XXVII. *On Supersaturated Saline Solutions.* *By* CHARLES TOMLINSON, *F.R.S.*

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I. *History.*

THE phenomena of supersaturation have been studied chiefly with reference to solutions of GLAUBER'S salt. In 1809, ZIZ of Mayence[†] showed that the sudden crystallization of these solutions is not due to agitation; that the vessels containing them need not be hermetically sealed, but if put under a bell-glass, or loosely covered as with a capsule, they can be preserved during a long time; that solids brought into contact with the solutions act as *nuclei* and produce instant crystallization, especially when dry; if wet or boiled up with the solution they become *inactive*. The best nucleus is a crystal of the salt itself. Air, if artificially dried, ceases to be a nucleus. Three varieties of the sodic sulphate are noticed, *i. e.* the *anhydrous*, the ordinary 10-*atom hydrate*, and also a modified salt formed when supersaturated solutions are left to cool down in closed vessels. This salt contains less water of crystallization than the ordinary salt, and is more soluble. If the vessel in which it is formed be suddenly opened, or a nucleus touch the mother-liquor, this instantly solidifies into the 10-atom hydrate, and the crystals of the more soluble salt become opaque, like the boiled white of egg.

In 1819 GAY-LUSSAC[‡] referred the state of supersaturation to the inertia of the saline molecules, the molecular condition of the sides of the vessel, and other causes. He also showed that solutions of some other salts besides GLAUBER'S salt exhibit the phenomena of supersaturation. In 1832 the number of such salts was stated by Dr. OGDEN[§] to be not less than 21.

In 1825 FARADAY[||] published some experiments on the supersaturated solutions of GLAUBER'S salt. GRAHAM[¶], TURNER[**], URE, and others also contributed new facts; but the most elaborate inquiry was made by M. LÖWEL between the years 1850 and 1857, the results of which are contained in six memoirs[††]. According to this writer, the modified salt is formed in consequence of a molecular change which takes place when a solution saturated at 218° FAHR. cools down to 64°. The modified salt is much more soluble at ordinary temperatures than the 10-atom hydrate, its maximum solubility being at 80°·6. The sodic sulphate has three maxima of solubility, viz. 93°·2 for the 10-atom hydrate, 78°·8 to 80°·6 for the 7-atom hydrate, and 62°·6 to 64°·4 for the anhydrous salt. At

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[*] Rewritten by the author from the original paper in a more condensed form.

[†] Schweigger, Journal for 1815, Band xv.

[‡] Annales de Chimie et de Physique, 2nd ser. vol. xi.

[§] Edinburgh New Philosophical Journal.

[||] Quarterly Journal of Science, vol. xix.

[¶] Transactions of the Royal Society of Edinburgh.

[**] Elements of Chemistry.

[††] Annales de Chimie et de Physique, 3rd ser. vol. xxix., xxxiii., xxxvii., xliii., xliv., xlix.

these three temperatures the saturated solutions are about equally rich in salt. The 7-atom hydrate and the anhydrous salt can only maintain their molecular constitution when in contact with the mother-liquor in closed vessels, in which they are sheltered from the air and from other bodies that act upon them as nuclei. No sooner are they exposed to the air than they become opaque and warm, and assume the molecular constitution of the 10-atom hydrate as well as its solubility. Hence the conclusion is that supersaturated solutions of the sodic sulphate are not really so, since they hold a salt of much greater solubility at common temperatures than the ordinary salt. It is also stated that the solutions of the sodic carbonate and of the magnesic sulphate form salts of a lower degree of hydration, and of greater solubility than the normal salts. LÖWEL'S general conclusion is that all cases of supersaturation are such in appearance only, and not in fact. As to the function of nuclei and the inner sides of the flasks in determining crystallization, he regards it as the effect of one of those mysterious contact actions known as *catalytic*, of which science has not yet been able to give a satisfactory explanation. Bodies that appear to be active in inducing crystallization are designated *catalytic* or *dynamic*; while bodies that are apparently inactive are termed *non-catalytic* or *adynamic*. "It appears certain," he says, "that but for the mysterious action which the air and other bodies exert on supersaturated solutions, we should obtain sulphate of soda only in the modified state; that is, crystallized with seven equivalents of water, and possessing at ordinary temperatures of the air a much greater solubility than that of the ordinary 10-atom salt."

Later inquirers have endeavoured to explain the action of nuclei. GERNEZ* tried 220 solids, and of these he selected thirty-nine that were active in inducing crystallization, of which eighteen were insoluble: these were carefully washed in distilled water, and dried out of contact with air. When dry they were found to be inactive. The twenty-one soluble substances were purified by recrystallization, and they all became inactive. Hence it is concluded that sulphate of soda is the only nucleus for solutions of the same salt. That is to say, whenever a glass rod or other body acts as a nucleus, it is contaminated with minute portions of the salt itself, which is supposed to exist in the air, not only of towns, but in the country. According to this view, the supersaturated solution of any other salt can only be crystallized by a saline nucleus of its own kind.

