III. *On Supersaturated Saline Solutions.*—Part II. *By* Charles Tomlinson, *F.R.S.*

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I have already in former papers considered the conditions under which gas[1] or steam[2] or salt[3] is separated from its supersaturated solution, and have endeavoured to show that a body is *active* or *inactive* as a nucleus, according as it is chemically *unclean* or *clean*. An objection to these terms has been started, on the ground that a stick of tallow, for example, may be as chemically clean as a catharized glass rod. In the first Section of this paper an attempt is made to define with rigour the terms *clean* and *unclean*, and to settle the conditions on which nuclei really act. In the second place, an attempt is made to confirm the conclusion arrived at in Part I., that supersaturation depends mainly on the absence of a nucleus, by a number of examples in which highly supersaturated saline solutions, when reduced to temperatures at and below the zero of Fahrenheit's scale, rather solidify than crystallize, and in melting reassume the condition of clear, bright, supersaturated solutions.

Section I.—*On the Functions of Nuclei.*

I have already endeavoured to show that the obscure and often contradictory behaviour of solids as nuclei in separating gas or vapour or salt from their supersaturated solutions, becomes clear by considering whether the solids used as nuclei were or were not *chemically clean* as to surface at the moment of contact with the solution into which they were placed.

A *nucleus* was defined as a body that has a stronger attraction for the gas or the vapour or the salt of a solution than for the liquid that holds it in solution.

A body is *chemically clean* the surface of which is entirely free from any substance foreign to its own composition.

It is to be observed that I speak of *surface* only, and shall hereafter omit the expression of surface in referring to nuclei. I call, for instance, a glass rod chemically clean, although a particle of carbon or of oxide of iron or other matter be enclosed and shut up within it; but not so if that particle reach and form a portion of the surface itself. So, also, I call a stick of tallow, stearine, paraffine, &c. chemically clean, so long as its surface falls under the definition just given.

In like manner, liquid oils, both fixed and volatile, and other liquids are chemically clean, provided they are chemically pure, and contain no substance, mixed or dissolved,

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[1] Phil. Mag., August and September, 1867.

[2] Proceedings of the Royal Society, No. 108, 1869.

[3] Transactions of the Royal Society, 1868, p. 659.

that is foreign to their composition. But in considering such bodies, there is a distinction to be made with respect to their nuclear functions, whether they exist in the mass, such as a lens or globule, or in the form of thin films.

Catharization[4] is the act of clearing the surface of bodies from all alien matter; and the substance is said to be *catharized* when its surface is so cleared.

As every thing exposed to the air or to the touch takes more or less a deposit or film of foreign matter, substances may be conveniently classed as *catharized* or *uncatharized* according as they have been, or not, so freed from foreign matter.

And it is perhaps not taking too much licence with language to extend the term *catharized* (denoting, as it does, the condition of pure surface) to those substances whose surface has not required the process. Thus a flint stone in the rough has an uncatharized surface; but split it and the inner surface of the pieces will, for a time, be clean. There can be no impropriety in speaking of the new surfaces as in a catharized or chemically clean state.

Referring to the definition of a nucleus, substances may be divided into *nuclear* and *non-nuclear*.

The nuclear are those that may, *per se*, become nuclei; the non-nuclear are those that have not that quality.

The nuclear substances would seem to be comparatively few, the larger number of natural substances ranking under the other division.

Under nuclear substances are included those vapours and oily or other liquids that form thin films on the surfaces of liquids and solids; and generally all substances in the form of film, and only in that form. Thus a stick of tallow, chemically clean, will not act, but a film of it will act powerfully; and, again, a globule of castor-oil will not act if chemically clean, but in the form of a film, whether chemically clean or not, it will act powerfully.

If a drop of a liquid be placed on the surface of another liquid, it may mingle with it; or it will either spread out into a film or remain in a lenticular shape, according to the general proposition that if a drop of a liquid B, whose surface-tension is b, be placed on the surface of another liquid A, whose surface-tension is a, the drop will spread into a film, if $a > b + c$ (c being the tension of the common surface of the liquids A and B); but if, on the contrary, $a = < b + c$, the drop will remain in the form of a lens. Hence if B spread on A, A will not spread on the surface of B. c has no value whenever the liquids A and B mingle in all proportions, as in the case of water and alcohol.

In the case of supersaturated saline solutions, the spreading of the drop may in some cases be slow, on account of the *superficial viscosity*, or the greater or less difficulty of the superficial molecules to be displaced.

A glass rod drawn through the hand becomes covered with a thin film, or the same rod by exposure to the air contracts a film by the condensation of floating vapour, dust, &c., and in either case is brought into the nuclear condition.

[4] From *καθαρίζω*, to purge, purify, or clean—from *καθαρὸς*, pure, clean.

A second class of nuclear bodies are permanently *porous* substances, such as charcoal, coke, pumice, meerschaum, &c. The action of these is chiefly confined to vaporous solutions, and, if catharized, they have no power of separating salts from their supersaturated solutions.

Under the non-nuclear, forming by far the larger class of substances, are glass, the metals, &c., while their surfaces are chemically clean; and by chemically clean is meant, as already noted, wholly free from any substance foreign to their own composition.

Among the non-nuclear will be found air; for its ascribed nuclear character is due, not to itself, but to the nuclear particles of which it is the vehicle. Thus, as stated in former papers, if air be filtered through cotton-wool, it loses its apparent nuclear action; so also if heated.

