Colloidchemistry. — *"Researches on the Nature of the So-Called Adsorptive Power of Finely-Divided Carbon."* I. *The Binding of Water by Animal Carbon*. By Dr. J. R. KATZ. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of June 30, 1923).

I. *Introduction.*

The power of finely divided carbon to bind all kinds of substances is evidently in connection with the degree of fineness of division; for in not finely divided condition the carbon does not show this property. At present the phenomenon is almost universally considered as a typical example of real surface adsorption, i.e. as the accumulation of a substance in the boundary layer simply in consequence of the surface-forces.

This surface adsorption is generally considered as in sharp contrast with the formation of a solid solution. In the latter case the bound substance is not only found in the boundary layer solid-liquid, but through diffusion it gradually penetrates between the molecules of the solid substance, so that finally the principal quantity of the absorbed substance is not found in the boundary layer, but homogeneously distributed throughout the solid body.

A clear realization of the questions that can be solved by experiments on the nature of this binding to carbon only dates from the time of physical chemistry. BANCROFT [1]) and others have considered the possibility that the substances would have been absorbed by the carbon in solid solution; but the further development of this thought failed on account of the form of the binding-isotherm. If we had to do with a solid solution, — this was the opinion some twenty years ago — the laws of HENRY and NERNST must be valid, hence the quantity of absorbed substance must be in direct ratio to the concentration of the vapour and liquid phase, with which it is in equilibrium. A curve is, however, obtained which is almost horizontal at first, and which then turns its convex side downward. This might be explained by the assumption that the absorbed substance dissociates in the carbon into many (e.g. four

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[1]) The Phase Rule.

or ten) molecules. In most of the substances bound by carbon such a hypothesis has no sense. Besides it does not become clear why the carbon works the better as it is more finely divided; this must then be accounted for as a consequence of the easier diffusion.

In 1907 FREUNDLICH showed [1]) that the binding isotherm can be represented by the formula:

$$\frac{x}{m} = a \cdot c^{\frac{1}{n}}$$

for not too great values of c (m is the quantity of carbon, x the substance bound by it, c the concentration of this substance in the solution which is in equilibrium with the carbon, a and n are constants). He showed that we had to do here with *real* equilibria which are established within a very short time. The degree in which a solid substance binds, varies greatly with the absorbed substance, but is little dependent on the nature of the solid phase. FREUNDLICH demonstrated that these facts become perhaps most easily comprehensible when it is assumed that the binding rests on surface adsorption, on a becoming denser of the surface of the solid phase. But in 1909 he himself does not exclude the possibility that the phenomenon rests on the formation of a dissociable chemical bond or a solid solution: he only calls these explanations "wesentlich unvorteilhafter" [2]).

In course of time, however, in default of new arguments for the other conceptions, this view has gained so many adherers that it often makes the impression as if it were an established fact that the sorption by carbon rests on a real surface-adsorption.

In 1910 I succeeded [3]) in showing that a deviation from the laws of HENRY and NERNST in solid solutions can have another cause than the dissociation of the bound substance into molecules, viz. when the mixing in solid solution is *chiefly* caused by the *attraction* between the molecules of solvent and dissolved substance; whereas in the ordinary diluted solutions the mixing is brought about particularly by the *diffusion impulse* (because mixing is a more probable state, one that takes place with increase of entropy — also when the attraction may be neglected). In this case the decrease of free energy is about equal to the heat effect that takes place in the

[1]) Zeitschr. f. physik. Chemie **57**, p. 385 (1907).

[2]) Kapillarchemie, 1ste Aufl. p. 289, Akadem. Verlagsgesellschaft Leipzig 1909.