II. *Definitions.*

In the present memoir the terms *chemically clean* or *chemically unclean*, or simply *clean* and *unclean*, are to be taken with the following limitations:—

1. A chemically clean surface is one that has not a greater attraction for the dissolved matter than for the liquid which dissolves it. A supersaturated aqueous solution, for example, whether of a salt or of a gas, will adhere perfectly to such surface, and there will be no separation of salt or of gas.

2. But as there is little or no adhesion between water and a fatty, oily, or greasy

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* Comptes Rendus, vol. lx. p. 833. See also Schiff, Ann. der Chem. und Pharm. vol. cxi. p. 68.

surface, while there is strong adhesion between a salt or a gas and such surface, the presence of such a surface in a supersaturated solution will cause a separation of the salt, or of the gas.

3. Hence a surface contaminated ever so slightly with oily, fatty, or greasy matter will act as a nucleus in such solutions.

4. A nucleus may be defined as a body that has a stronger adhesion for the salt or the gas than for the liquid which holds it in solution.

5. Bodies that have been exposed to the products of respiration or of ordinary combustion, or that have been handled or wiped with a cloth, are covered more or less with a greasy film, and act as nuclei in aqueous solutions. So also the dust of the room raised into the air is more or less contaminated with greasy or organic matter, and acts as a nucleus.

6. By washing such bodies in a solution of caustic alkali, in sulphuric acid, in ether, &c., such oily or greasy film is got rid of. In this way the sweepings of a room may be made inactive as nuclei. It is proposed to name bodies or surfaces that have been treated in this way *catharized*, from καθαρός.

III. *Action of Nuclei.*

This action may first be illustrated by taking care to ensure the absence of nuclei. Previous observers insist on the great sensitiveness to cold of sodic sulphate solutions; but if precautions be taken to ensure chemical purity, this sensitiveness disappears. For example:—Two ounces of large crystals of this salt (which had been purified by repeated crystallization) in a dry and slightly efflorescent state were put into a clean flask with one ounce of distilled water, and the flask was carefully heated so as to avoid the deposit of anhydrous salt, and then boiled. Two thin glass test-tubes, each of $1\frac{1}{2}$ oz. capacity, and about $\frac{3}{4}$ inch in diameter, were filled with strong sulphuric acid, emptied, and left to drain with their mouths under water. A glass funnel washed with spirits of wine, had a clean filter adapted to it, and the boiling solution was passed through the filter into the two tubes. These were immediately plugged with cotton-wool, and passed over the flame of a spirit-lamp, when one of the tubes gave a kick, and threw down a small quantity of anhydrous salt. Both tubes were now placed in a vertical position in a rack, and left to cool. At about 50° F. they were put into a freezing-mixture in which a thermometer rapidly sank to 10°; the tubes were moved about in the mixture, and then left in it during some hours, while the temperature slowly rose from 10° to 40°, when the solution in one tube was still liquid, bright, and transparent; and equally so in the other tube, only at the bottom there was a small group of 7-atom crystals, built, as it were, on the deposit of anhydrous salt already referred to. The cotton-wool was now taken out so as to admit a nucleus from the air, and crystallization instantly set in at the surface, spreading rapidly downwards, and carrying with it sufficient water to convert the whole solution into the 10-atom hydrate, and also to impart to the 7-atom hydrate three additional equivalents of water. There is a considerable rise of temperature accompanying this action. By cautiously fusing the salt after each experiment, these phenomena may be repeated with the same solution a number of times. It is very possible, however, that the tube may cease to retain its condition of chemical purity perfect; in which case the ordinary phenomena consequent on reduction of temperature will take place. It is not easy to maintain a chemically clean surface. A short exposure to the air, or a mere touch, will often suffice to impart a greasy film, or motes or dust, which prevent or lessen adhesion, and render a so-called "inactive" solid "active." When a glass rod has been kept in water or passed through flame and dried, or cooled not in contact with the air, it is more or less chemically clean, and remains so while being sheltered. When Herr ZIZ found that a knitting-needle was "active" in one solution, and that by passing it through the cork which confined another solution it became inactive, he simply made the wire chemically clean by the friction.

Some liquids, such as spirits of wine, act as nuclei by combining with a portion of the water of the solution, and liberating a little salt which acts as a nucleus.

My experiments lead me to the conclusion that air, in its pure state, is not a nucleus; for not only may a supersaturated solution be briskly shaken up in a bottle half-full of air*, but air if previously passed through water may be made to bubble through a supersaturated solution without producing any separation of the salt.