I have already published numerous examples from the recorded experiments of OERSTED, SCHÖNBEIN, LIEBIG, LÖWEL, and others; and I have also shown by new experiments[5] that Class II., namely the non-nuclear, are really so, and have only been thought otherwise for want of adverting to the condition to which I first called attention, namely their being in a catharized state or not. To run through all the substances of which this may be predicated were impossible. To treat of a few will answer the purpose if we show that those which have been thought to have the quality of nucleus do not possess it, but only seem to do so, by having their surfaces soiled with foreign matter or films that really do possess the power. The only answer that such a view admits of as to those substances is manifestly to show that they had been catharized previously to experiment, and yet were found to be active as nuclei.

My former papers contain sufficient details as to the general action of nuclei in separating gases, vapours, and salts from their supersaturated solutions. When the nucleus is catharized or clean, it has no such separating action, because the solution adheres to it as a whole, that is, there is the same adhesion between the gas or vapour or salt and the nucleus as between the liquid part of the solution and the nucleus; but when the nucleus is non-catharized or unclean, the gas or vapour or salt adheres to the surface more strongly than the liquid part of the solution, and hence there is a separation of gas or vapour or salt from solution. My present purpose is to show that an active nucleus, or unclean or uncatharized surface, is contaminated with a film of foreign matter, which filmy condition is necessary to that close adhesion which brings about the nuclear action; for it can be shown that a liquid, such as an oil, is non-nuclear in its action when in the form of a lens or globule, but powerfully nuclear when in the form of a film.

There are certain liquids which form films, and act as nuclei by separating water instead of salt from supersaturated solutions. Absolute alcohol acts in this way. Other liquids, such as glycerine, diffuse through the solution without acting as nuclei. Saline solutions may also saponify fatty oils, or otherwise act chemically upon them,

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[5] Journal of the Chemical Society for April 1869. Chemical News, 1868, 1869, 1870. See also notes (1), (2), (3).

without any separation of salt due to nuclear action. Cases of this sort will be illustrated experimentally.

In preparing the flasks and other apparatus for the exhibition of the properties referred to, attention must be paid to cleansing, by means of caustic alkali, sulphuric acid, or spirits of wine, as insisted on in former papers; but in the experiments on the action of nuclei the flasks are not to be plugged with cotton-wool, but merely covered loosely with watch-glasses. Solutions may thus be kept supersaturated in a quiet room during weeks, and even months. Cotton-wool answers admirably where the flasks have to be kept, as it were, in store, and then opened only once for the purpose of determining crystallization; ·but when the flask is to be opened with a view to the insertion of a nucleus, cotton-wool is objectionable for several reasons, such as the liability to detach a few fragments in taking out the plug; and this is certain to happen if in filtering the solution a little of it get into the neck and become entangled and crystallized with the fibres; moreover, in taking out the cotton-wool, an equivalent volume of air enters the flask, and this is almost certain to deposit a nucleus on the solution. In the following experiments a solution of one, two, or three parts of GLAUBER'S salt to one of water was made in a large flask, and filtered while boiling into a number of three-ounce flasks made clean. Each flask received about two ounces of the solution, and was covered with a watch-glass, and left to cool during some hours, or until the next day.

Experiment 1. Four ounces of GLAUBER'S salt in four ounces of water was boiled and filtered into four flasks, covered with watch-glasses and left till cold. A clean glass rod was dipped into a bottle of clear pale seal-oil, and the watch-glass being gently removed from off one flask, a drop of the oil was carefully delivered to the surface of the solution; the glass rod was withdrawn, and the watch-glass restored to its place. The drop of oil expanded into a well-shaped film, with a display of iridescent rings; and immediately from the lower surface of the film there fell large well-shaped flat prisms with dihedral summits of the ten-atom sodic sulphate, being the normal salt. The prisms were an inch or an inch and a half in length, and three eighths of an inch across. The crystallization proceeded from every part of the lower surface of the film, and as one set of crystals fell off another set was formed, until the whole solution became a mass of fine crystals in a small quantity of liquid. This effect is entirely different from the usual crytallization which takes place when a supersaturated solution of GLAUBER'S salt is subjected to the action of a nucleus at one or two points in its surface, as when motes of dust enter from the air, or the surface is touched with a nuclear body. In such cases small crystalline needles diverge from the point touched, and proceed rapidly in well-packed lines to the bottom, the whole being too crowded and too rapid to allow of the formation of regular crystals. But in the case before us, where the whole surface of the solution, and the surface only, is subjected to nuclear action by the spreading of the oil-film, the action is not so rapid as in the former case, because it is not downwards but parallel with the surface; the crystals mould themselves, as it were, upon the oil-film, and falling off, allow fresh portions of the solution to come into contact with the film, until at length a very fine crop of crystals is produced. This experiment was repeated on the solutions in the other three flasks with the same result.

Similar experiments were tried on solutions of GLAUBER'S salt of different strengths, with drops of ether, absolute alcohol, naphtha, benzole, oil of cajeput, oil of turpentine, and other volatile oils, herring-oil, sperm-oil, olive-oil, castor-oil, and some other fixed oils of animal and vegetable origin, with this general result, that, whenever the oil spread out into a film, it acted as a powerful nucleus.

Experiment 2. A solution of two parts of GLAUBER'S salt to one part of water[6] was boiled and filtered into three flasks, which were covered with watch-glasses and left until the next day. A drop of castor-oil was then placed upon the surface of each: it formed a lens which gradually flattened; but there was no separation of salt, even when the flasks were shaken so as to break up the oil into small globules.

