

Thus we see that the same periods of certain disturbances are manifested very differently in two stations so near each other as Kew and Lisbon. The modification is the greatest, particularly in the periods which depart from the general rule at Lisbon, and are doubtless also abnormal at Kew.

From the examples here quoted, it is evident that a great value would be attached to the curves from another intermediate station; for the little vertical-force *peaks* and *hollows*, being opposed at Lisbon and Kew, it would be very interesting to see if these peaks would be wholly or nearly absent at some intermediate station.

With a certain number of these magnetographs very discreetly placed, we may one day analyze the different forces acting on the needle in the different places on the earth—a manifest desirability.

II. "On Supersaturated Saline Solutions." By CHARLES TOMLINSON, F.R.S. Received April 21, 1868.

(Abstract.)

This memoir is divided into six parts. The *first* part contains a definition of the subject; the *second* an historical sketch; the *third* is on the action of *nuclei* in inducing crystallization, and the effect of low temperatures on a number of supersaturated solutions contained in chemically clean vessels; the *fourth* is on the formation of a modified salt, as in the case of zinc-sulphate and sodic sulphate; the *fifth* contains an inquiry as to whether anhydrous salts form supersaturated solutions; and the *sixth* and last part is a summary with a classified list of the salts examined.

1. *Definition*.—When water at a high temperature is saturated with a salt, and, on being left to cool in a closed vessel, retains in solution a larger quantity of the salt than it could take up at the reduced temperature, the solution is said to be supersaturated.

2. *History*.—During many years the phenomena of supersaturation were studied 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 the solutions do not require to 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, but that such solids act best as nuclei when dry; if wet or boiled up with the solution they become *inactive*. The most efficient 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* and the ordinary 10-atom *hydrate*, and also a peculiar salt formed when supersaturated solutions in closed vessels are left to cool down. This

* Schweigger, 'Journal,' 1815, vol. xv.

x salt, as it is termed, 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 the mother-liquor touched with a nucleus, the mother-liquor instantly solidifies into the 10-atom hydrate, and the x crystals become opaque, like the boiled white of an 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 exhibit the phenomena of supersaturation. In 1832 the number of such salts was shown by Dr. Ogden† to be not less than twenty-one.

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 by M. Löwel between the years 1850 and 1857, the results of which are contained in six memoirs¶. According to this writer, the ordinary 10-atom sodic sulphate increases in solubility from 32° to 93°·2 F., at which latter temperature it begins to fuse in its water of crystallization, and to deposit the anhydrous salt. This salt follows an inverse order of solubility as compared with the 10-atom hydrate, its solubility diminishing as the temperature rises; or, what is the same thing, from 218°, the boiling-point of a saturated solution, down to 64° the solubility increases; but at 64° the solution undergoes a new molecular modification, and begins to form crystals of the 7-atom hydrate (the x salt of Ziz). This salt is much more soluble at ordinary temperatures than the 10-atom hydrate, its maximum solubility being at 80°·6. Thus the sodic sulphate has three maxima of solubility; viz. 93°·2 when it is under the molecular constitution of the 10-atom hydrate, 78°·8 to 80°·6 when it is under the molecular constitution of the 7-atom hydrate, and 62°·6 to 64°·4 when it is under the molecular constitution of the anhydrous salt. At these three maxima 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 ordinary temperatures than the normal 10-atom salt. Löwel extends his inquiry to sodic carbonate and magnesia sulphate, and endeavours to show that in their supersaturated solutions salts of a lower degree of hydration and of greater solubility than the normal salts are formed; and his general conclusion is

* Annales de Chimie et de Physique, 2nd ser. vol. xi.

† Edinb. New Phil. Journ.

‡ Quarterly Journal of Science, vol. xix.

§ Trans. Roy. Soc. Edinb.

|| Elements of Chemistry.

¶ Annales de Chimie et de Physique, 3rd ser. vols. xxix., xxxiii., xxxvii., xliii., xliv., xlix.

that all cases of supersaturation are 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 as *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 normal 10-atom salt."

Later inquirers have endeavoured to explain the nature of the force exerted by nuclei in inducing crystallization under certain conditions, and their passivity under others. Gernez* tried no less than 220 solids, and of these he selected 39 that were active in inducing crystallization: 18 were insoluble; these were carefully washed in distilled water, and dried out of contact with air. When dry they were found to be without action on the solutions they had previously caused to crystallize. The 21 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 M. Gernez believes 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. But, as M. Jeannel† has pointed out, if this theory be true, we must have floating in the air specimens of all kinds of salts that form supersaturated solutions, and crystallize by the introduction of a solid nucleus; whereas there are some such salts which cannot exist in the presence of the oxygen or of the ammonia of the air. M. Jeannel shows that a few drops of an ordinary solution of a salt will induce crystallization in a supersaturated solution of the same salt without contact of air.