When air appears to act as a nucleus, I believe that it is simply performing the part of a carrier of some solid particle not chemically clean. If a boiling solution be poured into a bottle, which is then tightly corked, or the stopper inserted, the solution in cooling down will have a partial vacuum over it. If, now, the cork be loosened, air will rush in, and almost certainly drag in with it a solid nucleus. But if the flask be plugged with cotton-wool, motes &c. will be kept back while the air streams in as the solution cools, and the plug may be removed without always producing immediate crystallization. Thus a solution opened in a garden, on a fine clear still day, is less likely to crystallize than if opened in a room, where a step across the carpet raises a cloud of solid particles. So also a narrow-necked bottle is less likely to catch nuclei than a wide one. LÖWEL found that he could keep his solutions from crystallizing longest in tubes of narrow bore. Those in tubes of from $\frac{1}{2}$ to $\frac{3}{4}$-inch bore, crystallized on being opened; in those of less than half an inch the solutions remained longer in the liquid state, and they could be kept for weeks exposed to the air in tubes of $\frac{1}{4}$-inch bore. All this seems intelligible without recurring to any mysterious undiscovered force, such as M. LÖWEL so frequently refers to.

By using chemically clean vessels and thermometers, we get rid of various anomalous cases of crystallization referred to by previous observers. And not only so; but we reduce most of the phenomena of supersaturation to the case of nucleus or no nucleus. In chemically clean vessels there is no nucleus, and the modified salt, if formed at all,

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* In such a case it is a long time before the air becomes disengaged and the solution clear—an effect which belongs to many saline solutions a familiar example of which is afforded by the long white foaming trail left behind a steamer in sea-water. This effect is not produced in river-water.

is the result of certain conditions which will be examined in the next section. But it by no means follows that supersaturated solutions in cooling down undergo any change in molecular condition, or produce a modified salt of a lower degree of hydration. Strong solutions of many salts may be cooled down below the freezing-point of water, and become viscous without crystallizing. For example:—Five parts of sodic acetate to one part of water were boiled, filtered, and boiled again at 240°, in a flask, with a thermometer in the solution, the neck being plugged with lamp-cotton. The solution was left in a cold room during about twenty hours, and then placed for some hours in a freezing-mixture. The solution remained some time at 14°, when the thermometer being gently lifted up several times, without being taken out of the flask, the viscous solution ran off from the bulb like a thickish syrup. The thermometer was restored to its place, and a wire passed down so as to touch the liquid. It immediately and rapidly crystallized into an amorphous mass, and became quite solid; the temperature rose to 104°, thus showing a sudden rise of 90°.

Now here is a solution which in an open evaporating-dish crystallizes at 150° and becomes solid a few degrees below this; yet it can be cooled down to 14° or lower, and be kept in that state for hours without crystallizing. It becomes viscid at this low temperature, and so far it undergoes a molecular change; but this solution has no tendency, so far as I am aware, to form a salt of modified character. It may be cooled at least 140° below its point of crystallization and yet not crystallize, simply because there is no nucleus to start the action. In the open evaporating-dish, on the contrary, no sooner is the boiling solution in contact with the air, than its surface becomes dotted with specks and filaments that are floating about. If these be carefully watched, one or more of them will be seen to increase in size by the aggregation of saline particles about it, and suddenly from this point fans of crystals begin to radiate. In the meantime the sides of the vessel are active in separating the saline molecules, and the more so in proportion to the absence of chemical purity.

The sodio-potassic tartrate also gives remarkable results. Two ounces and a half of newly formed crystals were fused in their water of crystallization, one ounce of water was then added, and the solution raised to the boiling-point. The solution cooled down to the temperature of the air without depositing crystals. The flask was then kept for some hours in ice and water, and afterwards in ice and salt until the temperature of the solution was 14°. The flask was repeatedly moved round and round in the freezing-mixture, but the solution remained perfectly fluid. The flask was now taken out, and the thermometer lifted up several times, then quite out of the flask; the solution was also touched with a wire, but crystallization did not set in until the side of the flask had been scratched with a wire not chemically clean. (If clean, it would have had no effect.) The scratches instantly became chalky white, and crystallization set in very gradually; each crystal as it was formed dragged a viscid line as it slowly descended. There was at first but little rise of temperature, but in the course of half an hour the mercury gradually rose to 64°, thus showing a rise of 50°.

The sodic arseniate may be taken as another example. Two parts of this salt to three of water were boiled at 223°, and filtered into a clean bottle with a thermometer passing through the plug. As the solution cooled it became viscid; but at 35° there was no sign of crystallization. The thermometer was taken out of the flask for an instant, and then reinserted. The effect was striking. The thermometer had caught up some chemically unclean particles from the air, and these acted as nuclei. The whole of the immersed portion of the thermometer became at once covered with crystalline tufts which propagated their action, and the temperature rose to 54°.

Cases like these may be multiplied; for it must not be supposed that I am dealing with exceptional instances with respect to these motes and particles. The air of every house is full of them (as a sunbeam often reveals); they come in contact with solutions and start crystallization, or they enter by the necks of flasks and bottles, and render their inner surfaces "active."