The necks of some clean flasks were oiled inside with castor-oil, and the boiling solution of GLAUBER'S salt filtered into them: the oil formed into globules, and some of it ran into the solution. Next day there was no separation of salt. The flask was turned round quickly so as to form a whirlpool, in which the globules of oil descended to the bottom and were broken up and diffused so as to form a kind of emulsion; but by repose the solution became clear again, the oil collected into larger globules, and there was no separation of salt.

If, while the flask is being turned round, a sudden jerk be given to it, so as to flatten some of the globules against the side into films, the whole solution instantly becomes solid; or if by strong pressure with the finger against the interior of the neck a smear of oil be made, the solution crystallizes as soon as it is brought into contact with such smear. But if it be objected that the finger may introduce nuclear matter, then a catharized wire, which dipped into the solution is inactive, will, if rubbed against the side so as to flatten some of the small oil-globules, leave a number of minute crystals of a chalky white colour filling up the lines traced by the wire, and these serve as nuclei to the rest of the solution.

Experiment 3. Stearine from sheep-tallow produced immediate crystallization in supersaturated solutions of GLAUBER'S salt. The solutions were gently heated and gradually raised to boiling. In cooling, the stearine, now catharized, collected into disks; but it was no longer nuclear, even when the vessel was shaken. When the flask was uncovered, a nucleus from the air produced immediate crystallization.

Of course, unless the oils be chemically clean, according to the definition, they induce crystallization, whether they form a lens or a film on the surface of the solution. Thus a specimen of sperm-oil placed on the centre of the surface of a supersaturated

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[6] This solution, it will be seen, contained twice as much salt as the solution used in Experiment 1, and hence was much more sensitive to the action of nuclei. This sensitiveness also increases as the temperature falls; and at low temperatures the crystals are more rapidly formed, more crowded and hence less distinct, than when formed from weaker solutions and in summer weather, as in Experiment 1.

solution of GLAUBER'S salt produced a well-shaped lens, from the under convex surface of which crystals of the salt radiated rapidly downwards. The flask was heated and gradually raised to near the boiling-point, and in cooling the oil formed a number of lenticular disks on the surface; but they produced no separation of the salt, even when the flask was shaken.

Also in the case of volatile oils containing products of oxidation, dust, &c., they may form lenses on the surface of the solutions and yet act powerfully as nuclei. If such oils be redistilled they still form lenses on the surface, but are no longer nuclear.

Experiment 4. A dark-coloured oil of bitter almonds formed a lens on the surface of a solution of GLAUBER'S salt, and the lens immediately became bristled with crystals. The crystallization was so vigorous that crystals projected above the surface, supporting the oil, as it were, on a platform. The oil was distilled into a limpid colourless liquid, of which about twenty drops were allowed to fall in succession on the surface of a supersaturated solution of GLAUBER'S salt. The drops coalesced into a beautiful, lustrous lens; but there was no longer any separation of salt. After half an hour or so the lens became surrounded with an opaque white disk or halo of benzoic acid. On shaking up the solution the oil was diffused in globules through it, and in the course of some days became converted into flakes of benzoic acid, which rotated vigorously on the surface of chemically clean water, after the manner of camphor. There was no separation of salt until the flakes were taken out with a non-catharized spatula, the contact of which with the solution caused it to solidify.

Newly distilled turpentine formed a lens on the surface of a supersaturated solution of GLAUBER'S salt, and remained so during some days. A drop of the old oil, from which the new oil had been distilled, was placed on the surface; it spread into a film, displacing the lens and producing immediate crystallization.

Experiment 5. Carbonic disulphide and also chloroform formed well-shaped lenses on the surface of the supersaturated solution of GLAUBER'S salt, and slowly evaporated without producing crystallization.

Glycerine and wood-naphtha mixed with the solution, rendering it dull, without separating the salt. Of course, on touching the solutions thus treated with a wire they immediately crystallized.

Experiment 6. A solution of 1½ part of potash-alum and one of water was boiled and filtered into a number of flasks. When cold the solutions showed great viscosity. A drop of a limpid pale seal-oil spread out into a film on the surface of the alum solution. Crystallization set in from every part, and the junction of the planes of crystallization gave the surface the appearance of a central point and six radii forming six angles, some of 30° and some of 60°.

Experiment 7. Oleine of tallow, the oleine of fish-oil, and oleic acid from palm-oil formed well-shaped lenses on the surface of the alum solution without any separation of salt.

Experiment 8. Benzole, naphtha, oleum anethi, turpentine, and some other liquids formed films, on the under surface of which octahedral crystals of alum were formed.

Experiments were also tried with supersaturated solutions of ammonia alum, of the magnesic sulphate, and the sodic acetate. Although these are not so well adapted as GLAUBER'S salt for the display of the phenomena in question, yet by carefully separating anomalous cases, as where a lens of old oil is not chemically clean, or where a mote from the air, in loosely covered vessels, produces crystallization, the result of a large number of experiments with a variety of liquids leads to the conclusion that liquids are nuclear in the form of films, and non-nuclear in the form of lenses, globules, or drops.