3. *On the Action of Nuclei*.—With respect to the action of nuclei on saline supersaturated solutions generally, the author refers to a theory of his‡ which seems to account for the liberation of gases from their supersaturated solutions (soda-water, seltzer-water, champagne, &c) when a solid nucleus that had been exposed to the air is immersed in them; while such nucleus becomes inactive if kept long in water, or passed through flame &c., and dried or cooled out of contact with air. The action of nuclei is referred to adhesion. Nuclei are active in inducing crystallization,

* Comptes Rendus, vol. lx. p. 833. A similar method was adopted by Schiff, Ann. der Chem. und Pharm. vol. cxi. p. 68.

† Ann. de Chim. et de Phys. 4th ser. vol. vi. p. 166; and Comptes Rendus, Jan. 2, 1866.

‡ Phil. Mag. July and August 1867.

or they are inactive, according to the state of chemical purity of their surfaces. In the case of a supersaturated saline solution, the sides of the vessel may act as nuclei, or any solid, and some liquid, bodies brought into contact with it. Now suppose the inner surface of the vessel to be made chemically clean, either by well washing it with strong sulphuric acid, or caustic alkali, or spirits of wine, or, as often happens, by boiling the saline solution in the vessel in which it is intended to be kept. In such cases there is perfect adhesion between the sides and the solution, and no salt will be liberated; the sides may in fact be regarded as merely a continuation of the liquid itself, and no salt can be formed there any more than in the central parts of the liquid. But suppose the sides to be not chemically clean, to be more or less dirty in fact; in such cases adhesion is diminished or destroyed, and the surface of the liquid next to such sides is virtually as free as its upper surface. Salt will be deposited there, other circumstances being favourable, really from want of adhesion between the side and the liquid that holds the salt in solution. Now apply this to the case of a so-called "adynamic," "non-catalytic," or "inactive" glass rod, or coin, or fragment of glass or of flint, &c. A glass rod placed in the solution does nothing more than form new sides, as it were, to the vessel, and its effect is merely that of the sides. If chemically clean, the rod will form no crystals about it, and hence it is "inactive" because its adhesion is perfect. If dirty, the surface of the solution in contact with it will be as free, or almost so, as the upper surface. It requires special means to produce a chemically clean surface; and when produced, it is not easy to maintain it. A short exposure to the air, or a mere touch, will suffice to cover it with an organic film, or with motes or dust that prevent or lessen adhesion between it and the aqueous part of the solution, and apparently render an inactive solid active. When a glass rod &c. has been kept in water or passed through flame and dried, or cooled out of contact with the air, it is more or less chemically clean, and remains so while being sheltered. When Ziz found a knitting-needle active on one solution, and by passing it through the cork which confined a similar solution it became inactive, he simply made the wire chemically clean by the friction. Air is not a nucleus, and when it appears to act as such, it is simply as a carrier of some solid particle not chemically clean. Hence narrow-necked flasks when opened retain their solutions liquid longer than wide-necked ones, as the former are less likely to catch motes &c. from the air than the latter. Supersaturated solutions are best preserved by plugging the necks of the flasks &c. with cotton-wool, since in cooling down the air is filtered in passing through the plug, and motes and dust are thus kept back.

Tubes made chemically clean by the action of strong sulphuric acid may be filled with a strong solution of sodic sulphate, and when cold the tubes may be placed in a freezing-mixture at 10° F. without any separation of the salt. Hence the author differs from M. Löwel's theory, which supposes a molecular change to take place when strong solutions of the salt are

cooled down below 60° . Supersaturated solutions of various salts were cooled down to various temperatures from 32° to 0° F. without crystallizing. Sodid acetate, for example, was kept for some hours at 14° , when on touching it with a wire it became solid, and the temperature rose to 104° . Sodid arseniate, sodid succinate, sodid borate, sodio-potassic tartrate, potash alum, and other saline solutions were treated in this way. Some of these solutions become viscid at a low temperature, and do not immediately crystallize on removing the cotton-wool plug. If they be touched, or the side of the flask scratched with a chemically clean wire, there is no action; but if the wire be not chemically clean, the scratches immediately become chalky white by being covered with minute crystals of the salt, and the action then spreads until the solution becomes solid.

Some salts that are not very soluble in water, such as the plumbic acetate, form highly charged supersaturated solutions, and retain their liquid state below ordinary atmospheric temperatures. When at a certain point they suddenly solidify. Other solutions merely deposit the excess of salt above the condition of supersaturation, leaving the mother-liquor saturated; the cupric sulphate is an example of this.

