

Citation:

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Chemistry. — "*On the behaviour of gels towards liquids and the vapours thereof.*" II. By Dr. L. K. WOLFF and Dr. E. H. BÜCHNER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of April 24, 1914).

In continuing the experiments mentioned in our first communication about this subject¹⁾, we hit upon two observations which have given us the key to the solution of the problem. Firstly it was found that, when leading saturated water vapour over gelatine which at the same temperature had swollen in water, the weight of the gelatine does not change; secondly it appeared that the amount of decrease with the experiments made in the previously described way — in desiccators according to VAN BEMMELEN — depended upon the size of the desiccator, and besides that in this way of experimenting pure water also lost in weight. These things found, we came to the following conception of VON SCHROEDER's phenomenon:

1. the state attained in water vapour is *no* equilibrium; even though the quantity of water absorbed does not visibly increase for days and days, one must suppose an extremely slow absorption still to be taking place, at least if the experiment is made in the exact way which will be presently described. However, it may be several years, before the true equilibrium is reached, which in liquid water appears within some days. So the so called vapourequilibrium is only a "false equilibrium".

2. the curve which indicates the connection between the water content and the vapourtension, runs almost horizontally as soon as the point which represents the vapour equilibrium, is passed; the tension being taken as ordinate, the concentration as abscissa.

3. The observation formerly advanced by VON SCHROEDER, BANCROFT, and also by us against the hypothesis mentioned under 1, viz. that the watercontent of gelatine swollen in the liquid, decreased again in vapour, (from which was concluded that the "equilibrium" was attained from two sides), is founded on an unsatisfactory way of experimenting. This conception seems to give a satisfactory explanation of the whole of the phenomena; we can support it by a great number of experiments.

We shall now first of all treat the proof of the third thesis. As

¹⁾ These Proc. 15, 1078 (1912/13).

we doubted about the exactness of the method with desiccators, we made experiments in another way. We let a piece of gelatine swell under water until the equilibrium was attained, put it into a U-tube with ground stopcocks, hung this tube in a thermostat, and sucked a stream of air saturated with watervapour through it. In order to fully saturate the air with watervapour, we let it pass in extremely fine bubbles through four tubes of water which were also hanging in the thermostat. We made sure of the vapour really being saturated by placing a U-tube filled with water before the U-tube with gelatine, and by also weighing the former before and after the air had been led through.

T A B L E I.

Time	Weight of U-tube + water	Weight of U-tube + gelatine	
	30.130	30.779	
24 hours	30.127	30.781	Temp. 19°.0
26 "	30.126	30.779	(in thermostat)
18 "	30.123	30.778	
72 "	30.117	30.780	

It will be seen, that the gelatine, contrary to our former experiments, showed no decrease of weight: it was in equilibrium and it remained so, and there was not the slightest abnormality. Now which method, the old or the new one, is more reliable? The answer cannot be dubious, for we succeeded in improving the old method to such an extent that it gives the same results as the new one.

Formerly we used to place little dishes of gelatine in a SCHIEBLER-desiccator, at the bottom of which was some water, and which stood in a room of a fairly constant temperature. In order to exclude the possibility that the water from the gelatine, under the influence of gravity, should distill to the water at the bottom, we have now, instead of pouring the water into the desiccator, placed a dish of water at the same level as that with gelatine. And, thinking of FOOTE's experiments mentioned in our first communication, we also weighed this dish, expecting, of course, that the water lost by the gelatine, should be found back here. However it appeared that both gelatine and water equally decreased in weight; (it is to be noticed that the desiccator was not evacuated).

TABLE II.

Time	Weight of dish + water	decrease	Weight of dish + gelatine	decrease	
	47.458		48.391		temp. 22° (room).
24 hours	47.238	.220	48.209	.182	
24 "	47.031	.207	48.009	.200	
24 "	46.868	.163	47.863	.146	
48 "	46.567	.301	47.525	.338	

2nd experiment (three dishes of water).

time	weight n°1	decrease	weight n°2	decrease	weight n°3	decrease	
	81.129		64.399		45.888		temp. 22° (room).
24 hours	80.868	.261	64.041	.358	45.591	.297	
24 "	80.601	.267	63.709	.332	45.291	.300	

We see from this that, in taking the experiment in this way, a dish of water decreases in weight 200 to 300 mG. in 24 hours, and that consequently the experiments thus made with gelatine, do not prove anything whatever.