In the form of films, as when a drop placed on one of the solutions spreads out and covers the surface with a display of colour, the surface-tension of the solution is so far diminished as to allow the film to come into contact, when that differential kind of action takes place whereby, the salt of the solution adhering more strongly to the film than the water of the solution does, the action of separation and crystallization thus once begun is continued and propagated. A similar action takes place with solid bodies that have contracted filmy nuclei by being drawn through the hand or touched or merely exposed to the air; they are active, or nuclear, by virtue of the films of matter which more or less cover them.

On the other hand, when a drop of oil, or many drops, is placed on the surface of a supersaturated solution, and it assumes the lenticular form, or even flattens down into disks, which more or less cover the surface, such lenses or disks retain their surface-tension, and do not greatly interfere with the tension of the solution on which they rest. The adhesion is, indeed, very different from that of a film, as may be made manifest by pouring, say, thirty or forty drops of freshly distilled oil of turpentine on the chemically clean surface of water in a shallow glass vessel about 3½ inches in diameter. The oil will nearly cover the surface of the water without being in contact, so to speak, with it; for contact is prevented by the surface-tension at the boundary of the two liquids. If, now, upon the oil thus resting on the surface of the water some fragments of camphor be scraped, these will be immediately wetted by the turpentine and be covered with a solution of camphor in that oil. This solution of camphor will form a film with iridescent colours on the surface of the water; a fragment of camphor will sail about, and being bounded on each side by nearly symmetrical films of iridescent colour, it has the appearance of a tropical butterfly. As it moves over the surface of the water it displaces the turpentine, and cuts it up into numerous lenses, until the surface-tension of the water is so far reduced, that no force is left to give rotation to the camphor.

The lens of oil &c. is not then sufficiently in contact with the surface of the supersaturated solution to allow of that differential kind of action taking place whereby salt is separated. Even when, by shaking, the oil is broken up into globules, and these are submerged, the conditions of the case are not greatly altered, since a submerged globule and the solution moulded upon it are separated by surface-tension, which prevents actual contact. When, however, by a sudden jerk the globules are flattened against the wall of the flask and form films, the solution instantly becomes solid.

A body may also be said to act as a nucleus when the cohesion of its own particles is weaker than its affinity for one or other of the constituents of the solution. In a solid or in a liquid globule the cohesion of its own particles is greater than that affinity; but in a film (which has extension only, length and breadth, the thickness being small enough to be disregarded) cohesion acts but laterally and not in every direction, and therefore the substance, coming into actual contact with the solution, yields to the attraction of one or other of the constituents of the solution for which it has the greater affinity, that attraction acting at right angles to the plane of the cohesive action of the film, and consequently meeting little or no resistance. Separation of the constituents of the solution then sets in. For example, the affinity in the case of a film of alcohol is for the water of the solution, and in the case of an oil-film for its salt, &c.

But if the film have no preferential affinity for one or other of the constituents of the solution no separation results, as when glycerine diffuses through the solution[7].

This would suggest that *form* and affinity were the elements in nuclear action. If a film of glass, for example, could be reduced to a sufficient state of tenuity, would it act as a nucleus? But at any rate it may be supposed that *contact* and affinity are the sole elements.

It will be gathered from the foregoing details that the distinction between *unclean* and *clean* resolves itself into the condition of *filmy* and *globular* in the case of liquids; and when solids act as nuclei, they are more or less contaminated with *films* of matter foreign to their composition.

Although in general the surface-tension of those liquids that form lenses, instead of films, on the surface of the solutions may be less than that of the solutions, yet the viscosity of the solutions retards their spreading. But if a globule of oil, such as castor-oil, instead of being allowed to drop from the end of the glass rod upon the surface, be delivered to it so that it does not for an instant become an independent globule, it may spread on the surface and form the usual cohesion-figure; under such a condition it instantly acts as a nucleus, and the solution becomes solid.

But not only the viscosity of the oil, but a similar property on the part of supersaturated saline solutions interferes with those strict relations between the surface-tensions of liquids which several distinguished physicists are just now endeavouring to establish. The surface-viscosity greatly diminishes when the supersaturated saline solutions have been kept from twelve hours to a couple of days, and the more watery parts seem to come up to the surface, so much so that I had long supposed that horizontal sections of the solution contained in a wide tube 10 or 12 inches in length were unequally rich in salt; but on drawing off portions of the solution from various parts into tared cruci-

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[7] It has often been stated that a solution of GLAUBER's salt acts as a nucleus to a supersaturated solution of the same salt; but I have shown (Chemical News, February 4, 1870) that if the conditions of chemical purity be attended to, the solution merely diffuses through the supersaturated solution, without acting as a nucleus.

bles and evaporating to dryness, the same quantity of salt was found to exist at four different parts of a column, 11 inches high, of a supersaturated solution of GLAUBER'S salt.

The internal viscosity of such a solution will probably account for a case mentioned in the next section, where a highly supersaturated saline solution of GLAUBER'S salt was reduced to about 20° FAHR. without any deposit of the 7-atom salt.

SECTION II.—*On the Action of low Temperatures on Supersaturated Saline Solutions.*

I propose in this place to show that the solutions of certain salts which remain liquid and supersaturated at and about the freezing-point of water, by a further reduction in temperature to about the zero of FAHRENHEIT'S thermometer, become solid, but on being restored to the temperature of 32° recover their liquid state without any separation of salt.

