XXXIX.—*Supersaturation of Salt Solutions.*

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IN previous papers on this subject (*Phil. Mag.*, 1885, June and September), I brought forward the view formerly advanced by Loewel (*Ann. Chim. Phys.* [3], 49—51), that solutions usually regarded as supersaturated are not really so, but owe their formation to the fact that the salt dissolved is not the same as that which crystallises out in the solid state. Considerable support is given to this view by the fact that the salts which exhibit the property of forming supersaturated solutions are all hydrated when crystallised from solution at the ordinary temperature, no well authenticated instance existing, so far as I am aware, of supersaturation of a solution of a salt which crystallises without water.* While on the other hand, if the solutions of anhy-

* Gmelin (*Handbook*, vol. i, page 11), it is true, states that potassium dichro-

drous salts are examined at low temperatures, temperatures at which hydrates are formed, then supersaturation is readily produced (Guthrie, *Phil. Mag.* [4], **49**, 1).

Supersaturation has been frequently compared to superfusion, the analogy being suggested by the usual method of preparing supersaturated solutions by cooling hot solutions, but it has been shown by de Coppet (*Compt. rend.*, 1871, **73**, 1324) and myself (*loc. cit.*) that supersaturated solutions can be readily prepared by dissolving cold dehydrated salt in cold water, and I have shown (*loc. cit.*) that such solutions are identical, so far as amount of dissolved salt is concerned, with solutions prepared by the aid of heat. Thus the analogy breaks down; in addition, supersaturated solutions are perfectly stable; so long as air is excluded, they may be shaken, either alone or with sharp particles such as broken glass; a current sufficiently strong to decompose the water is without effect on them, and finally they may be frozen without formation of the hydrate, which is at once produced by the addition of a crystal of the solid salt. In fact, the sole cause, which *never* fails to terminate the state of supersaturation, is contact with a crystal of the hydrate, or of a salt isomorphous with it.

In the papers referred to, I ascribed the formation of supersaturated solutions to the existence in solution of what may, for want of a better term, be called the anhydrous salt. According to this view, supersaturated solutions differ in no way from ordinary solutions, they are merely saturated or non-saturated solutions of the anhydrous salt, combination with water to form the hydrate taking place only at the moment of crystallisation. These views have met with but little acceptance, however, by those who are interested in the subject, the colour of some dissolved salts being regarded as positive proof of the existence of the hydrate in solution, moreover, stress has been laid on the fact that the experiments were made in one case with sodium sulphate, which is regarded as an exceptional salt; but on the other hand, these experiments were borne out by others on sodium thiosulphate, which exhibits no apparently exceptional behaviour in its solubility.

In order to bring more experimental evidence to bear on this difficult problem, I venture to lay the results of further experiments before the Society. These naturally fall into two groups.

mate and silver nitrate are exceptions to the above; and F. Kohlrausch (*Ann. Phys. Chem.*, **6**, 28) claims to have prepared a supersaturated solution of ammonium chloride, while elsewhere I have seen it stated that potassium nitrate exhibits this property. I have myself attempted in vain to prepare supersaturated solutions of anhydrous salts; and Dr. Tilden informs me that he also has been uniformly unsuccessful.

1. Experiments showing that ordinary and supersaturated solutions of the same salt have the same constitution; and

2. Those which show that solutions of a salt do not contain the hydrate which is known in the solid state.

The first of these cases can be approached from two sides. It is possible to pass from an ordinary solution to a supersaturated one, either by lowering the temperature of a solution containing a definite amount of salt, or by increasing the amount of salt dissolved at a definite temperature. Each of these methods yields evidence which is only partially conclusive, but the two together make the proof complete.

Amount of Salt Constant, Temperature Falling.

A solution of a salt saturated at any one temperature is supersaturated when the temperature falls, and non-saturated if it rises. With such a solution 10° or more above its saturation temperature, it will be possible by examination of the curves representing the various physical constants as the temperature falls to ascertain whether these exhibit any change in direction, gradual it may be, but still decided, in passing the saturation temperature.