The cotton-wool used in plugging the vessels is not chemically clean; it induces crystallization if the solution touch it for an instant, as it may sometimes do on inclining or shaking the flask for the purpose of watching the effects of cooling. We can also induce crystallization in any part of the vessel by making that part chemically unclean. For example, a large tube was washed out with a caustic alkaline solution, rinsed first with water, then with spirit, and again with water, when a boiling solution of sodic phosphate was poured into it, and in another experiment sodic sulphate (5 salt to 1 water); but before plugging it, the upper part of the inside of the tube was touched with a finger slightly greased. When cold the solution was brought into contact with different parts of the tube that were clean, without producing crystallization; but the moment the solution came upon the edge of the finger-mark, crystallization set in, and the solution became solid.

I believe this experiment will explain the statement so often made as to the necessity of keeping supersaturated solutions quite still; for if stirred or agitated they suddenly deposit the excess of salt. In such cases, no care having been taken to produce chemically clean surfaces, the solution itself does something in that direction to the extent that it occupies in the vessel; but agitation brings a portion of the solution against the upper and more "active" part of the sides, or the rod used for stirring is equally "active," and either may perform the part of a nucleus accordingly.

The salt used for making a solution is likely to be unclean. During its formation in an open evaporating-dish, and its subsequent handling, packing, &c., it contracts various impurities, among which may often be found hairs and other greasy substances, which do not always lose their property of becoming nuclei during the boiling of the solution. They may be removed by filtration; but as they often contaminate the vessel in which the salt is boiled, it is desirable to filter the hot solution into a second clean flask, in which it may be boiled up again. In the case of the acetates, a few drops of acetic acid should be added to the second flask to make up for any loss during the boiling. But in such case the temperature may pass beyond the boiling-point without giving any signal whatever, until the liquid bursts into vapour with explosive violence, or is simply turned out of the flask without any noise at all. Five ounces of sodic acetate were fused in its water of crystallization, boiled, and set aside to cool. The liquid contained a number of hairs or motes. At 150° it began to crystallize, and the whole solution became filled with crystalline needles. The salt was again raised to the boiling-point, and it boiled quickly and readily with the usual symptoms, both before and during the boiling. The solution was now filtered into a chemically clean flask wet with acetic acid, and again placed over the lamp. It rose to 240° without any sign, and a few degrees above this it suddenly burst into vapour. I have not repeated this experiment; but have no doubt that, instead of crystallizing at 150°, the clean solution might be reduced to a very low temperature without crystallizing, simply from the absence of the nuclei which were so abundant in the unfiltered solution.

*[It is said that the most powerful nucleus is a crystal of the salt itself. This statement must be received with reference to the condition of clean and unclean. When supersaturated solutions are lightly covered, so as to allow a portion of the water to escape, a crystalline crust often forms on the side of the flask. This crust does not act as a nucleus, because it is clean; and the solution, being supersaturated, does not dissolve it. I have kept such a solution of ammonium-phosphate in contact for days together with the crystalline crust that had formed above it with little or no corroding action. These crusts may be readily formed in the case of the magnesic sulphate solution (2 salt to $1\frac{1}{2}$ water) in clean tubes placed in strong sulphuric acid under an exhausted receiver. A crust will form on the surface of the cold solution in about twenty minutes, and this may be allowed to fall through the solution without acting as a nucleus. Or a solution of the magnesic sulphate (4 salt to 4 water) may be made in a flask, and filtered into a clean flask; and while this is boiling, perfectly clean crystals (made so by washing in sulphuric acid and rinsing in water), contained in a clean, short tube, are to be suspended by a clean wire in the neck of the flask while steam is pouring off from it. The cotton-wool plug may now be inserted, the lamp removed, and the flask left to cool during twelve hours or so. The tube may then be lowered into the solution, and the crystals will not act as nuclei in inducing crystallization.

In a similar experiment with sodic sulphate the salt in the short tube became, of course, converted into the anhydrous salt; but it was quite inactive as a nucleus on the cold solution. Exposed to the air for a few moments it acted powerfully as a nucleus.]

Such cases as the above lead me to the conclusion that the state of supersaturation is simply a case of no nucleus. There is nothing to start the action which produces change of state, and there is no reason why the state should change, unless indeed, as may sometimes happen, mere reduction of temperature is the efficient agent in inducing crystallization by bringing the particles so close together that cohesion can prevail over adhesion. But in such cases it more often happens that the solution completely solidi-

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* Those paragraphs within [ ] formed the subject of a Note sent in to the Royal Society, August 13, 1868.

fies into the normal salt than partially into a salt of a modified character. The formation of the modified salt, which has given rise to much speculation, will next be considered.

