Chemistry. — "*On the behaviour of gels towards liquids and their vapours*". By Dr. L. K. Wolff and Dr. E. H. Buchner. (Communicated by Prof. A. F. Holleman) [1]).

(Communicated in the meeting of December 28, 1912).

A paper by Mr. Bancroft [2]), which came to our notice only a short time ago, induces us to publish the following account of an investigation, which we do not yet consider completed. It concerns a phenomenon, discovered by von Schroeder, [3]) who found that gelatine, swelling in water vapour, behaved differently from gelatine, swelling in liquid water: in the first case it absorbs much less water than in the second. This phenomenon seems to contradict the second law of thermodynamics, which immediately leads to the principle, that, if a certain number of phases are in equilibrium, the equilibrium will not be disturbed, if one of the phases (in our case, the water) is taken away. Being convinced of the validity of the second law, and not satisfied by the given explanations, we started this research.

We can at once refute a seemingly obvious remark. It might be supposed, that the absorption of water vapour finally takes place so slowly, that the equilibrium would only be reached after a very long time, *i. e.* that we have a false equilibrium. The erroneousness of this suggestion is immediately proved by the fact, that gelatine, swollen in water, loses water, when brought into a space saturated with water vapour.

Von Schroeder found, that agar-agar showed the same phenomenon, though not so markedly, but he observed the reverse in the case of filter paper. As far as we know, no other experimental investigation of the subject has been published after von Schroeder's paper, though theoretical considerations have been given by Freundlich and Bancroft, which we will treat of later on.

We first repeated von Schroeder's experiments, concerning gelatine and agar; and we obtained the same results.

Both substances, when used in the proper concentration, can be quite easily dried with filter paper, which is an essential point, as it was suggested that mechanical adhering of water to the surface of the gelatine might serve as a means of explaining the phenomenon. When the plates grew mouldy or the growth of bacteria was noticed,

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[1]) Although much work has been done, since the original paper was written (Dec. 1912), we prefer only to present the translation of the Dutch communication and to postpone the publication of our new results.

[2]) J. physic. chemistry **16**, p. 395.

[3]) Z. physik. Chemie **45**, p. 76.

the experiments were rejected. We used very pure gelatine (Nelson), the same as von Schroeder used. The agar too was very pure and freed as far as possible from foreign substances by continuously treating it with water. The substances were placed in desiccators in a room, which was as much as possible kept at temperature.

The data of an experiment on gelatine will be found in the following table; a solution of about $2^o/_o$ gelatine was solidified into a plate.

		Weight of the fresh plate	1.797 Gr.
,,	after 8 days in water vapour	0.056	,,
,,	,, 8 more days in vapour	0.056	,,
,,	,, 3 days in liquid	0.728	,,
,,	,, 11 ,, ,, vapour	0.039	,,
,,	,, 4 ,, ,, liquid	0.758	,,
,,	,, 8 ,, ,, vapour	0.043	,,
,,	,, 6 ,, ,, liquid	0.800	,,

Whereas gelatine in water vapour absorbs not yet half its weight, we see that it takes up more than twenty-five times its own weight in liquid water. The experiment was repeated with other plates and always with the same result. A similar proportion is found with agar-agar.

Weight of the freshly prepared plate	2.111 Gr.
,, after 8 days in vapour	0.032 ,,
,, ,, 8 more days in vapour	0.037 ,,
,, ,, 3 days in liquid	0.422 ,,
,, ,, 11 ,, ,, vapour	0.033 ,,
,, ,, 4 ,, ,, liquid	0.358 ..
,, ,, 8 ,, ,, vapour	0.040 ,,
,, ,, 6 ,, ,, liquid	0.395 ,,
,, ,, 22 ,, ,, vapour	0.035 ,,

It will be observed that in our experiments agar shows the phenomenon much more distinctly than in von Schroeder's. This author also tried the experiment with filter paper; we however did not, because we found it impossible to free this material from the water adhering to the surface.

Then we investigated, whether other substances show the same phenomenon, and we found a very striking example in nitrocellulose. Celloïdin Schering was used, which is known to be very

pure. This substance swells strongly at room temperature in 98 °/₀ ethylalcohol, without being solved to any considerable degree; placed in saturated alcohol vapour at the same temperature, it loses a great part of the absorbed alcohol.

Celloïdin in ethylalcohol.