Taking the various physical constants, so far as they have been determined in this connection, we have first the electric conductivity, as examined by Heim, the results of whose experiments have been recently published (*Ann. Ph. Chem.*, 1886, **27**, 643). His observations were made with solutions of the salts, zinc sulphate, sodium sulphate, magnesium sulphate, sodium carbonate, and calcium chloride, and are thus fairly representative of the various hydrated salts which form supersaturated solutions. The method of experimenting was that indicated above; a solution of the salt under examination was prepared saturated at some intermediate temperature, such as 30° ; it was then heated to 60° , and the specific resistance was determined at every few degrees as the temperature fell to 10° , or even lower. The results are summed up by Heim, as follows:—

“The published experimental figures and the curves representing these clearly show that none of the salt solutions examined exhibit any sudden change in their specific resistance, as they pass into the supersaturated condition. . . . It is not possible, by the mere inspection of the curves, to determine whether or from what point the solution was supersaturated.”

Heim believes that this is proof of Loewel's view that a solution contains the anhydrous salt, and that there are no truly supersaturated solutions. In this I believe he is mistaken; his results furnish proof that the constitution of a solution is not altered in passing from the

nonsaturated to the supersaturated condition by fall of temperature; this is only one half of the proof.

Secondly, we have the specific viscosity as a means of examining this subject. I have made experiments on solutions of sodium sulphate, phosphate, and carbonate, saturated at about 30°. The form of apparatus employed and the precautions taken will be described in a future communication on the specific viscosity of salt solutions. The principle was the same as that of Heim. The results are contained in Table I, where the strength, saturation temperature, and the specific viscosity are given, the last being the time of flow of the salt solution, multiplied by 100, and divided by the time of flow of pure water at 20°. The temperatures of observations were 20°, 25°, 30°, 35°, 40°, and in the case of the sodium sulphate solution every degree between

TABLE I.

t° .	Na_2SO_4 .	t° .	$\text{Na}_2\text{S}_2\text{O}_3$.	t° .	Na_2HPO_4 .
20·0°	459·4	20°	834·4	20°	405·4
24·9	388·2	25	685·2	25	340·4
30·0	332·9	30	574·5	30	291·3
31·1	322·9	—	—	—	—
32·2	313·2	—	—	—	—
33·2	304·6	—	—	—	—
34·2	297·1	—	—	—	—
35·1	289·8	35·1	487·1	35	251·3
40·0	254·2	40·0	420·7	40	220·3
Strength	45/100	79/100		26/100	
Saturation t°	31·2°	28°		31°	

30° and 35°. The curves corresponding to the results are shown in Plate I, a vertical dotted line indicating the saturation temperature. In this case also the curve is perfectly continuous; there is nothing to indicate any change in the constitution of the solution.

Thirdly, there is the rate of expansion of supersaturated solutions. This I determined only qualitatively in the following way:—A solution of the salt saturated at about 30° was placed in a bulb furnished with a hollow stopper, to which was attached a long glass tube of uniform bore, graduated in millimetres. This last was surrounded by a glass jacket, through which water from the main flowed in a constant stream. The solution, nearly filling the bulb, was covered with a layer of paraffin oil, and the stopper inserted. The bulb was then

placed in a bath, side by side with a thermometer divided into tenths, the approximate ratio of the contents of each mm. of the tube to the contents of the bulb was 1.5 : 100,000. No attempt was made to take account of the amount of paraffin present, as the experiments were intended solely to ascertain whether the expansion between 20° and 40° was uniform or not. I therefore give only the curves corresponding to the results, as read in mm. of the tube. Salts were examined of the following concentration and saturation temperature:—

Salt.	$x/100$.	Sat. t° .
Sodium sulphate.....	44/100	30
Zinc sulphate.....	64/100	30
Sodium carbonate.....	38/100	30
Magnesium sulphate.....	41/100	30

The solubility of these at 20° and 40° being—

Salt.	20°.	40°.
Sodium sulphate.....	19.5/100	48.8/100
Zinc sulphate.....	57/100	72/100
Sodium carbonate.....	21.4/100	46.2/100
Magnesium sulphate.....	36.2/100	45.6/100

Here, again, it is impossible to detect the saturation temperature by mere inspection of the volume curves (Plate II).