The memoir contains a number of details respecting the action of nuclei, whether derived from the air, from the flask, from the salt itself, from the filter, or the cotton-wool used in closing the vessels. If the solution touch the wool, crystallization immediately sets in; or if the upper part of a chemically clean tube be touched with a finger slightly greasy before filtering into it the hot solution, the latter will cool down to the temperature of the air without crystallizing, nor will there be any effect if the tube be inclined so as to touch the clean portions of the inner surface; but the moment the solution comes upon the edge of the finger-mark, crystallization sets in, and the solution becomes solid. Solutions not filtered that begin to crystallize at above 100° in open vessels, or even in closed flasks, may by filtration be freed from nuclei, and so cooled down in the latter to low temperatures without any separation of the salt.

4. *On the formation of a modified salt.*—The readiness with which sodid sulphate parts with its water of crystallization, and two or three other considerations, make it more than probable that a solution of sodid sulphate at high temperatures is really a solution of the anhydrous salt. But M. Löwel supposes that a supersaturated solution in cooling down below 60° assumes a new molecular constitution, viz. that of the more soluble 7-atom hydrate which it then holds in solution. The author gives an experiment to show that such cannot be the case, but that the solution continues to hold the anhydrous salt until a portion of it actually separates. If a boiling solution of two parts salt to one part water be filtered into vessels made chemically clean by being washed out with spirits of wine instead of sulphuric acid, and if these vessels, when cold, be placed in water at 32° , or from that to 40° , a few octohedral crystals of the anhydrous salt will be thrown down. The temperature will slightly rise; and if the tube be now

set aside in a moderately warm air, the anhydrous salt will enter into solution, forming a dense lower substratum, from which the 7-atom hydrate will be produced in small quantity, there not being sufficient water present to form the ordinary 10-atom salt. The rest of the solution is still supersaturated, and if the plug be removed from the vessel, crystallization will set in from the surface and proceed rapidly downwards, carrying down enough water to convert the whole solution, as well as the 7-atom, into the 10-atom hydrate.

This process may be conveniently watched in the case of the zinc sulphate. When a saturated solution of this salt cools down from the boiling-point to about 70° , the monohydrated salt is thrown down in quantity, and, as the solution cools, a portion of this dissolves and a crop of acicular crystals is produced which readily melt down at about 100° . On removing the cotton-wool from the tube, crystallization sets in from the surface, and the ordinary 6-atom hydrate is produced.

The author examines M. Löwel's experiments on solutions of the sodic carbonate in which two modified hydrates are pointed out, viz. the $7\text{H O } a$ and the $7\text{H O } b$, which differ in solubility from each other and from the 10-atom salt; but as M. Löwel attaches great importance to the peculiar catalytic properties of the sides of his vessels in determining the formation of these salts, the author cannot help thinking that M. Löwel's results were due to portions of the sides of his vessel, not chemically clean, acting as nuclei. In chemically clean vessels M. Löwel's results have not been reproduced; for on reducing the temperature to a certain point depending on the strength of the solution, the whole became suddenly solid, with a rise in temperature of 35° or 40° . M. Löwel also points out two modifications produced from supersaturated solutions of the magnesia sulphate. The author has placed boiling saturated solutions, when cold, in freezing-mixtures at 10° without producing any separation of the salt.

The ammonia phosphate throws down from its supersaturated solution an anhydrous powder, which, again entering into solution, forms a dense lower stratum in which a modified transparent crystallized salt is formed in small quantity.

The strontic nitrate also deposits an anhydrous salt in cooling down to about 62° ; but as this salt is not soluble in the solution, the modified salt is not formed.

Some solutions on being cooled down in freezing-mixtures suddenly become solid; others freeze and sometimes thaw again without any separation of the salt, as in the case of the cupric sulphate; but if a boiling saturated solution of this salt be prepared with strict attention to chemical purity, it may be cooled down to near 0° F. without any separation of the salt.

5. *Anhydrous Salts*.—The method adopted to ascertain whether an anhydrous salt forms a supersaturated solution was to make a solution of known strength, as indicated by some good Table of solubilities, raise it to

the boiling-point, and then note whether salt began to be thrown down when the solution cooled down to the temperature indicated by the Table. For example, according to Poggiale's Table, 100 parts of water at 158° will dissolve 129·6 of sodic nitrate. This is the same thing as 622·22 grains of the salt in 1 ounce water. Such a solution on cooling down from the boiling-point began to deposit salt at 160°.