IV. *On the Formation of the modified Salt.*

Two ounces of zincic sulphate and one ounce of water were heated in a clean flask until the solution boiled briskly. The solution was then filtered into chemically clean test-tubes, made so by washing them out with strong sulphuric acid. The tubes were plugged with cotton-wool and set aside to cool; they were bright and transparent; but on cooling to about 70° they became troubled by the formation of a monohydrated salt, which gradually subsided and formed a small deposit at the bottom of the tubes. Upon this deposit, after some hours, a fine crop of acicular crystals had sprung up, leaving the mother-liquor clear, but still supersaturated; for on taking out the cotton-wool from one tube, crystallization set in from the surface. On gradually raising the other tube to the temperature of 100°, or from that to 106°, the acicular crystals melted down and formed a dense lower stratum.

This experiment throws much light on the behaviour of those supersaturated saline solutions that form salts of a modified character, and of greater solubility than the normal salt. When the richly hydrated salts, which best display the phenomena of supersaturation, enter into solution at high temperatures, they give up all, or nearly all, their water of crystallization to the aqueous solvent. In the case of the sodic sulphate, for example, I quite agree with the accepted theory, that from the boiling-point of an aqueous solution down to about 60° it is the anhydrous salt that is held in solution; but I differ from that theory which supposes a molecular change to take place in the supersaturated solution at and below 60°, and the molecules to arrange themselves into the constitution of the 7-atom hydrate. There is no experimental proof that such is the case. We can get the 7-atom hydrate, it is true, when a strong solution is cooled down below 60°; but this is no proof that the solution passed through the molecular change which has been insisted on.

I have already given a case in which a strong solution of the sodic sulphate, contained in a tube made chemically clean with special precautions, was cooled down to 10° F. without any separation of the salt, in consequence of the absence of a nucleus, and the strong adhesion of the solution as a whole to the sides of the tube. If a strong solution of sodic sulphate be filtered into a tube washed without any special precautions to make it chemically clean, and the mouth be closed with cotton-wool, such a solution may be cooled down to 50° or less without depositing any salt. If we now place this tube in ice-cold water, and watch it carefully, a small number of octahedral crystals (the form of the anhydrous salt) will separate from the solution and subside, liberating heat-currents as they fall and when resting at the bottom. This experiment has been performed with supersaturated solutions of sodic sulphate of varying strengths and with the same result, unless crystallization set in from the surface by the dragging in of a nucleus consequent on the cooling, or on the separation of a fragment of cotton-wool, and then the whole solution immediately became solidified into the 10-atom salt. The deposit of a few anhydrous crystals, as stated above, is, I think, a sufficient proof that the solution undergoes no molecular change at 60° or under, but continues to be a solution of the anhydrous salt until, by a proper reduction of temperature, it deposits the excess that it can no longer hold.

That which takes place in the case of the zincic sulphate solution applies equally here. The anhydrous sodic sulphate thus thrown down at 32° liberates heat, and the crystals partially enter again into solution. Or should the atmospheric temperature rise a few degrees, the operation is further assisted; the anhydrous crystals become wholly or partially dissolved, and a dense lower stratum is thus formed, containing not water enough for the formation of the 10-atom hydrate, but only sufficient for the 7-atom; and thus we have a comparatively small group of crystals of the 7-atom hydrate formed at the bottom of the solution.

In this way, as it appears to me, the formation of the 7-atom hydrate may be accounted for and rendered intelligible without having recourse to the doctrine of molecularity of which we really know so little. The mother-liquor resting on this 7-atom hydrate is still a supersaturated solution; so that if the flask be opened crystallization proceeds rapidly from the surface downwards, and carries down sufficient water to form the 10-atom salt throughout, and also to convert the 7-atom hydrate into the 10-atom; and in appropriating the three additional equivalents of water, the 7-atom hydrate becomes of an opaque white, from the breaking up of the mass into a multitude of minute 10-atom crystals. It is important to bear in mind the difference of locality in the formation of the two hydrates; the 7-atom hydrate originates at the bottom of the solution under circumstances which do not allow of sufficient water being present to form a salt of a higher degree of hydration than the 7-atom; whereas the 10-atom salt originates at the surface, and carries down in close well-packed crystalline lines sufficient water to form the 10-atom salt. These lines form so quickly, and are packed so closely together, that there is neither time nor space for the formation of the usual crystal; they pass to the very bottom of the vessel, and seem to penetrate while they render opaque the transparent crystals formed there.

M. Löwel states that supersaturated solutions of the sodic carbonate form two modified hydrates, viz. the 7HO *a* and the 7HO *b*, which, he says, not only differ in solubility from each other, but also from that of the 10-atom salt. He admits that the sodic carbonate differs in behaviour from the sodic sulphate, since the carbonate does not deposit crystals from the supersaturated solution merely by a reduction of temperature; "but such solutions remain saturated until, in consequence of lapse of time, and above all of low temperature, the inner surfaces of the flask have recovered their peculiar catalytic properties of determining crystallization which heat had deprived them of, the cause of which remains unknown." In chemically clean vessels I have not been able to reproduce M. Löwel's results. I have tried numerous experiments with solutions containing

5, 4, 3, and 2 parts salt to 1 of water: the solutions have been left to themselves, or they have been placed in freezing-mixtures at various temperatures; but the general result is a sudden crystallization from some point near the surface of the solution, rapidly converting the whole into a solid, with a rise of temperature of 35° or 40°.