	I.	II.
	Weight of dry substance 0.774 Gr.	Weight of dry substance 0.561 Gr.
	In *liquid*	In *vapour*
	after 2 days 4.591 Gr.	after 2 days 0.806 Gr.
	„ 5 „ 5.440 „	„ 5 „ 0.924 „
	„ 7 „ 5.430 „	„ 7 „ 0.972 „
	Composition of the gel 14.3 °/₀ cell.	„ 12 „ 1.073 „
	Then in *vapour*	„ 14 „ 1.060 „
	after 2 days 5.139 Gr.	Composition: 52.9 °/₀ celloïdin
	„ 4 „ 4.953 „	Then in *liquid*
	„ 6 „ 4.750 „	after 2 days 3.270 Gr.
	„ 9 „ 4.598 „	„ 5 „ 3.388 „
	„ 11 „ 4.510 „	„ 7 „ 3.391 „
	„ 16 „ 4.316 „	Composition: 16.5 °/₀ cell.
	„ 18 „ 4.200 „	This quantity, now once more
	„ 27 „ 3.949 „	placed in saturated vapour,
	„ 113 „ 3.140 „	lost weight as in exper. I.

Weight in equilibrium, calculated from experiment II, 1.601 Gr.

It was noticed, that, when the swollen celloïdin, taken from the liquid and well dried off, was placed in the vapour, a few drops of alcohol were found after some days on the bottom of the weighing-bottle; these were removed before weighing.

Celloïdin also shows the phenomenon in methylalcohol; the absorption in liquid, as well as the loss in vapour are nearly equal to those in ethylalcohol. It was also found with rubber ("gummi elasticum" Ph. Ned. IV) in xylene and in chloroform. In these systems a difficulty presented itself viz. that the swollen rubber almost became liquid; we succeeded in separating it from the xylene or chloroform by centrifuging. Rubber is more soluble in these liquids than the other substances investigated are in water or alcohol, but that does not decrease the results of our experiments.

Laminaria and cornea of the ox show the phenomenon quite clearly in water; from the latter, though well dried after being taken out of the liquid, big drops were found on the bottom of the

dish. The structure of these two substances, however, is so complicated, that we must allow for the possibility, that their behaviour may be explained in quite a different way.

Until now we have only treated colloïds; we thought it quite worth while to examine, if the phenomenon could also be found in crystalline bodies. A paper of FISCHER and BOBERTAG[1]) drew our attention to myricyl alcohol[2]), together with chloroform and amylalcohol. We are inclined to conclude, that this substance really shows the phenomenon, but the differences, which we found, are much smaller, and absolute certainty about the fact has not yet been obtained. The principal error in these experiments lies in the liquid adhering to the surface, and its influence will grow, according to the decrease of the total difference. Besides this substance we investigated stearic acid with acetic acid and anthracene with ethylalcohol; the differences in these systems are still smaller and the uncertainty therefore is still greater.[3])

All the above mentioned substances show the phenomenon more or less; a few others do not do so or at least they show differences, not exceeding the experimental errors; viz. silica jelly, (as could be seen from VAN BEMMELEN's investigations), coagulated albumen (serum-albumen, MERCK) and amongst the crystalline bodies stilbite; the latter absorbs only $3\,^o/_o$ water in toto. We did not investigate the hydroxydes of the heavy metals, because we did not think it possible, to free them from the surface water. Therefore we do not wish to oppose ourselves to the researches made by FOOTE[4]) and RAKOWSKI[5]). A word must be said, however, concerning a remarkable observation of FOOTE, to which Mr. RAKOWSKI drew our attention. FOOTE found, that a crucible, containing pure water, placed in a well closed weighing bottle, on the bottom of which was some water, and which was pending in a thermostat, lost some weight. Now theoretically the water on the highest level must evaporate wholly, but, if we do not consider this fact, we notice, at all events,

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[1]) Jahresber. d. Schles. Ges. f. Vaterl. Kultur 86, 36.

[2]) This substance was prepared for us of carnauba wax in Prof. HONDIUS BOLDINGH's laboratory; a crystallographic examination by Dr. B. G. ESCHER proved that it was wholly crystalline. We wish to express our hearty thanks to these gentlemen for their kindness.

[3]) Whether the phenomenon also appears in two normal, non miscible liquids, is a question, directly connected with the above. Experiments about this problem have been commenced.

[4]) J. Amer. Chem. Soc. 30, 1388.

[5]) Zeitschr. für Chem und Industrie der Kolloïde. 11, 22.

that the difference, which Foote speaks of (7 m.G.), is out of proportion to the differences, found by us (a hundred and more m.G.).