In like manner, according to Gay-Lussac's Table, 100 parts of water at 150° F. contain 125 of potassic nitrate. A solution of 125 parts salt to 100 of water began to deposit salt at about 149°. The deposit first began to be made on the side nearest the window, or the coldest side, when the flask was suspended in air; but if the flask were placed on metal, or any other good conductor, a ring of salt was first formed at the bottom, some 6° or 8° earlier than if the flask stood on a block of wood.

It has been frequently stated that the potassic bichromate forms a supersaturated solution. According to Kremer, 200 of water at 140° F. dissolve 100 parts of the salt. Such a solution, on cooling from the boiling-point began to throw down crystalline flakes at 138°. The remarkable deepening in colour of this solution under the influence of heat is pointed out.

Sal-ammoniac, potassic chlorate, and some other salts were also examined, the conclusion being that anhydrous salts do not form supersaturated solutions.

6. *Conclusion and Summary.*—The author refers to the prevailing theory that supersaturation exists in appearance only and not in fact, since it is supposed to be the modified and more soluble salt that is in solution. If this were true, it ought to apply to all cases of supersaturation, and it has only been claimed in the case of a very few salts, and in them much importance has been attached to the active or the inactive condition of the sides of the vessels containing the solutions.

The author, while admitting, in the case of a very few solutions, that a modified salt may be deposited, denies that it is due to any molecular change that takes place in the solution, either from reduction of temperature or any catalytic property of the sides of the vessel. His theory is that when these modified salts are formed, it is the anhydrous salt that is held in solution, a portion of which is thrown down as the temperature falls; and this anhydrous deposit, entering again into solution, forms a dense substratum containing less water than the upper portions, so that when the modified salt forms in it, it is out of the reach of sufficient water to form the normal salt. When, on the contrary, under the influence of a nucleus, crystallization sets in from the surface, the normal salt is formed, and the crystals carry down sufficient water to convert the whole into the ordinary hydrated salt.

As to the action of nuclei or the sides of the vessel, when chemically clean the solution adheres to them as a whole, and there is no separation of the salt; when not chemically clean there is a stronger adhesion between the salt and the nucleus than between the salt and the solvent, and there

is a separation of salt; and the action of separation once begun, may be rapidly propagated throughout the whole solution. Boiling saturated solutions may be cooled down in chemically clean vessels and kept for any length of time, not because they undergo any molecular change or hold a salt of greater solubility than the normal salt in solution, but they retain their fluid form simply from the absence of a nucleus.

The salts examined in this memoir are arranged into five groups according to their behaviour.

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

Examples:—Sodic sulphate.

Sodic acetate.

Sodic arseniate.

Sodic succinate.

Sodic borate.

Sodio-potassic tartrate.

Potash alum.

Magnesia 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:—Zinco-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:—Zinco-sulphate.

Sodic sulphate.

Magnesia sulphate.

Ammonia phosphate.

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

V. Anhydrous salts examined in this memoir that do not form supersaturated solutions :—

Potassic nitrate.
 Potassic bichromate.
 Sal-ammoniac.
 Sodie nitrate.
 Potassic chloride.
 Potassic ferrocyanide.
 Baric nitrate.
 Plumbic nitrate.
 Ammonium nitrate.

III. “ On the Impact of Compressible Bodies, considered with reference to the Theory of Pressure.” By R. MOON, M.A., Honorary Fellow of Queen’s College, Cambridge. Communicated by Prof. J. J. SYLVESTER. Received April 22, 1868.

(Abstract.)

Suppose that we have two *rigid* cylinders of equal dimensions, which have their axes in the same straight line; suppose, also, that one of the cylinders is at rest while the other moves towards the first with the velocity V in a direction parallel to both the axes; the consequence of the collision which under such circumstances must take place, will manifestly be that half the momentum of the moving cylinder will be withdrawn from it, and will be transferred to the cylinder which originally was at rest.

The mode in which velocity or momentum will thus be collected from the different parts of the one cylinder, and distributed amongst those of the other, is obvious. Exactly the same amount will be withdrawn from the velocity of each particle of the impinging cylinder, and exactly the same amount of velocity will be impressed on each particle of the cylinder struck.

And the reason of this is equally obvious; since, if such were not the case, the particles of each cylinder would *contract*—a supposition which is forbidden by the very definition of rigidity.

But if, instead of being perfectly rigid, each cylinder is in the slightest degree compressible, a variation in the effect will occur.

As before, momentum of finite amount will be transferred from the one cylinder to the other, but the mode of collection of the velocity withdrawn from the one, and the mode of distribution of that injected into the other, will no longer be the same as before.