[3]) These Proc. Vol. XIII, p. 958; Address at the Meeting of the Bunsen-Gesellschaft. Kiel, 1911; Gesetze der Quellung, Kolloidchem. Beihefte Bd 9.

binding. If the differential binding heat is great, and if it decreases on absorption of the substance, then follows from the equality of the variations of free energy and of binding-heat that the binding isotherm must have a course as FREUNDLICH must have found, i. e. that it begins pretty well horizontally, and then turns its convex side downwards. This appears to be the case in aqueous solutions of sulphuric acid and phosphoric acid, and in the swelling albumens and polysaccharides. In all these cases FREUNDLICH's formula appears to hold as approximating formula for small concentrations, even particularly well in aqueous solutions of sulphuric acid and phosphoric acid, though we have certainly not to do here with real surface adsorption, but with real mixing.

Hence it is clear that the validity of FREUNDLICH's *formula does not furnish the proof that we have to do with surface adsorption.* Inversely the equality in the variation of free energy and heat-effect is no proof either that there exists an ideal concentrated solution. It does not seem improbable to me that this equality *also* exists with pure surface adsorption, and possibly with many complicated intermediary phenomena called *sorption* at present. I found it confirmed in the absorption of water by cupri ferro cyanide, in which a strong change of colour from violet black to light brown is found [1]). The next step is now in my opinion to test this relation by a number of typical examples of genuine surface adsorption and of sorption. For if it appears to be valid everywhere, this is an important contribution to the knowledge of the sorption phenomena; and if it holds in some cases and not in others, it may be studied on what this depends. But apart from this it leads to a better method of analysis of sorption and adsorption phenomena : *the simultaneous determination of the sorption isotherms and of the sorption heats.* This method gives a much deeper insight than the prevalent one, which is restricted to the determination of the sorption isotherm for small concentrations. That FREUNDLICH's formula is of such universal validity at these small concentrations, will probably appear to mean that (in a system in which the variations of free energy and of heat-effect are equal in approximation) the differential sorption heat is very great at first, and diminishes gradually during the absorption; the longer the (almost) asymptotic horizontal initial part of the isotherm, the longer the differential sorption heat will preserve a great value. What is important in this method of investigation of the sorption phenomena is further that

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[1]) Verslag van de gewone vergadering der wis- en natuurk. Afd. Kon. Akad. v. Wet. Dl. XXXI, Nos. 9—10, p. 542.

it can take into account not only the course of the isotherm for small concentrations, but the whole course. And besides it has the advantage that it does not bind itself beforehand by a preconceived opinion on the question which can at present mostly not be decided, of what nature the sorption phenomonon is (solid solution real surface adsorption, dissociable chemical combination, or two or three of these possibilities at the same time). The simultaneous determination of the two curves does, however, supply a collection of facts important for the decision of this question, which every theory has to take into account.

2. *Experiments.*

The purest animal carbon of MERCK was used for the investigation It was placed in air-dry condition in a wide-mouthed glass jar; its water content was determined at 230° C. after 3 hours' drying. It is not impossible that in this way the water percentage is found slightly too high, the weight of the carbon having possibly been slightly diminished by oxidation. As in most hygroscopic substances of this kind it remains somewhat arbitrary *what* is considered to be "dry" substance.

For the determination of the *sorption heats* quantities of from 5 to 12 grammes of carbon were weighed in *air-dry* condition, which can easily be done accurately, as the substance is not particularly hygroscopic in this condition; the carbon cannot be weighed accurately when quite dry. In crystallisation dishes these samples of carbon were brought in exsiccators over sulphuric acid-water mixtures of different strengths; we then waited till equilibrium had been approximately established. In this way samples of carbon were obtained in which the water was very uniformly distributed. Where the water-content of the air-dry carbon was known, the increase or decrease of weight of the sample of carbon yields its water content at the known vapour tension.

This carbon was placed in a glass tube, which was closed with a tight-fitting rubber stopper and placed in a calorimeter vessel filled with water. The experiments were made in a room in which the temperature was particularly constant. After temperature equilibrium had been established, the course of the thermometer was followed; then the contents of the tube were emptied into the water of the calorimeter vessel, after which the temperature was again observed. After from 2—4 minutes the generation of heat did not increase appreciably any longer.

