

# THE ACTION OF WATER VAPOR ON GELATINE

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It was found by von Schroeder,<sup>1</sup> in Ostwald's laboratory, that a piece of gelatine apparently did not reach the same equilibrium point in presence of saturated water vapor that it did when immersed in liquid water. Some gelatine was liquefied and then allowed to solidify in the form of a plate. The solidified mass consisted of 0.679 gram gelatine and 0.122 gram water. This plate was immersed in water with the result shown in Table I.

TABLE I  
Weight of dry gelatine, 0.679 gram

Time of immersion	Water content of gelatine plate	
	Grams	Percent adsorbed
0 min.	0.122	17.0
5 min.	2.282	336.1
10 min.	2.934	432.1
20 min.	3.669	540.3
30 min.	4.072	599.7
40 min.	4.300	633.3
50 min.	4.415	650.2
60 min.	4.506	663.6
2 hours	4.941	727.7
24 hours	6.911	1018.0
48 hours	7.734	1139.0

The experiment was stopped after forty-eight hours and another gelatine plate containing a large amount of water was placed in a space saturated with water vapor, the temperature being the same as in the preceding experiment. It was supposed that the gelatine would not lose water under these circumstances; but this proved not to be the case. The data are given in Table II.

<sup>1</sup> Zeit. phys. Chem., 45, 109 (1903).

TABLE II  
Weight of dry gelatine, 0.433 gram

Time in vapor phase	Water content of gelatine plate	
	Grams	Percent adsorbed
0 day	—	—
1 day	4.659	1076
2 days	4.400	1016
3 days	4.322	998
4 days	4.276	988
5 days	4.241	979
7 days	3.730	861
9 days	3.346	759
11 days	2.687	621
14 days	2.088	482
	1.484	343

By standing for fourteen days in saturated water vapor, the gelatine went down to about the water concentration which fairly dry gelatine would have had after standing five minutes in liquid water at the same temperature.

Other experiments were made with gelatine plates which had only been allowed to stand a relatively short time in water and which, therefore, had not taken up anything like the maximum amount of water. These also lost water when placed in the vapor phase. A similar result was obtained with an Agar-agar plate which had been allowed to swell in water. On the other hand, a piece of filter paper which had been left for an unspecified time in water gained a little in weight when placed in the vapor phase.

Von Schroeder then tried placing a dry gelatine plate in presence of saturated water vapor. The results are given in Table III.

This plate had apparently reached equilibrium in presence of saturated water vapor; but it increased rapidly in weight when immersed in water at the same temperature, as can be seen from the data in Table IV.

TABLE III  
Weight of dry gelatine, 0.904 gram

Time in water phase	Water content of gelatine plate	
	Grams	Percent adsorbed
0 day	0.0 ?	0.0?
1 day	0.154	17.1
2 days	0.218	24.1
3 days	0.277	30.7
4 days	0.294	32.6
5 days	0.347	36.2
7 days	0.357	39.5
8 days	0.366	40.5
15 days	0.372	41.2
17 days	0.368	40.7
18 days	0.369	40.8
20 days	0.374	41.4

TABLE IV  
Weight of dry gelatine, 0.904 gram

Time of immersion	Water content of gelatine plate	
	Grams	Percent adsorbed
0 min.	0.374	41.4
15 min.	3.283	363
30 min.	4.739	524
45 min.	5.397	597
60 min.	6.002	664

If a gelatine plate is placed vertically with the lower part in the water and the upper part in the vapor, the lower part will swell much more than the upper part; and the dividing line will be quite sharp. Von Schroeder points out that these experiments show that the vapor pressure of water in gelatine must be higher than the vapor pressure of pure water because water distills from the gelatine to the vapor phase. He also points out that the vapor pressure of the water in the gelatine can be lowered by allowing the gelatine to swell in a salt solution instead of in pure water. By making

the salt solution concentrated enough, the gelatine should then take up more water when placed in a vapor phase saturated with respect to pure water. This proved to be the case. If the gelatine plate was allowed to swell in a N/100,000 sulphate solution, it increased further in weight when placed over pure water. If allowed to swell in a N/1,000,000 sulphate solution, the gelatine lost water when placed over pure water. Von Schroeder gives some data for the two cases; but they are rather unintelligible. He says that the gelatine, which had swelled in the N/100,000 sulphate solution, showed the following increases in weight when placed in the vapor phase:

After 24 hours	1.318 grams
After 48 hours	1.341 grams
After 72 hours	1.351 grams

There is nothing to show to what weight of dry gelatine this refers or how much water the gelatine took up while in the sulphate solution. It seems probable that the unknown amount of gelatine, containing the unknown amount of water, took up 1.318 grams water in the first twenty-four hours and 0.0033 gram in the next forty-eight hours; but it may be that the gelatine plate took up 4.010 grams (1.318 + 1.341 + 1.351) in seventy-two hours. This last guess is perhaps the more probable in view of the fact that von Schroeder says that "with a N/1,000,000 sulphate solution there was a distinct loss of water:

After 24 hours	1.210 grams
After 48 hours	1.107 grams
After 72 hours	0.814 gram

This ought to mean that the gelatine lost 3.131 grams (1.210 + 1.107 + 0.814) in seventy-two hours unless von Schroeder by mistake has given the actual weight of the gelatine plate; but in that case he ought to have given the initial weight. Fortunately, it is quite immaterial what his real data were. The essential thing is that the difference between the vapor pressure of pure water and of N/100,000 sulphate solution is apparently sufficient to keep a mass of

0.433 gram dry gelatine + 4.659 grams water from losing over three grams of water (cf. Table II) when placed in saturated water vapor. As von Schroeder justly remarks: "These experiments show that very considerable changes in the degree of swelling of a gelatine plate are caused by very slight changes in the vapor pressure of the swollen gelatine."

It seemed possible that these extraordinary results might be due to the action of gravity causing the liquid water to sink down in the meshes of the gelatine when this latter was placed in the vapor phase. I quote von Schroeder's<sup>1</sup> experiments in regard to this and also his tentative solution of the problem.

"A gelatine cylinder, which had swelled in water, was placed as a plug in an inverted flask having no bottom. The flask was supported on a tripod so that the neck dipped into a crystallizing dish filled with water. The flask was filled with water and, in order to keep a vapor phase saturated with respect to water, a large beaker lined with moist filter paper was inverted over the flask, the rim of the beaker resting on the bottom of the crystallizing dish. A trace of mercuric iodide kept the gelatine from spoiling. No formation of drops at the lower end of the gelatine plug could be detected though the experiment ran for over four months.

"Equally unsuccessful was another experiment along similar lines. A swollen gelatine cylinder was suspended in a vapor phase saturated with respect to water and was watched to determine whether the lower end of the cylinder formed drops or swelled more, and whether the upper end shriveled.

"I then had made a tubular vessel with a small side-vessel blown on. The gelatine plate was fastened on a glass frame and placed in the main vessel while the side-vessel was filled with water. The air was pumped out of the apparatus which was then sealed. When the water was in the side-vessel it was above the gelatine. By tipping the apparatus, water could be brought into the main vessel under the gelatine. By tipping the apparatus more, the gelatine could

<sup>1</sup> *Zeit. phys. Chem.*, 45, 114 (1903).

be flooded. If desired the water could all be poured back into the side-vessel. It was thus possible to let the gelatine swell while entirely in the water vapor, then to let the gelatine swell while half in the water, and finally to observe the swelling when the gelatine was completely immersed. When the water was poured back into the side-vessel, it was possible to note the shrinking of the gelatine even when the level of the water was higher than the gelatine. Even this experiment was not decisive.

“By determining qualitatively the rise in capillary tubes according to the method of Röntgen and Schneider,<sup>1</sup> it was found that the surface tension of a dilute gelatine solution against air is less than the surface tension of water against air. Quantitative measurements of the same sort have been made by Quincke.<sup>2</sup>

	Sp. g.	Surface tension against	
		air	water
Water	1.000	8.253	0
Gelatine (very dilute)	1.000	7.277	0
Agar-agar (very dilute)	1.000	7.842	0
Fish glue (very dilute)	1.000	6.790	0

“I have only found one reference in the literature to any difference in the degree of swelling in water and in water vapor. Volbehr<sup>3</sup> writes that it is not necessary that all the water, taken up by a substance when swelling, should be adsorbed by the frame work. There may also be interstices filled with water which ought not to be counted when considering the affinity between water and substance. Of course this water is much less in amount than the total which a swelling substance can take up. By this way of wording, Volbehr does not eliminate the apparent contradiction between the admitted facts and the second law of thermodynamics.

<sup>1</sup> Ostwald-Luther: Hand- und Hilfsbuch, 263.

<sup>2</sup> Wied. Ann., 35, 580 (1888).

<sup>3</sup> Untersuchungen über die Quellung der Holzfaser: Kiel, 1896.

“It is undoubtedly safe to say that the second law holds in this case and that is why I speak of an apparent contradiction. There may have been some experimental error, such as that the vapor phase was not saturated or that the temperature was not constant, in spite of the fact that I was particularly careful in regard to both of these points. If not, then there could not have been equilibrium between the swelling substance and either the water or the water vapor.