These experiments on the various physical constants prove completely that there is no change in the constitution of the solution in passing the saturation point. In other words, that a supersaturated solution has the same constitution as a saturated solution prepared in the same way. It remains to be proved that it is the same as that of a non-saturated solution prepared in the ordinary way.

Temperature Constant, Concentration Varying.

In this connection I can bring forward determinations of only two physical constants, density and specific viscosity. The results obtained by experiment on the densities of solutions of sodium sulphate and thiosulphate are contained in a previous paper (*loc. cit.*). But I introduce the curves here (Plate II) for the sake of completeness. It will be seen that the density curve is perfectly regular in the case of both salts, nothing indicates supersaturation. It must be remembered that determinations of the density of supersaturated solutions are liable to greater experimental error than ordinary determinations; loss of water is almost unavoidable in the preparation of such solutions, and twice the usual error is introduced, owing to the necessity for employing a liquid to protect the solution. Similar results were also obtained

by Schiff, so that it is certain that the density curves do not change their direction at the saturation point.

Secondly, the specific viscosity at constant temperature increases uniformly with uniform increase of dissolved salt. This is shown by the results in Table II. Experiments were made with sodium sulphate, carbonate, and phosphate, and the solutions were of such strength that they extended equal distances on either side of the saturation point. The amounts of salt are in parts per 100 of water, not percentages.* Plate III gives the corresponding curves, which are again perfectly uniform and continuous on either side of the saturation point.

TABLE II.

$x/100.$	$\text{Na}_2\text{SO}_4.$	$x/100.$	$\text{Na}_2\text{HPO}_4.$	$x/100.$	$\text{Na}_2\text{CO}_3.$
10.0	134.7	5.0	124.2	10.0	165.3
12.5	146.0	7.5	139.2	12.5	189.4
15.0	158.8	10.0†	156.6	15.0	219.2
17.5	173.1	12.5	178.2	17.5	253.4
20.0†	188.4	15.0	205.6	20.0†	292.9
22.5	205.7	—	—	22.5	342.3
25.0	224.2	—	—	25.0	401.2
27.5	245.5	—	—	27.5	466.3
30.0	268.4	—	—	30.0	546.3

These experiments show that supersaturated solutions have the same constitution as non-saturated solutions at the same temperature, and those in the first part of the paper proved that alteration of temperature produces no abrupt change when the solution passes from the one state to the other. There can thus be no doubt that dilute, saturated, and supersaturated solutions all have the same constitution. This being the case, supersaturation cannot be explained by the hypothesis that the state of hydration of the dissolved salt is different in the two cases, nor can we fall back on the "inertia" of Kremers, for I have shown that a supersaturated solution can dissolve dehydrated salt. Some other explanation must therefore be sought for. This is to be found, I believe, in the statements in my previous paper.

"The individual in solution is not the same as that in the solid state, when hydrated salts are considered.

"A supersaturated solution is a solution of the anhydrous salt, which may or may not be saturated."

* The solutions were prepared by dissolving weighed quantities of salt in *measured* quantities of water, and are thus only approximate.

† Nearly saturated.

There is a good deal of evidence in support of the former of these statements, thus:—

Loewel (*Ann. Chim. Phys.* [3], **49**, 32) found that a supersaturated solution of sodium sulphate deposited either the heptahydrate or decahydrate, according to which hydrate was used to terminate supersaturation, and he obtained similar results with other salts, such as sodium carbonate, magnesium sulphate.

Again, it has been found that a supersaturated solution of nickel sulphate deposits the pentahydrate or heptahydrate under similar conditions, while Gernez (*Compt. rend.*, 1867, **63**, 843) found that supersaturated solutions of the salts of racemic acid deposited dextro- or lævo-tartrate, according to which crystal was introduced into the solution.