It is not quite easy to say where this water goes to. It might be thought that it serves to saturate the whole space of the desiccator with vapour; but for this a much smaller quantity suffices, 1 L. saturated watervapour of 22° only weighing 19 mG. Nor are differences of temperature probable, because the changes we have found always go in one direction, and because we cannot think why the water in the middle of the desiccator should always be warmer than the walls thereof. Besides the temperature in the room was rather high¹⁾, only varying within 0,5°, and so the dishes, after being weighed, would sooner enter colder than warmer. It was also controlled if a loss of weight occurred during the weighing and the preparations for it; by working quickly however, this loss could easily be kept under 1 mG. The only explanations left are, either the watervapour diffuses to the outside, passing through the layer of grease which is between the desiccator and the lid, or water is adsorbed at the great glass surface of the desiccator. The latter explanation will be most probable, as in smaller

¹⁾ Except in two series of table III, where the differences are equally great all the same.

T A B L E III.
Small desiccator of FRESSENIUS; temp. room 22°.

Time	weight dish 1 + water	decrease	weight dish 2 + water	decrease	
48 hours	33.798		21.409		Volume of the desiccator: 700 c.c.
	33.745	.053	21.382	0.027	
48 "	33.722	.023	21.360	.022	
	dish 3 + gelatine		dish 4 + water		
24 hours	31.584		27.566		
	31.573	.011	27.545	.021	
24 "	31.561	.012	27.527	.018	
24 "	31.549	.012	27.510	.017	
120 "	31.505	.044	27.471	.039	
	water		water		
24 hours	31.621		27.834		temp. room 14°
	31.605	.016	27.819	.015	
24 "	31.585	.020	27.800	.019	
48 "	31.565	.020	27.777	.023	
	gelatine				
72 hours	27.764		27.777		temp. room 16° 5
	27.741	.023	27.759	.018	
48 "	27.724	.017	27.739	.020	

Bell-jar in pail; temp. room 22°.

Time	weight of weighing-bottle + gelatine	decrease	Time	weight of weighing-bottle + water	decrease
	36.116			40.407	
90 hours	36.052	.064	5 hours	40.411	(+.004)
30 "	36.026	.026	48 "	40.250	.161
18 "	36.009	.017	24 "	40.122	.128

desiccators — model FRESSENIUS — we found much smaller decreases, and as we also found a loss of weight when making the experiment differently. A glass bell-jar, in which was hanging a weighing-bottle with gelatine swollen in water, was partly placed in a pail of water, so that the gelatine remained some cm. above the water surface. There can here be no question of diffusion to the outside. Yet the adsorption hypothesis is not without its difficulties; for in taking the above mentioned experiments the desiccator or the belljar were first well rinsed out and moistened with water, so that one should think the glass surface to be entirely covered with a layer of water. Perhaps the two last mentioned causes of decrease of weight are cooperating

Whatever may be the cause of decrease, we can distinctly see by this table that both water and swollen gelatine decrease. So if we wished to really confirm VON SCHROEDER's observation, we first ought to have an arrangement with which water only does not diminish in weight.

A series of experiments, undertaken in consequence of Foote's communication which has been mentioned before several times, will illustrate how hard it is to make exact observations by the statical method. In a glass tube were two small tubes filled with water above one another, which had been weighed before. The tube was closed with a rubberstopper or it was sealed in the flame, and then placed in a thermostat; after two days the tube was opened, and the little tubes were quickly put in weighing bottles, and were weighed.

TABLE IV.

Time	weight lower tube	decrease	weight upper tube	decrease	
48 hours	22.098		24.000		
	22.090	.008	23.992	.008	temp. 18°0
48 "	22.081	.009	23.980	.012	rubberstopper
2nd experiment.					
	22.060		23.923		
48 "	22.051	.009	23.918	.005	id. id.
3rd experiment.					
	10.108		36.289		
48 "	10.098	.010	36.244	.045	sealed

So we again found a decrease of weight in all cases, be it less than with the experiments made before. As the amounts are so much smaller here, another circumstance, except the one of adsorption at the glass walls, must be taken into consideration, which, as we have found with the apparatus presently to be described, can account for differences to an amount of some mG.¹⁾ The tubes were opened outside the thermostat; the outer walls then cooled down a few degrees, while the inner tubes remained a little warmer. In those few moments a small quantity of water could distill to the wall of the great tube, and this may be the cause of the loss of weight.

Now in order to exclude adsorption we have passed on to another arrangement. We had a cylindrical box made of brass (measures: diameter 7.5 cm., height 7.5 cm., volume 320 c.c.), which was closed by an exactly fitting brass lid that could be still more strongly fixed on by screws. Both the box and the lid were silvered at the inside. The apparatus was entirely plunged into a thermostat, kept constant within 0°.1. In this apparatus too we began with weighing-bottles, which only contained water; we again had to state a loss of weight. With these experiments the vessel was taken out of the thermostat, and was quickly unscrewed after which the weighing-bottles were taken out and weighed with their stoppers closed. When a closed weighing-bottle with water was placed in the vessel, the weight remained constant; when taking it out, some slight moisture was to be seen against the stopper. A refrigeration evidently took place here, by a colder stream of air entering when the lid was taken off. In order to avoid this as much as possible, we placed the apparatus rather high in the thermostat; when it had to be opened we made the water run out of the thermostat through a siphon, so far that the lid appeared just above the watersurface. Meanwhile the screws were unscrewed so that the lid could be taken off as soon as it was above the waterlevel; in this way the whole kept the same temperature until the very last moment. The then obtained results were satisfactory (cp. table V), and we therefore repeated our experiments with gelatine-water, agar-water, and celloidin-alcohol in this way.