“The fact that the phenomena could be repeated as often as desired is an argument against the assumption that the error is due to any irreversible process. We must seek an explanation of the apparent anomaly in the fact that the rate with which a reversible process takes place plays an important part in the calculation of the work-equivalent of that reversible process. If we keep in mind the principle put forward by Maxwell, Gibbs, Le Chatelier, and van't Hoff, in regard to the resistance of a system to a compulsory change [theorem of Le Chatelier] and if we keep especially in mind the theorem of Gibbs that a suddenly decreased surface has temporarily a smaller surface tension than the equilibrium one, we can at any rate give a qualitative explanation of this apparently puzzling phenomenon.

“To illustrate this, I will cite a concrete case in which one passes from the same original state to what appears to be the same final state isothermally and reversibly with two different expenditures of work, in apparent defiance of the second law of thermodynamics. We start with a cylinder in which there is a movable piston so that we can change the volume and pressure relations of the water vapor in the cylinder at will. The cylinder is connected by a capillary, having an infinitely small cross-section, to a water reservoir which is filled with water up to the capillary. The whole apparatus is supposed to be in a thermostat so that all changes take place isothermally. Let the water vapor have the volume  $v_1$  and then raise the piston by the volume  $v$ , the piston being raised infinitely slowly. In this case the work done by the

machine is  $p v$  where  $p$  is the pressure of the saturated vapor. If, however, the piston rises only so slowly that temperature and pressure are always at equilibrium values but fast enough so that there is not time for a perceptible amount of water to evaporate from the reservoir into the cylinder through the capillary, the work done during the same expansion  $v$  will be  $v_1 p \log \frac{v_1 + v}{v_1}$  and it will be done practically reversibly. Although the system is now externally in the same state (the piston is exactly in the same position), the system is, nevertheless, not in definite equilibrium and the two amounts of work are different.

“In our particular case this would mean that the gelatine with its extremely high viscosity is readily susceptible to hysteresis effects with reference to surface tension. The rapid expansion of the swelling gelatine when in the water would correspond to the rapid movement of the piston, and would involve more work than was necessary for the slow swelling of the gelatine in the vapor phase which corresponds to the slow movement of the piston. This difference in the work-equivalents would then be the cause of the gelatine losing water when placed in the vapor phase.”

It is doubtful whether this alleged explanation has ever satisfied anybody. Freundlich<sup>1</sup> gives a different one.

“The different behavior of an elastic gel towards liquid water and towards saturated water vapor is not easily accounted for. In the vapor phase water will unquestionably be adsorbed by the wetted walls of the gel as shown in the diagram.<sup>2</sup> In accordance with what we have said about cotton and in accordance with the steep pitch of the curve it is probably very difficult to reach a definite equilibrium because the adsorbed water gradually dissolves in the walls of the gel, reacts with them, etc. In liquid water these changes take place very much more rapidly: the water dissolves in the walls of the gel (and the gel dissolves to some extent

<sup>1</sup> Kapillarchemie, 496 (1909).

<sup>2</sup> Freundlich: Kapillarchemie, 179 (1909).



in the water), the walls change their volume, new surfaces are formed, etc. Swelling takes place and reaches a not very definitely marked limit when the elastic contracting forces of the gel just balance those forces which tend to increase the volume. It is also to be noticed that the gel, which has swollen to the maximum amount, is under water and that the outer, limiting parts of the gel are under the influence of the attracting forces of the adjoining, surrounding portions of the water and that they are therefore just as much under a uniform pressure as a particle of liquid in the midst of the liquid.

"This state of things changes when the swollen gel is brought into the saturated vapor phase. It is no longer surrounded by liquid in mass and the pull due to that drops out. Therefore, the elastic walls of the gel press on the water inside the gel. Since these walls are presumably more permeable to water vapor than to liquid water, the vapor pressure of the water in the cavities of the gel is increased and consequently we have evaporation and a shrinking of the gel. From this it follows that it is not a matter of indifference whether the swollen gel is removed slowly or rapidly from the liquid. If it is removed infinitely slowly, the part projecting into the vapor phase must shrink. That portion of the water which is held weakly, will not be carried along. The surface tension between the walls of the water or the air is changed and, therefore, the work-equivalent is different. There is no violation of the second law of thermodynamics, though there seems to be when we say that a system which is in equilibrium with liquid water is not in equilibrium with saturated water vapor. The rapid transfer<sup>1</sup> of the gel from the liquid phase to the vapor phase is not a reversible process."