Ferrous sulphate ($Fe\,SO_4$, 7Aq) was dissolved in hot water, 1·25 of the salt to 1 of water, and was cooled rapidly, first, by placing the tube containing the filtered solution in water at 50°, then in snow-water, and lastly in a mixture of salt and snow at 0°. Beautiful tetrahedral crystals formed at the surface of the solution, and were propagated downwards, until the contents of the tube became solid. In snow-water at 32° the solid mass shrank from the sides of the tube, formed into a smooth rounded mass, and gradually melted, leaving the solution clear and bright without any deposit. On removing the cotton-wool from the mouth of the tube, small but well-shaped rhomboidal crystals soon filled the solution.

The double salt formed by mixing in atomic proportions solutions of the *zincic* and *magnesic sulphates* retains all the water of crystallization of the constituent salts, namely, 14 equivalents, and hence is well adapted to display the phenomena of supersaturation; since, in general, the more highly hydrated a salt is, the more readily does it become supersaturated. One reason for this is that the water of crystallization adds to the volume of the menstruum and so assists solution. So much is this the case, that while the salt readily undergoes the watery fusion, the addition of a very small quantity of water is sufficient to cause the solution to remain entirely liquid in closed vessels, even under considerable reductions of temperature. On the other hand, if too much water be added to the salt in making the solution, saturation, and not supersaturation, is produced, so that on lowering the temperature the behaviour of the solution is quite different in the two cases. For example, 246·3 grains of the magnesic sulphate, 287 grains of the zincic sulphate, and one ounce of water, boiled and filtered into clean tubes, forms only a saturated solution at ordinary atmospheric temperatures. If such a solution be reduced to 0°, or from that to −5° or −8°, a portion of the solution solidifies. It first forms an opaque growing mass of snowy whiteness, adapting itself to the smooth curved surface of the tube, but within, directed towards the axis, covered with well-shaped tetrahedral crystals. If at this low temperature the tube be transferred to a mixture of snow and water, it will of course be thickly encrusted with ice, the mass of crystals within the tube will become deformed, and rising to the surface, quickly melt; but if before plunging the tube into snow and water it be held for a short time in air, say, at about 50°, the crystals break up, and throw down a quantity of anhydrous salt, which, occupying the bottom of the tube, begins to combine with water and to heat, so that, on putting the tube into snow-water, the middle portion becomes quickly encrusted with ice, as before, while the bottom of the tube for about $\frac{1}{4}$ to $\frac{3}{8}$ of an inch is protected from ice.

By detaining the tube long enough in the freezing-mixture the solution becomes entirely solid, and on transferring it to ice-cold water it rapidly melts into a very bright, highly refractive liquid, without any separation of salt; and the same liquid may be solidified and melted any number of times with the same results, provided the solution be protected from the action of nuclei. If the cotton-wool be taken out of the tube, even when the contents are solid, and be restored again to its place, there will be a separation of salt during the melting, in consequence of a nuclear particle being admitted from the air.

Such is the behaviour of the solution made with one ounce of water. Although not supersaturated at ordinary temperatures, and not sensitive to the action of nuclei, yet it soon reaches a temperature at which it becomes supersaturated, and then it is very sensitive to such action. For example, in the case in hand, when the solution is at 50° or thereabouts, it may be touched, or the tube below the solution rubbed with a wire or a glass rod, and show no disposition to crystallize; but at the temperature of 20° the same nuclei are powerfully active in inducing crystallization, crystals instantly attach themselves to the nucleus, or the part of the tube rubbed becomes at once chalky white, from which mark crystallization spreads[8].

Next, as to the behaviour of the solution made with half an ounce instead of an ounce of water. Such a solution, after being boiled and filtered, remains clear and bright, but retains its viscosity after twenty or thirty hours. Unlike the former solution, made with one ounce of water, this begins to crystallize at the temperature of the room, as soon as the cotton-wool is removed. The crystallization sets in from the surface in the form of minute needles spreading out like tufts of thistle-down and soon closing in the surface, so that the tube can be inverted, and the heat-currents generated in the viscous fluid consequent on change of state can be seen.

But if, instead of subjecting such a solution to the action of the aërial nuclei, it be

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[8] Supersaturated solutions of GLAUBER's salt &c. are much less sensitive to the action of nuclei in warm than in cold weather. This has led to a good deal of misapprehension as to the real functions of nuclei, and has caused some observers to produce lists of bodies which will or will not induce crystallization; whereas the same body, under the same conditions, only varying with the temperature of the solution, will induce crystallization at one time and not at another. This is strikingly shown in the case of calcic chloride ($CaCl$, 6 aq); the same nuclei which are inactive when the solution is at the temperature of the room act at once when the solution is reduced to from 24° to 34°. A strong solution of this salt in an open evaporating-dish, which under ordinary circumstances becomes weaker by absorbing moisture, will, if the dish be put into a freezing-mixture, give a splendid crop of well-formed crystals.

reduced in temperature to about 16° FAHR., there is a deposit of anhydrous salt, as in the case of GLAUBER'S salt and one or two others, and the subsequent behaviour is similar. Upon this deposit are built rhomboidal plates of a lower degree of hydration than the double salt of the solution. If, now, the cotton-wool be removed and crystallization sets in from the surface, the fully hydrated salt, on coming into contact with the modified salt, renders it opaque without altering its form. If before crystallization sets in the upper part of the solution[9] be poured off, and the crystals be taken out and dried between folds of filtering-paper, with a view to ascertain their state of hydration, they become hot from the fixation of an additional quantity of water, and pass at once into the condition of hydration of the normal salt.