Now it does not seem probable that were the salt in solution combined with its maximum amount of water of hydration, that mere contact with a crystal of lower hydration could effect the separation of two or three or more molecules of water, more especially in presence of excess of water. But in addition I am able to bring forward evidence, in one case at least, which proves that the individual in solution is not the same as that in the solid state. In my previous paper I described the formation of crystals in a supersaturated solution of sodium thiosulphate which had been prepared several years before, by fusion of the solid salt, and probably by boiling before sealing the tube; of this last I am not certain. These crystals contained less than 2 mols. H_2O , though they were only partially separated from the mother-liquor. This led me to try evaporation of a supersaturated solution at the ordinary temperature over sulphuric acid, and as sodium thiosulphate forms very stable supersaturated solutions, I fused some crystals, and exposed the solution over sulphuric acid for two days, at a temperature between 16° and 21° , with the result that an abundant crop of crystals was obtained. On decanting the mother-liquor into a dish, it immediately solidified, and the crystals were again exposed over sulphuric acid for 24 hours; at the end of that time they were surface-dry, were perfectly transparent, and not effloresced in the least, showing that they were in the same state of hydration as when deposited from the solution. When, however, they were touched they crackled, grew warm, and slightly opaque. On heating they liquefied partially, and a liquid was obtained which contained solid transparent crystals; this showing that the substance contained mother-liquor, which had crystallised as pentahydrate. Two analyses of the crystals gave 15.6 per cent. of water, corresponding with 1.6 mol. H_2O to 1 mol. of the anhydrous salt. Thus the crystals produced by the evaporation of a supersaturated solution of sodium thiosulphate have at the most the formula

$(\text{Na}_2\text{S}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$, or more probably $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$, the latter formula indicating the presence of about 25 per cent. of the pentahydrate. In any case, the results show that the salt deposited from the supersaturated solution is not the pentahydrate, and that consequently the pentahydrate is not present in the solution. I hope soon to be able to describe the results of similar experiments with other salts. But what I have said, taken in conjunction with the experiments formerly described, when I prepared supersaturated solutions by dissolving cold salt in cold water, or in cold non-saturated solutions of the same salt, put it beyond question that such solutions do not contain the hydrate which exists in the solid state.

The second statement that supersaturated solutions are saturated or non-saturated solutions of the *anhydrous* salt is not so easily proved. It must stand or fall with the hypothesis that all solutions contain the *anhydrous* salt, and I must emphasise here once more that by this I do not mean anhydrous in the sense when applied to a solid salt, but as opposed to the view that any portion of the water is connected with the salt in a way different from the rest of the water.

This homogeneity, so to speak, of the solvent water is so clearly proved by experiments on vapour-pressures, freezing points, molecular volumes, electric conductivity, and other physical constants of solutions, that I think we ought to hesitate before asserting that hydrates exist in solution, the sole evidence in the support of this being heat evolved on solution of dehydrated salts as opposed to the absorption of heat attending the solution of the hydrates, and the colour-changes attending the warming or other treatment of solutions of certain salts.

The thermal argument I have already treated of at some length in a previous paper (*Chem. News*, 1886, **54**, 1403), and I am still convinced that all the thermochemical results relating to Thomsen's "*Acidität*," or Ostwald's "*Affinität*," tend to prove by their concordance the non-existence of hydrates in solution.

The colour-changes are at first sight an insuperable difficulty, but I believe that as our knowledge of the phenomena of solution increases, we shall find that these are due, not to hydration or dehydration, but to some rearrangement of the molecule of the salt itself, similar it may be to the rearrangement in the case of chromium sulphate, but differing from it in being more easily reversed, in fact the experiments of Wagner (*Wied. Ann.*, 1883, **18**, 286) on the specific viscosity of copper chloride before and after heating lend much support to this view.

SPECIFIC VISCOSITY
T° VARYING.
CONCENTRATION CONSTANT

SPECIFIC VISCOSITY $T^{\circ} = 20^{\circ}$

CONCENTRATION VARYING.