Let us call i the degree of sorption (gr. of water per 1 gr. of dry substance), and W the heat of sorption (generation of heat in cal. when 1 gr. of dry substance absorbs 1 gr. of water). Then I found:

i	Quantity of heat at maximum sorption per 1 gr. of dry carbon	W
0.—	20.91	0.—
0.049	17.66	3.25
0.090	15.34	5.57
0.218	11.79	9.12
0.350	7.90	13.01
0.437	6.05	14.86
0.563	3.12	17.79
0.659	1.59	19.32
0.718	1.09	19.82
0.753	0.29	20.62
sorption-max. 0.93	0.—	20.91

This is the integral heat of sorption. From this I calculate the differential heat of sorption for $i = 0$

$$\left(\frac{dW}{di}\right)_{i=0} = 75 \text{ cal.}$$

This value is considerably smaller than was found in swelling substances (250 to 400 cal.). At the heat of mixing of sulphuric acid (with water) it amounted to 550 cal., of phosphorus 100 cal., of glycerine 20 cal.

The curve of the integral sorption heats is graphed in fig. 1; it starts as the ordinary curve of the heats of imbibition and of mixing, as a hyperbola, then follows a flattened, almost rectilinearly rising part, the end again being a hyperbola. Accordingly it is distinctly different from the curves described by me formerly for bodies that can swell up.

I have not yet succeeded in calculating the differential sorption heat in its full course from these measurements. The curve of the integral sorption heat has so complicated a shape that a formula with a great number of parameters is required to give any description of it. The greater the number of parameters, the more arbitrary is

the calculation of the differential quotient $\dfrac{dW}{di}$. But this at least may
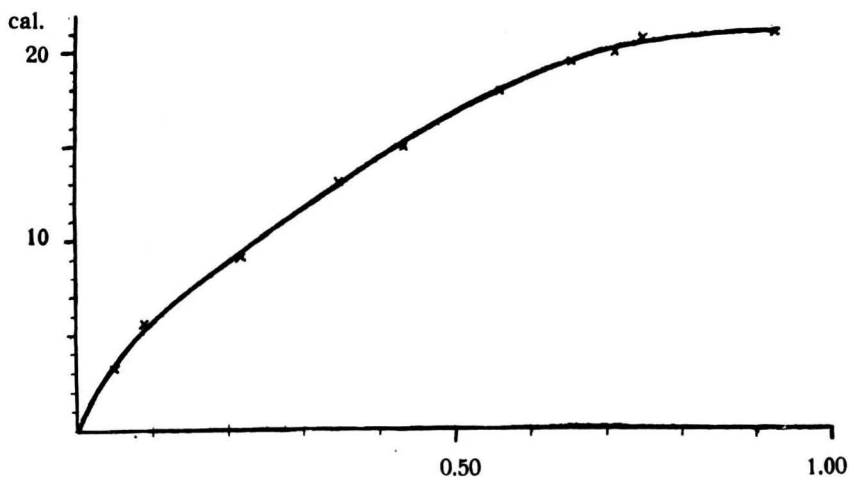

Fig. 1.

be said now that the curve begins with $\dfrac{dW}{di} = 75$ cal., then decreases pretty rapidly, in a way, which corresponds pretty closely with the course of this quantity in the heats of mixing (of sulphuric acid or phosphoric acid with water). At $i = 0.10$ to $i = 0.15$ it begins to assume a more or less constant (albeit slowly diminishing) value, amounting to about 23 cal., which diminishes again greatly past $i = 0.65$, and converges to zero.

It would be very important also to study the volume contraction at the absorption of water; for, where in expansible and in miscible substances the relation $\left(\dfrac{c}{W}\right)_{i=0}$ always appeared of the same order of magnitude (between 10 and 30×10^{-4}), it would be important to examine what the order of magnitude of this quotient would be in animal carbon. Unfortunately it is not possible to determine these volume contractions, as carbon probably acts as an adsorbent on *every* pycnometer liquid, at least in anhydrous condition.