All these phenomena closely resemble the behaviour of a supersaturated solution of GLAUBER'S salt on a proper reduction of temperature. The anhydrous salt passes into solution, a portion of it is thrown down when the solution cools sufficiently (and this varies with the solubility of the salt and the strength of the solution), and it partially enters into solution at the bottom of the vessel; the heat thus generated further assists the solution, until at length a dense solution is formed occupying the lowest stratum, and, in the case of sodic sulphate, containing only water enough to form the 7-watered instead of the usual 10-watered salt. The crystals of the modified salt thus formed occupy the bottom of the vessel, while the solution above is not its mother liquor, as is commonly supposed, but still remains a solution of the anhydrous salt, as may be proved by again lowering the temperature of the solution, when octahedral crystals of the anhydrous salt will again be thrown down. If at any time after the modified salt has been formed the solution be exposed to free air by taking out the cotton-wool plug, crystallization sets in from the surface, and proceeding downwards carries with it sufficient water to convert the 7-atom into the 10-atom salt; and in doing so it effects such a minute state of division as to change the transparent salt into an opaque white.

It is commonly stated that a supersaturated solution of GLAUBER'S salt forms the modified salt at temperatures between 60° and 40° F.; but if the solution be clean and contained in a clean vessel, a highly supersaturated solution, formed of two or three parts salt to one of water, may be reduced to 20° and under without throwing down any salt. Such a solution contained in an 8-oz. globular flask, the globe of which was quite full, was exposed all night to a temperature which fell to a minimum of about 20° F. In the morning the solution was perfectly clear and bright, and there was no deposit of the modified salt; but on shaking the flask it instantly became opaque, from the multitude of small octahedral crystals that filled the solution; these quickly subsided, and within a quarter of an hour a fine crop of the 7-atom crystals was erected upon them, while the solution above still remained that of the anhydrous salt.

The sulphate of zinc and magnesia is rich in water of crystallization, and hence its behaviour is different from that of a double salt containing only a small proportion of combined water, such as the double salt formed by dissolving the *zincic sulphate* in a

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[9] This, it should be observed, is not the mother liquor, but a solution of the anhydrous salt.

saturated solution of the *sodic sulphate*. As this double salt contains only four proportionals of water of crystallization, its supersaturated solutions are not very stable; but by mingling the salts in atomic proportions in a small quantity of water (such as 287 grains of zinc sulphate, 322 of the sodic sulphate, and half an ounce of water) so as to ensure supersaturation, raising the temperature to about 100° F. until the solution becomes clear, then boiling and filtering into clean tubes and plugging with cotton-wool, such a solution may be kept and even reduced to 10° F. without any separation of the salt, although on removing the plug for an instant crystallization sets in from the surface in tufts.

But by repose, even in clean tubes and in the absence of nuclei, long crystals of the separated salts occupy the length of the tube; but they are invisible on account of having the same refractive index as that of the solution in which they are immersed. By inverting the tube so as to drain off the liquor, the crystals become visible, air enters the interstices, and on restoring the tube to its original position the bubbles of air have a very solid appearance, and may be taken for amorphous masses of crystals. These air-bubbles may be driven away by gently heating the tube. By further repose of some weeks a portion of the water of the solution evaporates through the cotton-wool, and as the solution becomes more dense, the crystals become more and more visible. These crystals are easily fusible at about 90°.

It may happen that the anhydrous powder thrown down by the zincic sulphate during the cooling is not taken up again. If in this state the tube be suddenly heated, the sodic sulphate will throw down an anhydrous salt, and on attempting to boil the salt there will be much kicking of the tube. But as the temperature rises this kicking ceases, and the mixed anhydrous powders pass rapidly into solution, the one apparently assisting the solubility of the other; for in the case of strong sodic-sulphate solutions alone, when once the anhydrous powder is deposited by heat, the continued application of heat increases the quantity of the deposit and aggravates the *soubresauts*.

If a saturated solution of the double salt be reduced to a low temperature, such as that of 0° F., the anhydrous powder of GLAUBER'S salt is thrown down; but in very clean tubes the solution passes into a transparent jelly-like mass that has the appearance of a liquid. A platinum spatula plunged into it while the tube is inverted does not produce any flow of liquid. By repose the pulpy mass becomes crystalline, the mother liquor separates, and the crystals become invisible in it. If the tube be put into warm water at 75° or 80°, the crystals liquefy in a few minutes, but they form again in a freezing-mixture at 14° or 16° F.

The double salt fuses at about 140° into an opaque mass; if raised to about 180° there is much kicking of the vessel, the anhydrous powder separates, and the clear liquor collects above. The powder consists chiefly of anhydrous sodic sulphate. If a little water be added the solution may be boiled, but only a portion of the powder is taken up. By reduction of temperature, this powder, influenced by the solidification of the zinc salt, forms cauliflower masses which creep a little way up the tube. On opening the tube crystallization sets in from above and proceeds downwards, and the cauliflower masses become chalky white. Thus the presence of the two salts in solution affords a number of new phenomena which vary with the strength of the solution and the amount of reduction in temperature, and also the old phenomena belonging to GLAUBER'S salt modified by the presence of the zinc salt.

