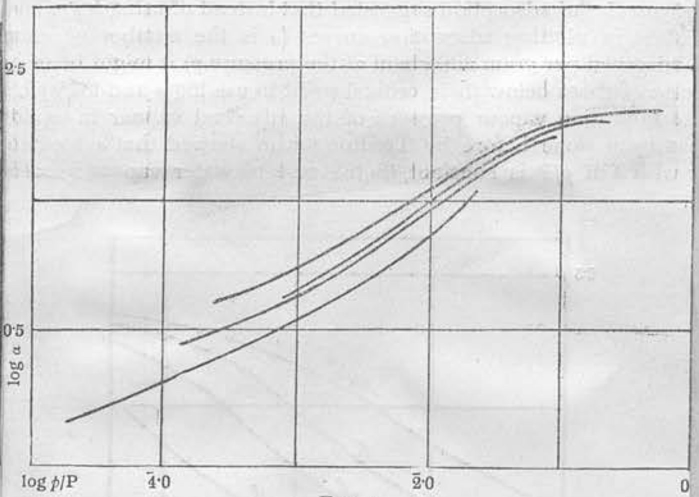


FIG. 2.

XII

Fig. XI. Fig. XII.

Trouton (Proc. Roy. Soc. (1905) 77 A, p.292) in studying the case of adsorption of water vapour by flannel was led to the conclusion that the (α , p/P) curve was independent of the temperature and/

and Masson and Richards (Proc. Roy. Soc. 78 A, p.412) concluded similarly. This would imply that the heat of immersion was zero since by analogy with solution the heat of adsorption of successive portions of fluid at constant pressure is equal to $R\,T^2\left(\frac{\partial \log p/P}{\partial T}\right)_\alpha$ (See Paper III, p.2, Paper V, p.27).

Since there is an appreciable heat of immersion the different (α, p/P) curves are not coincident but as shown in Fig. XII.

13. On examining the value of $R\,T^2\left(\frac{\partial \log p/P}{\partial T}\right)_\alpha$ the author was struck by the fact that it steadily diminished. Experimentally also the heat of adsorption of a vapour falls to the heat of condensation as the vapour pressure p increases to the saturated vapour pressure P. That is, if the adsorption is reversible and the surface extension negligible, $R\,T^2\left(\frac{\partial \log p/P}{\partial T}\right)_\alpha$ falls to zero.

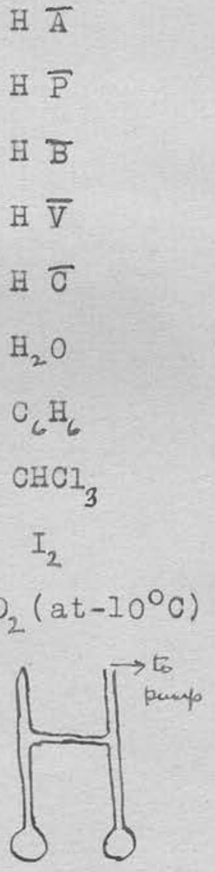
As will be seen(in Paper III) this leads to the conclusion that the amount adsorbed at the saturated vapour pressure is either infinite or finite and independent of the temperature. The author inclines to the opinion that the amount adsorbed is finite and it would be of interest to test if the amount is independent of the temperature. No evidence is at present available and extrapolation seems unwise from the reasons stated in Paper III.

14./

14. The author investigated (1912-13) the amounts adsorbed by 1 gram charcoal at 25° C of different substances at their saturated vapour pressure. In a desiccator were placed two weighing bottles containing charcoal and a third containing the substance to be adsorbed. The desiccators consisted of four ounze sample bottles closed by a waxed rubber cork and were kept in a thermostat after evacuation by a Töpler pump. The results were as follows for various fatty acids, etc.

Table XVI.

Charcoal	1.00 gm.	0.62 cc.
$H\overline{F}$	1.08	0.90
$H\overline{A}$	0.97	0.93
$H\overline{P}$	0.85	0.86
n $H\overline{B}$	0.77	0.81
n $H\overline{V}$	$>$ 0.69 (after 100 days)	$>$0.75
n $H\overline{C}$	$>$0.28 " " "	
H_2O	0.69	0.69
C_6H_6	0.72	0.83
$CHCl_3$	1.18	0.79
I_2	$>$0.43 (after 100 days)	
SO_2 (at-10°C)	1.39	0.97



On placing water and charcoal in a tube of the form shown and freezing the water in CO_2 and alcohol while evacuating/

evacuating the charcoal bulb at 100° C and then sealing off, equilibrium was apparently attained in a few days. After 2 days and 5 days the value 0.68 gm. was obtained - compare 0.69 above.

Assuming normal densities in the adsorbed layer we may compare the volumes adsorbed. It will be noticed that the volume adsorbed varies appreciably and hence it seems unlikely that the adsorption from the saturated vapour is a mere filling up of capillary pores as suggested by Langmuir (Jour. Amer. Chem. Soc. (1917) 39, p. 1848) from Gurwitsch's observations (Jour. Russ. Phys. Chem. Soc. (1915) 47, p.805) on the volumes of different vapours adsorbed.

Papers IV and V.

15. The author has studied the variation of the heat of adsorption with the amount adsorbed and his results are shown in Paper IV. He has also investigated the thermodynamical aspect and raises in Paper V the question of the effect of a possible variation of the extent of the adsorbing surface. Applying the thermodynamical formula to Titoff's results (Zeits f. Physik. Chem. (1910) 74, p.641) the author obtains a negative value for the surface energy of the adsorbent. Donnan (Zeits. f. physik. Chem. (1903) 46, p.197) has considered a negative surface tension and/

and shows how it may arise when two substances are present at the interface. In the above paper V the surface energy refers to the adsorbent in vacuo and it is not so easy to see how it should be negative. From the usually accepted ideas of molecular forces it would seem to imply either (1) the surface layer is denser than the substance in bulk - (a conclusion, by the way, reached by Lewis. (Phil. Mag. 1910 p.502) by what appears fallacious reasoning to the author) - or (2) the particles constituting the surface repel each other.

(Assuming the divergences tabulated in Paper V are real and not due to experimental error and that the thermodynamics are sound and applied to a reversible adsorption, a more conventional result would have been either a zero value or high positive value for the surface energy. Of these two the more likely value seems zero which would imply that there is no change in the density of the adsorbent in bulk and at the surface. In view of the observed divergences this would further imply a much greater initial expansion on adsorption.)