The *free energy* at the sorption can most easily be calculated from the vapour tension of the water at different degrees of sorption. These vapour tensions have not been determined directly, but indirectly by the method of GAY LUSSAC-VAN BEMMELEN (by bringing the substance into equilibrium with sulphuric acid-water mixtures of known strength till constancy of weight is reached). The absorption and loss of water then appeared to be a phenomenon of equilibrium, which presents *hysteresis*. This result is in striking

contrast with FREUNDLICH's experience that the absorption of *dissolved substances*, as iodine, dyestuffs, and organic acids, is an equilibrium, which is readily established independent of the condition from which one starts, and within a few minutes; this observation of FREUNDLICH's was confirmed for *dissolved* substances by many investigators.

In order to obviate the influence of hysteresis, the equilibrium had to be determined from two sides; then the approximative value of the state of equilibrium was calculated by taking the mean of the two values found in this way. Accordingly twice thirteen samples of air-dry carbon, each having a weight of about one gramme, were weighed off in crystallisation dishes. One half of these dishes were dried for one or two weeks in a vacuum exsiccator over sulphuric acid; they then contained no more than 1 or 2 parts of water to 100 parts by weight of dry carbon. The other half was placed over water in a vacuum exsiccator for the same length of time; they then contained about 90 parts of water to 100 parts of dry carbon. Then thirteen small exsiccators were arranged with sulphuric acid-water mixtures of known vapour tension; in every exsiccator there was placed a dry and a moistened carbon. These acids were refreshed a few times. After 40—90 days, when the dishes had become almost quite constant of weight long before, it was assumed that they had reached their onesided equilibrium. All the experiments took place at a temperature of 16—20° C. in a room in which the variations of temperature were particularly small (a room built specially for thermochemistry).

The vapour tension h was expressed as fraction of the maximum tension of water at the same temperature; the sorbed quantity i as grammes of water per one gramme of dry carbon. The free energy at the sorption of one gramme of liquid water is found from the relation $A = \dfrac{1252}{18} \, log^{10} h$.

Fig. 2 shows the isotherm. The curve begins as a real adsorption-curve (or as the isotherm of a concentrated solution), but with a *very* short horizontal initial portion[1]), at half its height, ($h = 0,40$ to $0,65$) it gets, however, an almost horizontal part; at $h = 0,65$ and $i = 0,57$ there begins a new part of the curve (which, however, issues from the preceding part without any abrupt transition), which again has an S-shape. It is remarkable how great the quantity

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[1]) This has probably been drawn too long; has the weight of the carbon not been somewhat diminished by drying at 200° C. through oxidation? The horizontal beginning, *if* it exists, is probably only little pronounced.

of water is which this form of amorphous carbon can absorb; over a sulphuric acid with a $h = 0,997$ the substance absorbed 0,929 parts of water per 1 part of dry substance! Accordingly an absorption of water of the same order of magnitude as in *greatly* swelling

| h	i			Difference between the two false equilibria
	after moistening	after drying	in equilibrium	
0.010	0.009	0.022	0.016	—
0.083	0.033	0.021	0.027	—
0.176	0.039	0.038	0.039	—
0.278	0.062	0.052	0.057	0.010
0.410	0.172	0.141	0.157	0.031
0.517	0.458	0.266	0.362	0.192
0.596	0.570	0.411	0.491	0.159
0.721	0.649	0.572	0.631	0.077
0.788	0.673	0.631	0.652	0.021
0.853	0.698	0.676	0.687	0.022
0.914	0.730	0.715	0.723	0.015
0.962	0.800	0.814	0.807	—
0.997	—	0.929	0.929	—
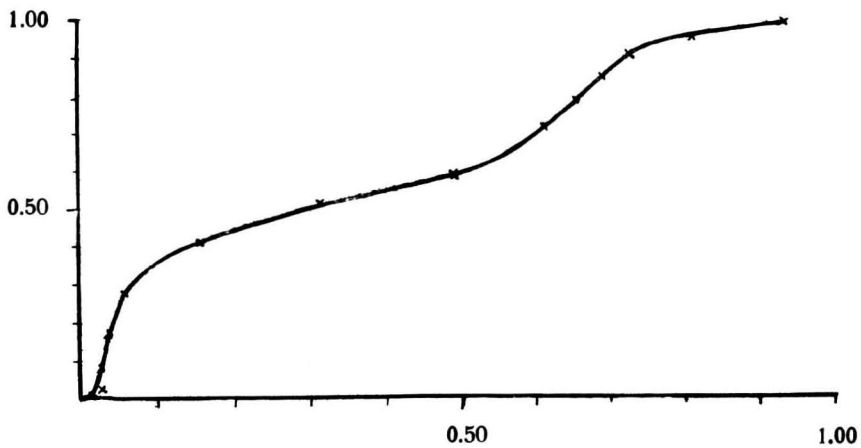
Fig. 2.