We now wish to proceed to consider the given explanations. In doing this the first question that suggests itself is, whether the examined substances are composed of one or of two phases. Since van Bemmelen and Hardy's investigations it is pretty generally assumed, that gels are systems of two phases. As to bodies like silica, we do not oppose this statement; but for gelatine, celloïdin and rubber, it does not seem to be at all certain. Let us examine the grounds, on which it is based:

1. the well-known "Umschlagpunkt" and the behaviour of silica jellies (van Bemmelen); agar, gelatine, celloïdin, and rubber do not show a similar behaviour.

2. the pressing experiments; these do not prove anything. In the same way, one can expel the water from a salt solution, by exposing it to a pressure that exceeds the osmotic one, in a pot with semipermeable walls. Under these circumstances some water is pressed out; but nobody will maintain this solution to be a system of two phases. In the case of agar the canvas, between which the agar is pressed, acts as a semipermeable membrane.

3. the analogy to mixtures of water, alcohol and gelatine, in which Hardy [1]) succeeded in observing the separation of small drops. Leaving the question, whether the drops appear just at the point of solidification, out of discussion, we are not allowed to apply results, obtained in a ternary system, to a binary one [2]).

4. the behaviour of gelatine and agar, which are soluble in water, when liquid, but insoluble, when solidified, whilst the solution generally solidifies as a whole. If one takes the hysteresis into account it does not seem impossible to explain this behaviour also in a system of only one phase.

5. the structures found by Bütschli. These however do not seem to be of much value, since they are on the limit of the power of the microscope and since they have to be called into existence by all sorts of artificial means. Moreover Zsigmondy and Bachmann [3]) have lately shown, by using the ultramicroscope, that both silica gel and gelatine are built up of much finer elements. It is doubtful though, if in this case we can speak of "phases". We too think it very likely, that molecular aggregates are formed in solutions of gelatine; but these are also to be observed (by means of the ultramicroscope)

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[1]) Z. phys. Chem. **33**, 326.

[2]) Bachmann, Z. Anorg. Chem. **73**, 125 expresses the same opinion.

[3]) Z. anorg. Chem. **71**, 356; **73**, 125.

in greatly diluted, non-solidifying solutions[1], which, then, ought also to be considered as systems of two phases, a view, which to us seems to be without any foundation whatsoever.

6. the forming of a membrane in gels by opposite diffusion of salts that give a precipitate[2]). It is not clear to us, why these precipitates should only arise in the cavities of the gel.

Let us first of all examine BANCROFT's explanation, which is identical with the one, originally put forth by us, but which we have rejected for the reasons, we shall presently discuss. It assumes two phases in the gel — one with much, the other with little water — which are separated by curved surfaces. The equilibrium in the vapour decides the composition of the second phase; the water, which is taken by the gelatine up in the liquid, forms the first.' According to our observations, the concentrated phase of agar would contain $50^o/_o$ agar, whilst 3 to $5^o/_o$ would follow from HARDY's pressing experiments. So this does not agree exactly! If we try to obtain — as is necessary — a more detailed conception of the structure of the gel, we have to choose between an open and a closed cell structure. Assuming the former, one could only accept BANCROFT's hypothesis, if the surface tension of the diluted phase with regard to the concentrated one is as that of mercury with regard to glass. We have investigated, whether this is the case by covering glass capillaries on the inner surface with a thin layer of gelatine, agar, celloïdin or rubber. We found a behaviour as that of water-glass; only in the case of vapour-swollen or dry gelatine we observed a convex meniscus; gelatine, swollen in liquid, behaved as the other bodies. An open cell structure is, therefore, not consistent with BANCROFT's explanation. Another fact may be mentioned, which also speaks against this assumption; a plate of gelatine, dipped half way and vertically in water, only swells for the lower part, while the part above the water surface presents exactly as gelatine in equilibrium with vapour. For if there were an open cell structure, the canals should fill themselves by capillary action. Whether an open or a closed structure is obtained, will depend on the question, which phase separates first. If this is the most concentrated and consequently the most viscous one, an open structure will arise and the water will have a concave surface; if, on the contrary, the latter appears first, it will of course show a convex meniscus. If, therefore, we accept BANCROFT's explanation, we are obliged to suppose that the phase with much water separates first in all the systems that show the phenomenon; of course, this

[1]) See especially BACHMANN, loc. cit.