From these experiments we learn that *gelatine, agar, and celloidin swollen in a liquid, do not undergo a loss of weight when placed in saturated vapour*, if the experiment is made rigorously. The results with the celloidin-alcohol system are not so good as with the others, it is true, but the decrease which reached an amount of 100—200

¹⁾ The greater difference in the upper tube of the 3rd experiment is evidently due to the heating during the sealing process.

T A B L E V.
Temperature 19°0; weighings every 24 hours.

	weight of weighing- bottle 1 + water	decrease	weight of weighing- bottle 2 + water	decrease
1st series water vessel opened <i>outside</i> the thermostat	26.045		25.096	
	26.033	.012	25.088	.008
	26.025	.008	25.081	.007
	26.012	.013	25.069	.012
2nd series water vessel opened <i>in</i> the thermostat	25.772		27.837	
	25.768	.004	27.834	.003
	weighing- bottle + gelatine			
3rd series gelatine	20.136		The gelatine had been swelling for a fortnight in water at a temperature of 19°0, and had been dried with filter paper before the experiment. (after 3×24 hours).	
	20.135	.001		
	20.135	0		
	20.135	0		
	20.133	.002		
Temperature 21°4.				
4th series agar	24.575		The agar had been swel- ling for 8 days under water at the same temperature, and had been dried as said above.	
	24.580	(+ .005)		
	24.582	(+ .002)		
	24.581	.001		

Temperature 21°4.

	No. 1		No. 2		No. 3		No. 4		
5th series celloidin- alcohol	12.202		12.122		12.389		11.310		
	12.200	.002	12.108	.014	12.379	.010	11.304	.006	after 42 hours
			12.095	.013	12.370	.009	11.301	.003	74 "
Temperature 0°.									
6th series celloidin	12.248		12.115		12.397				
	12.255	(+ .007)	12.113	.002	12.399	(+ .002)			after 61 hours
	12.249	.006	12.109	.004	12.396	.003		" 30 "	
	12.249	0	12.109	0	12.395	.001		" 24 "	

mG. with the old method, has been reduced to some mG. only; we must herewith remember that the vapour tension of alcohol is considerably greater than that of water. Therefore the 6th series of experiments was undertaken at 0°; according to our expectations the results were better than at 21.4°.

The experiments communicated here have taken away every actual ground of existence from the opinion expressed first by von SCHROEDER, viz. that here was a conflict with the second law of thermodynamics; the second law, as one might think, remains untouched. Of course the phenomenon of several substances swelling more in liquids than in vapours, remains; but we think this can be sufficiently explained by assuming that the absorption in vapour occurs extremely slowly in the end. We have also investigated if not totally swollen gelatine and celloidin, placed in vapour, would absorb more water in our new apparatus, and would come to the real equilibrium. This appeared not to be the case; e.g. with gelatine of the following compositions: 1 gelatine to 26 parts of water (in weight); 1:24,2; 1:18,8; 1:15,8; 1:6,5, (the "false vapourequilibrium" is about 1:0.7) no change of weight was found for five days¹⁾. So it goes without saying that the absorption takes place exceedingly slowly.

This is most probably connected with the fact, that the vapour tension of gelatine (and numerous other substances) is already very near to that of pure water when they have only absorbed a rather small quantity of water²⁾; consequently all the further water absorption of any importance is only of slight influence upon the vapour tension. Or in other terms, the difference of the vapour tension of pure water and of gelatine in "vapourequilibrium" is very small, and consequently the absorption velocity will also be very small. That it is yet very great in liquid water, may be easily explained from the density which is 50000 times greater.

We just wish to state that the determinations meant here have all been obtained by the statical method, the deficiency of which we have proved; a true opinion can only be possible if the experiments are taken along the dynamical way³⁾, and if the real equilibrium has been proved by placing the jellies alternately in vapour of higher and lower tension. The values given for the composition of the substances swollen in the vapour of pure water are never true

¹⁾ These experiments were also made in the dynamical method with U-tubes, yielding the same result.

²⁾ KATZ, these Proc. **13**, 958 (1910/11).

³⁾ Or in the apparatus described above.

equilibria; one ought to state the value which is attained in liquid water¹).