substances. BACHMANN [1]), who already determined an isotherm of carbon and water before me, found in cocoanut carbon a maximum water absorption of $i = 0,25$. BERL and ANDRESS [2]) also found in their carbon a considerably smaller value than I in mine.

The double-S-shaped curve of the isotherm obtained is practically the same form as that which van BEMMELEN has observed in gels of silicic acid and of iron hydroxide. The flat portion there corresponds to the part of the curve in which the gel, which is first transparent, becomes opaque.

3. *Comparison of Free Energy and Heat Effect.*

A simple comparison of the curves fig. 1 and fig. 2 shows that $\dfrac{dW}{di}$ and $log\ h$ must have an analogous course as function of i. Both curves have an almost horizontal, almost rectilinear (slowly descending) portion between $i = 0.10$ and $i = 0.60$ to 0.65; both curves have before and after this the shape as for liquids which mix with water with strong heat effect. By graphical determination of the differential quotient $\dfrac{dW}{di}$ this can be estimated for some values of i, for which $log\ h$ is known. Thus I find:

i	h	$\dfrac{1252}{18} log^{10} \dfrac{h_1}{h_2}$	$\left(\dfrac{dW}{di}\right)_1 - \left(\dfrac{dW}{di}\right)_2$
0.027	0.083		
		37 cal	11 cal
0.057	0.278		
		12 ,,	20 ,,
0.157	0.410		
		7 ,,	8 ,,
0.362	0.517		
		4 ,,	4 ,,
0.491	0.596		
		6 ,,	4 ,,
0.631	0.721		
		5 ,,	5 ,,
0 687	0.853		
		3.5 ,,	6 ,,
0.867	0.962		

These are only rough estimations; but they show nevertheless with sufficient probability that in the large middle portion of the curve (from $i = 0.05$ to $i = 0.80$) the variation of the free energy

[1]) Zeitschr. f. anorgan. Chemie **100**, p 32 (1917).
[2]) Zeitschr. f. angewandte Chemie 1921. Bd. I.

is of the same order of magnitude as the heat effect. But with small i the heat effect is much smaller than the variation of the free energy. This latter is probably in connection with the small value of the first differential heat of sorption in this substance. Most likely there is no equality in the middle piece either, but only correspondence in the order of magnitude. The experiments are, however, not accurate enough to set forth this difference clearly.

4. The Analogy of the Curves with those for Newly-made Silicic Acid and ZSIGMONDY and ANDERSON's Explication.

As I already observed, the isotherm has the same typical shape as that found by VAN BEMMELEN and later by ANDERSON for silicic acid gel. The "turn", the point where the second S-shaped curve begins, lies at $i = 0.57$ and $h = 0.65$ for carbon. Also BACHMANN found a curve with a horizontal portion for the cocoanut carbon examined by him (possibly even with two such pieces). And BERL and ANDRESS found a curve of the same shape as mine in the carbon examined by them.
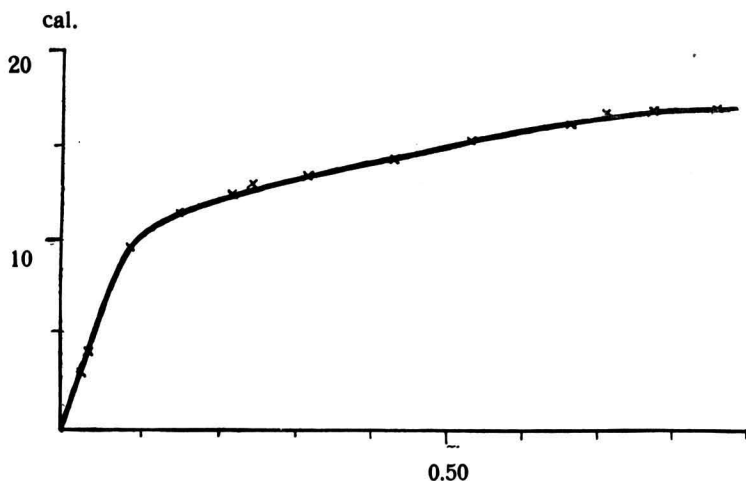