[2]) BECHHOLD, Z. phys. Chem 52, 185.

is not impossible. In the case of silica and alumina jellies, where the concentrated phase separates, an open structure is to be expected. Since the surface tension will probably be similar to that of water-glass — the gel is completely moistened by water —, the gel will not show von Schroeder's phenomenon. In fact, we did not find it (nor did van Bemmelen), in opposition to Bancroft's declaration, that gelatine and aluminium gel are theoretically equivalent.

It is, therefore, possible to explain in this manner, why gelatine, swollen in water, loses water, when in a space saturated with vapour; we should even be able to calculate the size of the drops by the difference of the vapour pressures of the gelatine swollen in vapour and in water. Von Schroeder has tried to measure this difference by allowing gelatine to swell in salt solutions and by determining the concentration of the solution, in which the phenomenon no more appeared. He found this to be the case in a solution of sodium sulphate of a normality between 10^{-5} and 10^{-6}. This would give a difference in vapour pressure of $\pm 3.10^{-5}$ mm. of water, out of which the radius of the drops in the gel can be calculated to ± 9 mm.[1]), evidently an impossible result. In fact, we have, in repeating von Schroeder's experiments, obtained different results: celloïdin, swollen in a solution of $3\,^0/_0$ sublimate in absolute alcohol, does show the phenomenon. We intend to try to determine the difference of the vapour pressures by a direct method. If, on the other hand, we suppose the diameter of the drops in gelatine to be 5 $\mu\mu$[2]), we calculate, that the vapour pressures must differ ± 100 mm. of water, which to us seems a rather high amount.

There is, however, a serious objection to be raised against this explanation. The gel, swollen in liquid, loses water in the vapour; in consequence of which either cavities, filled with air and vapour, are formed, or the gel shrinks, according to its losing water. Silica jelly shows the first alternative, as is proved by its opaqueness, appearing at a certain point; gelatine, agar, celloïdin and rubber, however, remain quite clear, but their volume is diminished. *Now, if there are no cavities, we do not see, why they should be formed anew, when the gel is replaced in the liquid.* This objection, we think, entirely pulls down Bancroft's theory.

As to von Schroeder's remarks, we must observe, that they do not give an explanation in the proper sense of the word. Von Schroeder only wants to put an end to the controversy against the second law, by remarking, that the gel is taken from the liquid and

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[1]) According to the formula: $\Delta p = \dfrac{2ad}{DR}$ (see Chwolson, Lehrb. d. Phys. III, 744), and assuming that the drops are bulbs.

[2]) 5 $\mu\mu$ is the diameter of the capillary canals in silica jelly, as put by Zsigmondy.

placed in the vapour very quickly and that the velocity of this process influences the work done. As BANCROFT says, this alleged explanation is not likely to satisfy anybody; moreover it can be refuted by arranging VON SCHROEDER's imaginary experiment in a slightly different manner. Pour upon the gelatine (in equilibrium with vapour) as much water, as can be totally absorbed, and place the whole in saturated vapour, it will now lose weight, till the vapour equilibrium is reached again. In this way the excess work, in VON SCHROEDER's opinion necessary for taking the gelatine quickly out of the liquid, is eliminated.

FREUNDLICH [1] introduces special attracting forces of the surrounding liquid on the gel. As long as one does not enter into detail as to the nature of which these forces are, nor why they have so much influence especially with the gels, this explanation does not seem to be more than a circumscription of the facts, and we agree with BANCROFT, who declares it to be "neither very clear, nor very convincing".

We must acknowledge, however, that we ourselves are not able to give a better one. When looking for the directions, in which the solution might be sought, we find hysteresis, gravity, and capillary action. Hysteresis, of course, would do away with the possibility of a perpetuum mobile of the second kind; we should then have to assume, that every time slight changes are left in the gel, and that it would consequently be impossible to detect ad infinitum differences in water content, when the process of transferring the gel from liquid to vapour, and vice versa, is repeated. No fact, pointing in this direction, has however been found, neither by VON SCHROEDER nor by us; but it may be, that the process has not been repeated often enough; of course, this is not a more fundamental explanation either.

Concerning the influence of gravity, we wish to remark, that it might possibly explain the loss in the vapour, but never the gain in the liquid. Moreover, VON SCHROEDER made some experiments with regard to the influence of gravity, but with negative results. This would not, however, be a sufficient ground to deny the effect of gravity, since, as BANCROFT justly remarks, the effect might be too small for observation.

When, at last, we try to ascribe the phenomenon to the action of capillary forces, we do not make more progress than FREUNDLICH, though in this direction perhaps success will be most probable.

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[1] Kapillarchemie, p. 494—497.