The *ammonia* and *zinc sulphates* mixed in atomic proportions, boiled with an ounce or two of water, and filtered into an evaporating-dish, form a definite compound with six equivalents of water. It forms supersaturated solutions of moderate strength, but very sensitive to the action of nuclei, a shower of brilliant crystals falling as soon as the tube is opened. Eighty grains of the salt in three drachms of water, boiled and filtered into a clean tube, and exposed to the temperature of 4° F., formed large feathery crystals with a central quill formed by the junction of two planes of crystallization, the effect being very lovely and striking. In snow and water at 32° the crystals balled, ascended, and quickly melted. These alternate effects of solidifying and melting were repeated three times, when the tube was opened and inspected to see if the whole contents were solid. On reinserting the cotton-wool and placing the tube in water at 32°, the solid quickly melted with immediate separation of the salt, the act of opening the tube having introduced a nucleus from the air.

Nickel sulphate with 7 equivalents of water forms supersaturated solutions which resist a cold of 6°. Mixed with an equivalent weight of *cupric sulphate* with 5 equivalents of water of crystallization and one ounce of water, the mixture when hot is not to be distinguished from the solution of nickel sulphate, but when cold a faint shade of blue comes over it. The salts separate in cooling in the air; but the supersaturated solution is solid at 0° F., and produces the beautiful feathery crystals noticed in the case of the solution of the ammonia and zinc sulphates, and, like it, rapidly melts at 32° without any separation of salt, if nuclei be excluded.

A very beautiful display of the leaf-like crystals, and also of the so-called tetrahedral crystals, is furnished by a solution of *zinc sulphate* in one of *potash-alum*. The mixed solution, which contained the salts in atomic proportions, was evaporated to dryness, and 200 grains of the salt was boiled with 5 drachms of water and filtered into a clean tube. The solution was bright and viscous, but, as is usual in such cases, the viscosity became more equally diffused throughout the solution in the course of a few days. At 4° F. tetrahedral crystals formed on the surface, and were propagated downwards until the whole was solid; in snow and water it rapidly melted. The tube was left to repose during a week, when on examining it again it had thrown down a dense white powder, apparently of anhydrous zinc sulphate. On placing the tube in a freezing-mixture at 0°, the powder at the bottom increased in volume and formed acicular crystals, while in the solution above a series of large leaves resembling ivy gradually ascended to the surface of the solution, and even projected above it. In snow-water the ivy-leaves rapidly melted, and threw down small bright crystalline grains of alum, while the powder at the bottom remained.

The leaf-like crystals seem to be deformations of the so-called tetrahedral crystals produced by the action of cold on these solutions, highly supersaturated as they were at the low temperatures to which they were reduced. From the recurrence of similar forms during the solidification of solutions of different salts, it is reasonable to suppose that the water of the solution determines the form, and that the presence of the saline molecules modifies it. From the abundance of these saline molecules in comparatively so small a quantity of water, and in so confined a space as a glass tube, the water as a preparatory step to solidification is not able to eject the saline molecules; they therefore remain and influence the forms of the solid which results from the low temperature. My business, however, is only incidentally mixed up with the solidification of supersaturated solutions. What I wish to insist on is the fact that, in the absence of a nucleus, these solutions prefer rather to become solid than to crystallize; and that there is no real freezing (if by freezing is meant, as a necessary condition, the separation of salt during the act) is proved, I think, by those cases where the result of a moderate elevation of temperature is to produce a bright, clear, and still highly supersaturated solution[10]; while in other cases, where there is a separation of salt, it is the anhydrous or a salt of a lower degree of hydration than that employed to make the solution. But if, at any time during the process of solidifying or of melting, the solution be subjected to the action of a nucleus, crystallization is sure to set in, and the original fully hydrated salts are reproduced.

A solution of the *cupric* and *magnesic sulphates* at 4° F. produced the crystals already described, and when solid the outside of the tube displayed some elegant forms in different shades of blue.

The *sodic* and *magnesic sulphates* in atomic proportions form, with water, a supersaturated solution; but on reducing it to low temperatures, the salts are apt to separate. When such is not the case, an anhydrous salt is thrown down on greatly reducing the temperature; and as this salt takes up a portion of water, acicular crystals shoot out from it. Other interesting phenomena may be observed with solutions of this double salt at various degrees of supersaturation and at various temperatures; as also with the sulphates of other bases, such as those of *cadmium* and of *nickel*, either alone or in conjunction with other sulphates. The addition of *potassic sulphate* to other sulphates in atomic proportions leads to the formation of double salts, which, so far as I have examined them, do not form supersaturated solutions.

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[10] RÜDORFF (*Jahresber. der Chemie*, 1862, p. 20) showed that by employing saturated solutions of single salts and reducing them to low temperatures, ice is formed, together with a hydrated compound of the salt in question. In my experiments with supersaturated solutions in close vessels, chemically clean, the conditions are, of course, quite different, and no ice is formed. In some cases the solutions become viscid, like syrup.

ADDENDA.

[18th February, 1871.] Since the reading of the foregoing paper and the publication of the Abstract thereof in the Proceedings (vol. xviii. p. 533), some points connected with Section I. seemed to require further elucidation, which I am permitted to offer in this place by way of addenda.