Fig. 3.

That also the curves of the heats of sorption correspond is shown by fig. 3, in which I have represented BELLATI and FINAZZI's results [1] for newly-made silicic acid (temperature $12° - 20°$ C.). Unfortunately these carefully performed researches have so far escaped the notice of the writers of the books on colloid chemistry, whence they have not met with the recognition they deserve. The curve typically

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[1] M. BELLATI and L. FINAZZI, Atti d. R. Instituto Veneto, Serie VIII, Tomo 4, p. 518.

presents the same course as that found by me for carbon; the initial part as the curve for a heat of mixing, the almost rectilinear middle portion, the end in a curve with the concavity downward. Unfortunately we have no reason to believe that the silicic acid examined by BELLATI and FINAZZI possesses exactly the same constants as that on which VAN BEMMELEN and ANDERSON performed their determinations of the vapour tension, as the properties greatly depend on the preparation. This *is*, however, the case in the experiments with carbon, described above.

In the absorption of water vapour by carbon we have, therefore, to do with a system of which the isotherm and the curve of the heats of sorption are in perfect agreement with the same curves of those silicic acid gels that present a so-called "turn".

In silicic acid it is very probable that in the flat piece very fine capillaries are getting filled with water, for absorption of water causes the opaque substance to become transparent again. ZSIGMONDY and ANDERSON [1] pointed out that the radius of these fine capillaries can be calculated from the vapour tension of the water in the flat piece; they then arrived at values of the order of magnitude 1.3 10^{-6} mm. for the initial part, and 2.6×10^{-6} mm. of the end of the flat piece. And they showed further that when the same silicic acid gel is changed into an alcohol or benzene gel, and the radius of the capillary is calculated from the vapour tension of the alcohol or the benzene, values are obtained for this radius of the same magnitude as in water. This pleads very strongly in favour of the view that the flat middle piece is due to the filling of capillaries, which gradually become slightly wider, hence on micro-porosity.

PATRICK [2] repeated these experiments with liquid carbonic acid and liquid sulphur dioxide with silicic acid gel. Then he found, however, much less concordant values for the size of the capillaries; he tried to explain this by the greater thickness of the capillary layer near the critical point.

BACHMANN [3], working in ZSIGMONDY's laboratory, also explained the flat middle piece in the isotherm of carbon and water by a system of such fine capillaries. The substance being opaque, it cannot be ascertained if this property becomes stronger in the middle piece.

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[1] Zeitschr. f. physikal. Chemie, **88**, p. 191 (1914); ZSIGMONDY, Lehrbuch der Kolloidchemie, 4th edition, p. 219—234.

[2] PATRICK, Diss. Göttingen, 1914.

[3] BACHMANN, loc. cit.

My experiments lead to the following values for this radius:

$$i_1 = 0.157 \qquad h_1 = 0.410 \qquad r_1 = 1.24 \times 10^{-6} \text{ mm.}$$

(beginning of the
flat piece)

$$i_2 = 0.362 \qquad h_2 = 0.517 \qquad r_2 = 1.67 \times 10^{-6} \text{ mm.}$$
$$i_3 = 0.491 \qquad h_3 = 0.596 \qquad r_3 = 2.13 \times 10^{-6} \text{ mm.}$$
$$i_4 = 0.57 \qquad h_4 = 0.65 \qquad r_4 = 2.57 \times 10^{-6} \text{ mm.}$$

(end of the
flat piece).