Although this explanation is based on Schroeder's, it is an improvement on it. Even in this form it is neither very clear nor very convincing. The whole matter seems to me quite simple if one takes into account the structure

<sup>1</sup> Von Schroeder: *Zeit. phys. Chem.*, 45, 117 (1903).

of the gel. We are dealing with a cellular structure. If we place a dry paper bag in a space saturated with water vapor, the paper will adsorb a certain amount of water; but there will be no tendency for the water to condense inside the bag and to fill it with liquid water. If we put this same bag into liquid water, the paper will take up water as before; but water will also pass into the bag and fill it because then the surface between liquid and paper will be a minimum with reference to the mass of liquid inside the bag, the surface of contact remaining constant while the mass of water inside the bag increases. If we lift the bag into the vapor phase, and if the bag is so constructed that the actual dripping is negligible, the water will distill from the curved surface in the bag to the plane surface in the containing vessel. The smaller the bag is, the greater will be the curvature of the water within and consequently the higher the vapor pressure. With the microscopic spaces in solidified gelatine, the vapor pressure of the drops of water will be enough higher than that of water in mass to counterbalance the differences of level in von Schroeder's experiments. Since we know that a N/100,000 sulphate solution cuts down the vapor pressure of the drops to below that of water in mass, it would be a simple matter for anybody mathematically inclined to calculate what the vapor pressure of the drops is when they consist of pure water and from that what their dimensions are. Since filter paper and water do not form a gel, the abnormal phenomena were not obtained by von Schroeder in this case.

An objection to my explanation is that a paper bag full of water does bulge at the lower end and that von Schroeder looked for this effect and could not find it. The reason that he did not find it is because his methods of measurement were not sensitive enough. In the case of gelatine we have the equivalent of myriads of small paper bags. Each one undoubtedly bulges at the lower end when the gelatine is placed in the vapor phase. Since it is very difficult to make out the cellular structure even under the microscope, it is quite clear that one could not hope to detect a bulging at the

lower end by examining a strip of gelatine with the naked eye. In von Schroeder's experiments the lower ends, that he was looking for, extended practically to the top. His gelatine was all lower ends—and upper ends.

Another good point about the explanation I have offered is that it accounts for the relatively large amounts of water which are taken up by the gelatine when it swells under water. The amount of water which a paper bag will hold is out of all proportion to the amount of water which can be adsorbed by the paper itself. While some gelatine will dissolve or disintegrate in the water, we may neglect this and other disturbing factors for the present. As a first approximation it is probably safe to say that the water taken up from the vapor phase goes into the cell walls. The bulk of the excess taken up when the gel swells under water goes into the cavities. Assuming the facts to be as stated in Tables I-IV, water to the extent of about forty percent of the dry weight of the gelatine was taken up by the cell walls while water to the extent of at least eleven hundred percent of the dry weight of the gelatine was inside the cells. If we take an alumina jelly<sup>1</sup> with 1/600 of alumina by weight, only a negligible proportion of the water is in the cell walls. We cannot realize this experimentally as yet by letting alumina swell because we do not get sufficiently elastic cell walls in the case of precipitated alumina; but this dilute alumina jelly corresponds theoretically to the swollen gelatine.

The general results of this paper are:

1. The behavior of swollen gelatine in liquid water and in saturated water vapor is a necessary consequence of the cellular structure of the gelatine jelly, and does not involve any assumption of irreversible changes.

2. The microscopic globules of water in the gelatine cells have a higher vapor pressure, owing to their curvature, than water in mass. The swollen gelatine, therefore, loses water in contact with saturated water vapor.

3. When gelatine swells in a N/100,000 sulphate solution,

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<sup>1</sup> Crum: Jour. Chem. Soc., 6, 216 (1854).

the globules have a lower vapor pressure than that of water in mass. When gelatine swells in a N/1,000,000 sulphate solution, the globules have a higher vapor pressure than that of water in mass.

4. From the data in regard to solutions, it would be possible to make a first approximation as to the size of the water globules in a gelatine jelly.

5. As a first approximation we may consider that the equilibrium in contact with saturated vapor gives us the liquid in the cell walls. The excess amount taken up when the gel is immersed in the liquid represents, as a first approximation, the liquid inside the cells.

6. An alumina jelly is equivalent theoretically to a swollen alumina though it has never been prepared in that way.

7. All conclusions in regard to partial pressures of gels are subject to modification in so far as the colloidal substance forms a true solution under the conditions of the experiment.

8. Moistened filter paper is not a gel and therefore does not show von Schroeder's phenomenon.

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