M. Löwel also points out three varieties of the magnesic sulphate, the ordinary 7-atom salt, which he names 7HO *a*, a modified salt, 7HO *b*, and also a 6HO salt.

In the case of this salt also I have placed highly charged supersaturated solutions (2 salt to 1 water), contained in chemically clean tubes, in freezing-mixtures without any effect in producing crystallization. In one experiment a solution made with two ounces of salt and one of water was boiled and filtered into five tubes, four of which were chemically clean, while the fifth had been used for a solution of this salt and left lying on the table for two or three days. All five tubes on being filled were plugged with cotton-wool, and set aside to cool. When cold the four clean tubes were put into a freezing-mixture at 10°, and when this had slowly risen to between 30° and 40°, another freezing-mixture was prepared, to which the tubes were transferred; but still after another half hour the solutions remained perfectly bright and transparent. One tube was removed from the mixture and opened, when on touching the surface with a metal point, crystalline tufts, like thistle down, were propagated downwards, and soon the whole solution had solidified into the usual 7-atom salt. The fifth tube, which was not chemically clean, did not retain its solution in the liquid state: on examining it some hours after it had been filled, the contents had solidified into the ordinary salt. The other three tubes, on being removed from the freezing-mixture, showed no disposition to crystallize.

The magnesic sulphate parts readily with an atom of water and becomes milky white. A group of these milky crystals is sometimes deposited at the bottom of a long tube containing a strong and still warm solution of the salt, and partly immersed in cold water. A certain difference in density between the lower and upper portions of supersaturated solutions is favourable to this result. Indeed there is a tendency to stratification during the cooling of all these solutions, as may be seen on gently shaking the flask, when the effect is that of the mingling of layers of different densities, as when water is resting on syrup. I long thought that when a salt of a lower degree of hydration is produced, it was due to the formation of denser and more highly charged saline substrata. Gay-Lussac's experiment* teaches that saturated solutions contained in long tubes, and maintained at the same temperature during many months, are of the same density at every part of the column; and it seems probable that such is also the case with supersaturated solutions when cold and left undisturbed some time; but there are various difficulties in the way of determining this point experimentally. When the denser lower stratum is formed at all, it is, I believe, by the process already explained in the case of zincic sulphate and sodic sulphate. A salt of a lower degree of hydration, or an anhydrous salt, is thrown down on a reduction of temperature of the supersaturated solution, and the heat given out during a change of state, assisted by a rise of atmospheric

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* Annales de Chimie et de Physique, vol. vii. p. 79.

temperature, enables the salt to go into solution, and thus a dense lower layer is formed from which the modified salt is produced.

The ammonium phosphate is another example of this action. A solution saturated at 212° was filtered into a clean flask wetted with liquor ammoniæ, and left some weeks as a supersaturated solution. It was then placed in a freezing-mixture, when it threw down a white powder, probably the anhydrous salt: the flask was now set aside, when after a few days the powder had partially disappeared, and a crop of transparent crystals had formed. But this result is not so readily produced if special means be taken to secure clean vessels. Five tubes were filled with sulphuric acid, rinsed with water, filled up with liquor ammoniæ, emptied, and a boiling saturated solution of the ammonium phosphate filtered into them. When cold, these tubes were put into a freezing-mixture composed of sodic sulphate and hydrochloric acid, and after half an hour transferred to a similar mixture, without producing any immediate effect. On examining the tubes next day a small quantity of white powder was found at the bottom of three of the tubes, with transparent crystals in the form of flat quadrangular prisms.

Strontic nitrate would appear to be favourable to the exhibition of this class of phenomena, since a strong solution on cooling down to about 62° deposits anhydrous octahedral crystals. But these are bright, hard, and transparent, and apparently not affected when the tube is put into water at 212°, or into a freezing-mixture at 10°, or when the crystals are touched with a wire. On removing the cotton-wool and scratching the side of the tube, the scratches became immediately filled up with minute crystals, and a copious shower of the hydrated salt took place with the liberation of heat-currents. After a time these formed a considerable mass, and on putting the tube into water at 70° the salt melted down, but more rapidly at 90°; at 200° the remaining part of the mass fell down into an opaque white powder, from which the original octahedra emerged as sharp and transparent as when first formed.