The values found for the radius of the micro-capillaries, are in such close agreement as regards order of magnitude with the values of ZSIGMONDY and ANDERSON, and with those of BACHMANN, that it is astonishing that always *this* order of magnitude is again met with. (The second system of capillaries which BACHMANN thinks that he can derive from his curves, seems questionable to me).

The agreement in the form of the curves for the heats of sorption with their typically flattened piece corroborates that the flat part of the isotherm for carbon and for silicic acid has the same cause.

It is the more striking under these circumstances that BERL and ANDRESS have found that the same carbon which gives a flat middle piece in the isotherm with water, has *a curve without any flat middle piece,* and with a much longer horizontal initial part (for small l) *with organic liquids* (as benzene or methyl alcohol). If the correctness of these experiments is confirmed, they furnish the proof that ZSIGMONDY's explanation, cannot be the true one, at least for carbon. I am, therefore, occupied with a repetition of these experiments, and also with a determination of the heats of sorption.

Since ZSIGMONDY's explanation is inadequate to account for the flat piece in the isotherm and for the flattened piece in the heats of sorption, it is in my opinion natural to see a connection between the deviating form of the isotherm of water and the fact that *water moistens solid bodies, as carbon, much less easily than organic liquids,* as benzene or methyl alcohol, do. We should then have to do in water and carbon with surface adsorption at a surface that is not easily moistened, a phenomenon of which so far only one example has been studied somewhat more closely [1]), viz. the adsorption of watervapour to glass-wool which has been thoroughly dried beforehand, investigated by TROUTON [2]). The glass-wool had been previously

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[1]) FREUNDLICH, Kapillarchemie, 2nd edition, p. 223. Possibly there is solid solution present as a complication in the boundary layer also here.

[2]) FREUNDLICH, loc. cit.

treated by drying at 162° over phosphorus pentoxide, and then gave an isotherm with a flat middle piece (possibly even with a faint retrograde piece), which shows a close analogy with the shape of the isotherm for water and carbon. When the glass-wool had been well moistened beforehand, it gave an S-form, as they have been found in mixtures of sulphuric acid and water, and in swelling bodies with water as imbibition-liquid; characteristic is there the beginning with a strongly pronounced horizontal piece for small i, in which region FREUNDLICH's adsorption formula is valid. Similar curves were found by BERL and ANDRESS for the adsorption of those liquids that moisten the carbon well.

This conception might also be able to explain why the adsorption by carbon of water presents such strong hysteresis, whereas that of organic vapours seems to take place without hysteresis. It is, however, possible that solid solution in the boundary layers also plays a part in this [1]).

The experiments are being continued.

5. *Conclusions.*

1. In the investigation of the phenomena of sorption it is insufficient to determine the isotherm of binding; it is necessary to determine at the same time the heat of sorption as function of the quantity of absorbed substance at *the same* material.

2. The examined animal carbon appeared to have an isotherm with an almost flat middle piece, analogous to the isotherm of newly-made silicic acid. The sorption-heat had a course corresponding with this, a flattened middle piece.

3. By assuming that this course is explained by a system of micro-capillaries, I calculate the radius of these capillaries from the isotherm at 1.2 to 2.6 $\mu\mu$ (as for silicic acid). That this dimension agrees so closely with that for silicic acid, is somewhat strange and striking.

4. It is, however, doubtful whether this explanation by the assumption of a system of micro capillaries is the true one. It seems probable to me that the difficult moistening of the carbon by water accounts for it.

5. Very striking is the strong hysteresis in the isotherm [2]).

[1]) In the search for possible explanations for the deviating behaviour of *water* at carbon much light was thrown on the subject by conversations with Dr. M. POLANYI.

[2]) The complicated results of B. GUSTAVER (Kolloidchem, Beihefte, 1922) and HÄLLSTRONO's experiments (Diss. Helsingfors, 1920) will be discussed in a following paper. Not to lengthen this communication, I confine myself to only mentioning them here.