The explanation of the phenomenon becomes somewhat different, if we do not let the gelatine (celloidin) swell in pure water (alcohol) but in solutions. In case of the dissolved substance being volatile (example: celloidin-alcohol-water), the circumstances are exactly the same as above mentioned; but, if the substance is e.g. a salt, the thing changes. VON SCHROEDER has made some experiments about this question, and he ascertains that $1/100000$ -norm. sulphate solution already lowers the vapour-tension of gelatine so much, that there is not even a decrease in vapour, but an increase. After the results described above, VON SCHROEDER's argument loses all weight, and his result is sure to be due to chance.

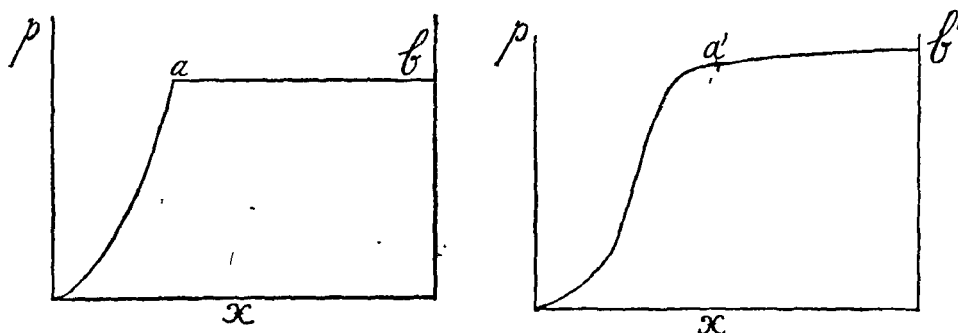
It is a fact we have repeatedly observed, that gelatine (celloidin) which had swollen in the vapour of a salt solution (NaCl in water, resp. HgCl_2 in alcohol) absorbs much more still, when brought into the liquid; 1 Gr. celloidin, e.g. gains 1.77 Gr. in weight in a solution of 4% sublimate in alcohol of 96%, whereas only 0.89 Gr. is absorbed in the vapour of alcohol, and consequently still less in the vapour of a solution in alcohol. The difference between the swelling in a pure liquid and in a solution finds its cause in a substance, when in the vapour of a solution, never being able to absorb anything but the solvent, as long as the dissolved substance is not volatile; when placed in the liquid itself, it also absorbs the dissolved substance.

This is a wellknown fact about gelatine; we have ascertained by the experiments with celloidin mentioned above, that this substance too had not only absorbed alcohol, but also sublimate. So in *these* cases it is clear for other reasons, that a substance swollen in vapour, when brought into the liquid phase, must still absorb more, and that the state attained in vapour is not a true equilibrium²). In vapour e.g. celloidin passes into celloidin + alcohol, until the vapour-tension of this phase has become equal to that of the liquid phase: alcohol + HgCl_2 . Now if one brings the celloidin phase under the liquid, the HgCl_2 diffuses into the celloidin; diminishes so to say the vapour-tension of the alcohol which is contained therein, and consequently a further absorption of alcohol must take place. If we

¹) Strictly speaking one must not speak of pure water, but of a saturated solution of gelatine, agar etc. in water; of course, the difference really is exceedingly minute.

²) Cf. TOLMAN's views, J. Amer. Chem. Soc. 35, 307 (1913). We have assumed with TOLMAN that every substance evaporates somewhat, no matter how little; if one objects to this, one must speak of an equilibrium which lies differently in consequence of passive resistances (GIBBS).

represent this by a figure, we obtain in the vapour a state a ; and after this the state b is reached in the liquid along an exactly horizontal line, for the vapour tension remains absolutely the same; only the composition of the celloidin changes. a lies of course at a lower pressure than a' in the figure, which stands for pure alcohol; in the latter $a'b'$ is only approximately horizontal.



It is evident that in this case the greater absorption in the liquid must be connected with the solubility of the salt in the gelatine or celloidin. According to the colloid absorbing more salt, the difference between the vapour and the liquid equilibrium will be all the greater. We believe a closer study of this subject may probably bear fruit with a view to the knowledge of the behaviour of jellies in different solutions. We intend to start experiments about this with celloidin, which, as to stability, has great advantages over gelatine with which suchlike experiments have been made up to the present¹⁾. We do not consider skinpowder an ideal substance for this purpose either²⁾.

As a summary we think, we can say that the pretended conflict with the second law of thermodynamics has been put an end to, and that VON SCHROEDER's phenomenon in the principal case is due to a slowly coming equilibrium; one may expect it in all cases where the vapour tension already approaches the tension of the pure liquid very nearly, a long time before the equilibrium has been attained. If the liquid absorbed is a solution of a nonvolatile substance, another explanation must be given.

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¹⁾ HOFMEISTER, among others.

²⁾ HERZOG and ADLER, Koll. Zeitschr. 2, Supplem. heft 2, (1908).