Many salts behave like the sodic carbonate in maintaining a state of supersaturation down to a certain temperature, and then suddenly becoming solid throughout. The rhombic sodic phosphate does this, as also the plumbic acetate. A boiling solution of plumbic acetate ($2\frac{1}{2}$ salt to 1 water) was left to cool slowly down to about 40° (the temperature of the room), when it suddenly crystallized with a considerable rise in temperature. The whole formed a solid mass, not amorphous, but consisting of needles of the normal salt, as is nearly always the case when crystallization commences at the surface. On gently warming the mass, these needles fell apart, and revealed the fibrous structure. This is a common case in salts that have considerable solubility. A boiling saturated solution of zincic acetate, on the contrary, not only cooled down to 40° without crystallizing, but continued liquid during some hours in a mixture of snow and water at 32°. On removing the thermometer crystallization did not set in until the inner side of the flask at the level of the solution had been scratched, when the marks became chalky white as usual, crystallization of the normal salt set in, and small well-shaped crystals continued to fall during some hours with but slight rise in temperature. The excess of salt beyond the point of saturation was deposited, and the mother-liquor was simply a solution saturated at the existing temperature. The cupric sulphate, citric acid, and other salts are examples of this action. In some cases supersaturated solutions, if not highly concentrated, may be frozen and thawed again, without any separation of the salt; whereas if such solutions are much stronger, they cannot be frozen at temperatures varying from 10° to zero. The cupric sulphate is a good example of this. According to POGGIALE, 100 parts water at 86° dissolve 48·81 parts of the salt; this is equivalent to 234¼ grains of salt to one ounce of water. A solution of this kind was put into a freezing-mixture and sank slowly to about 16°, when it froze, and the thermometer rose to about 25°. The solidified solution now appeared almost white, but on leaving the flask exposed to an atmosphere of 52° during some hours, the solution thawed, and recovered its former brightness. A much stronger solution was now made (468 grains salt to 1½ ounce water) and filtered into a tube that had been washed out with sulphuric acid; this was repeatedly kept in a freezing-mixture at 10° without any deposit of salt.

V. *Anhydrous Salts.*

The salts hitherto treated of in this memoir as presenting the phenomena of supersaturation are hydrated, and in general the phenomena are best exhibited in those salts which are richest in water of crystallization. Whether anhydrous salts display these phenomena in their solutions is a point by no means settled; for while some observers maintain that the solutions of a few anhydrous salts do become supersaturated, others deny that such is the case. In perfectly clean flasks, and with clean solutions, I have never been able to detect a case of supersaturation in an anhydrous salt. A few examples may be given. Two ounces of nitre crystals were added to two ounces of water in a clean flask, say 100 parts of nitre in 100 of water, and the solution was raised to the boiling-point, filtered into a chemically clean flask, made so by washing it out with strong nitric acid. In this flask the solution was boiled again; the neck was then plugged with cotton-wool with a thermometer passing through the plug. When the temperature of the solution had fallen to about 120°, crystals began to grow up from the bottom of the flask. These crystals were built up of short prisms, diminishing in width and becoming smaller as they rose into the hotter and weaker part of the solution above.

Now, according to GAY-LUSSAC'S Table, 100 parts of water at 131° F. contain 97·05 of nitre. My solution contained 100 parts. Supposing that, owing to the absence of a nucleus, the solution were supersaturated between the temperatures 131° and 118°, it could not remain so in consequence of the cohesive force of the saline particles prevailing over the adhesive force of the solvent; it begins to deposit crystals, and then the action goes on rapidly; the temperature rises a few degrees, then declines, and when cooled down to the temperature of the air, say 50°, the solution holds about 22 per cent. of the salt.

But is there any reason for supposing the solution to be supersaturated? When crystallization begins, it is at the coldest part of the flask that the action commences.

The coldest part is the bottom, and the coldest part of the bottom is that nearest the window. If the flask be suspended in the air crystallization will first begin on the window side. If the flask be placed on metal or other good conductor of heat, a ring of crystals will be formed at the bottom, while the thermometer is 6° or 8° above the point at which crystallization ought to take place; the bottom of the flask and the ring of solution in contact with it are prematurely chilled, while the rest of the solution is above the point of crystallization. If the flask be left on a thick block of wood or other bad heat-conductor, the crystals at the bottom will be formed later. A solution containing 125 parts of nitre in 100 of water ought, according to the Table, to begin to deposit salt at 150°. The flask containing such a solution at boiling heat was placed on a block of wood; at about 149° heat-currents suddenly rose like a cloud from the bottom of the solution to the surface, and crystallization instantly set in. If, before crystallization begins, the flask be plunged into cold water, the sides become coated with a shell of crystals, while the rest of the solution is still hot.

It might reasonably be expected, from its great solubility, that nitre would form supersaturated solutions; but it behaves as, I believe, anhydrous salts in general behave; its solution cools down until it is exactly saturated, and then it begins to deposit crystals of the normal salt without any modification whatever.

The potassic bichromate is cited, on the authority of OGDEN and others, as an example of an anhydrous salt that produces supersaturated solutions. My experiments do not confirm this view. According to KREMER's Table, 200 parts water at 140° F. dissolve 100 parts of the salt. Such a solution in cooling down from 212° ought to deposit salt at about 140°, unless it becomes supersaturated. One ounce of newly crystallized dry salt was boiled in two ounces of water, filtered into a clean flask and again boiled, and the flask was closed. At 138° an abundance of crystalline flakes was thrown down, heat-currents ascended, and the temperature continued stationary for a minute or so. The crystals formed a lining over about two-thirds of that part of the flask that was occupied by the solution, but the deposit was most abundant on the side nearest the window*.

Sal-ammoniac.—According to KARSTEN, 100 parts water at 65°·75 dissolve 37·02 of the salt, or, what is the same thing, one ounce water (480 grains) dissolves 177·6 grains of the salt. Such a solution in cooling from 212° began to deposit salt at about 66°, and just below this the salt separated abundantly.

Sodic nitrate was also tried. According to POGGIALE's Table, 100 parts of water at 158° will dissolve 129·6 of the salt, or $\frac{129\cdot6}{100}$ of $\frac{480}{1}=622$ grains. In such a solution raised to the boiling-point and allowed to cool down, the salt began to separate at 160°.

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* Saturated solutions of the potassic bichromate undergo a remarkable deepening in colour under the action of heat; they may even become black and opaque if boiled a second or a third time in the same flask; but they recover their usual colour on cooling. The salt deposited in an open evaporating-dish from a hot saturated solution is almost white. If this light-coloured portion be placed on filtering-paper and allowed to dry in the open air, it does not deepen in colour; but if put in a platinum crucible and gently heated over a spirit-lamp, it becomes very dark in colour, and in cooling assumes and retains the usual colour of the salt. The phenomena in question resemble those pointed out by Sir DAVID BREWSTER in the case of nitric peroxide.

Potassic chlorate, potassic ferrocyanide, baric nitrate, and plumbic nitrate gave similar results.

Ammonium-nitrate solution gave apparently some signs of supersaturation; but the observation is liable to error from the fact that at high temperatures ammonia is given off. According to KARSTEN, 100 parts of water at 64°·5 F. dissolve 199·54 parts of the salt. A hot solution (2 salt to 1 water) was filtered into a clean flask moistened with a few drops of *liq. ammon.* Such a solution remained during an hour or so at 40°, when it suddenly crystallized. I may, however, remark that a number of authorities differ in their determination of the solubility of this salt. But if the observation be correct, the behaviour of this anhydrous salt resembles that of some salts that crystallize with only a small proportion of water of crystallization. Baric chloride ($BaCl+2Aq$) is a case in point. According to BRANDE'S Table, 100 parts water at 99°·5 F. dissolve 51 parts of the salt. This is equal to 244 grains of salt to one ounce of water. A solution of this kind cooled from the boiling-point to 100° without depositing salt, and it was not until the temperature had fallen to about 66° that the salt separated, and then it did so abundantly.

VI. *Summary.*

My experiments lead me to the conclusions, first, that the state of supersaturation in saline solutions is a real and not an apparent one, and is due in the majority of cases, where the solutions are kept in chemically clean flasks, to the absence of nuclei or other predisposing cause to crystallization; 2nd, that in the few cases where salts of a lower degree of hydration are formed in such solutions, the effect is not due to a predisposing molecular change in the solution, but to the deposit of a portion of the anhydrous salt, or of a monohydrated salt, which, entering again into solution, forms a dense lower substratum from which the modified salt crystallizes out; 3rd, that anhydrous salts do not form supersaturated solutions.

The salts examined in this memoir may be arranged into five groups according to their behaviour:—

I. Salts of which the supersaturated solutions remain liquid at low temperatures.

Examples:—Sodic acetate.
Sodic sulphate.
Sodic arseniate.
Sodic succinate.
Sodic borate.
Sodio-potassic tartrate.
Potash alum.
Magnesic sulphate.
Baric acetate.
Calcic chloride.
Cupric sulphate.

II. Salts of which the supersaturated solutions suddenly solidify at low temperatures.

Examples:—Sodic carbonate.
Sodic phosphate.
Plumbic acetate.
Sodic hyposulphite.
Strontic chloride.

III. Salts of which the supersaturated solutions deposit their excess of salt at low temperatures, or under the action of a nucleus, leaving the mother-liquor saturated.

Examples:—Zincic acetate.
Cupric sulphate.
Baric chloride.
Potassic arseniate.
Antimonio-potassic tartrate.
Citric acid.

IV. Salts of which the supersaturated solutions form modified salts of a lower degree of hydration.

Examples:—Sodic sulphate.
Zincic sulphate.
Magnesic sulphate.
Ammonium phosphate.

It will be seen that the sodic sulphate and the magnesic sulphate also occupy a place in Class I.

V. Anhydrous salts that do not form supersaturated solutions:—

Potassic nitrate.
Potassic bichromate.
Sal-ammoniac.
Sodic nitrate.
Potassic chlorate.
Potassic ferrocyanide.
Baric nitrate.
Plumbic nitrate.
Ammonium nitrate.