(1) *On the definition of a nucleus.*—In the case of a supersaturated saline solution, a nucleus is defined as "a body that has a stronger attraction for the salt of the solution than for the liquid which holds it in solution." This is true in the great majority of cases; but in certain instances, such as those of absolute alcohol and washed ether, the nucleus has an attraction for the aqueous rather than the saline molecules of the solution. In order therefore to make the definition include such cases, it may be necessary to add to the definition, as given above, the following words:—"or a stronger attraction for the liquid than for the salt." In the case of supersaturated gaseous solutions, such as soda-water, Seltzer-water, champagne, &c., it has been shown[11] that a glass rod, or other body, covered with a film of foreign matter is active in liberating gas, while the same body in a catharized state is inactive. Similar phenomena are exhibited in the case of liquids at or near the boiling-point, which I regard as supersaturated solutions of their own vapour[12]. A catharized body is inactive; but if such body be drawn through the hand or in any other way covered with a film, it immediately produces a burst of vapour when placed in the vaporous solution. Hence in saline, gaseous, and vaporous supersaturated solutions the action of nuclei is the same, and may fairly come under the same definition, subject only, in the case of saline solutions, to the modification above given, and, in the case of vaporous solutions, to the additional fact that porous bodies, whether catharized or not, are energetic nuclei. Gathering up these various details, a nucleus may be defined as a body that has a preferential attraction for the salt or the gas or the vapour of a supersaturated solution, or for the liquid which holds any one of the three in solution, separation of the constituents of the solution being in either case the result; only in the case of vaporous solutions, porous bodies act as permanent nuclei.

(2) *On the pure substances capable of causing immediate crystallization.*—Conclusions cannot, obviously, be drawn from liquids that have contracted dust or products of oxidation &c., since such liquids are generally active as nuclei, whether in a lenticular or a filmy form. Fixed oils require to be refined or filtered, volatile oils to be distilled, and solid fats to be fused and filtered or passed through flame, alcohol or naphtha to be distilled, ether to be washed, and so on. Whatever the body that forms films, it must be treated in some way or other that shall ensure the deposit of a pure film on the supersaturated saline solution, and not a film containing a small speck of foreign matter that is likely to act as a nucleus. Moreover, in trying the action of a film of any one substance, the experiment should not be limited to one flask of solution, but to

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[11] Phil. Mag. July 1867.

[12] Proceedings of the Royal Society, vol. xvii. p. 240.

many solutions of the same, and of various degrees of supersaturation. There is also a difference in the mode of action of a speck, compared with that of a film. A speck or mote or point acts by determining the crystallization downwards at right angles to the surface, or radially, in closely packed crystalline lines; whereas in the case of a pure film crystallization proceeds from every part of its lower surface simultaneously, so as often to produce large well-shaped crystals parallel with the film.

(3) *Why should a film act as a nucleus, and a lens of the same oil not so act?*—It can be shown experimentally that a clean inactive rod immediately becomes active simply by drawing it through the hand; so also a clean surface, such as the inside of a flask, smeared with a little oil becomes powerfully nuclear; but if the smear on the surface of the rod or on the inner wall of the flask can gather itself up into globules, these are not nuclear. Phenomena of this kind seem to be explained by reference to the surface-tension of liquids. In the case of a film formed by depositing a drop of an oil on the surface of a supersaturated saline solution, the surface-tension of such solution being diminished at the point touched by the oil, the surface of the solution surrounding the point touched exerts a tractive force on the oil, and spreads it into a film, with adhesion to the surface and a nuclear action on the solution; because being brought into contact with the saline particles, but not with the aqueous (seeing that oil and water do not combine, while adhesion readily takes place between oil and salt), the saline molecules are separated from the aqueous, and the action once begun is propagated. When, on the other hand, an oil deposited on the surface of the solution assumes the form of a well-shaped double convex lens, or even a disk, there is no adhesion properly so called, and no nuclear action, since the lens is separated from the solution by surface-tension, and is not nuclear because it is really not in contact with the solution. Even when the solution is shaken so as to break up the lens into globules and to submerge them, each globule is as completely separated by surface-tension from contact with the solution as if it were outside the flask, at least so far as any nuclear action is concerned. Whether a drop of oil form a film or a lens depends on several variable circumstances, such as the temperature of the solution, its degree of supersaturation, its surface viscosity, and so on.

(4) *Is it possible to deposit a film on a supersaturated saline solution without its acting as a nucleus?*—In a recently published account of a series of experiments, it is stated that an oil, such as citronella, was dissolved in ether (approximately 1 part oil to 20 of ether), and a drop of this solution was allowed to fall upon a supersaturated solution of GLAUBER'S salt; as the ether evaporated, a film of the oil was left on the surface of the solution, and it did not act as a nucleus. In repeating this experiment, I found that in most cases the ether itself, or its vapour acting at a distance, formed a film on the surface of the solution, and produced crystallization; but when this effect was not brought about, and the ether evaporated, the oil was left in the form of a multitude of minute globules or lenses, which, as already stated, are not nuclear. But granting the result stated above to have been obtained, and that a film was actually deposited on the sur-

face of the solution without any nuclear action, the answer appears to me to be found in a highly ingenious experiment by Professor VAN DER MENSBRUGGHE, of the University of Ghent, contained in a Memoir on the Surface-tension of Liquids[13]. Some filaments of silkworm's cocoon were tied together at the ends so as to form an irregular circle, and being made chemically clean and pressed flat, the circlet was placed on the surface of water in such a way as to be exactly in contact with it, without being below the level. If, now, " a drop of ether be held above that portion of the surface limited by the coil of filaments, this coil immediately undergoes lively trepidations, and tends to assume the true circular form, evidently because the vapour of ether diminishes the tension of the surface within the silken boundary, and this, in its turn, yields to the superior traction of the portion external to it. The moment the drop of ether touches the surface within the flexible contour, the silk expands into a circular form; but it as quickly contracts, since the evaporation of the ether cools the surface and so restores the contractile force. When, on the other hand, the ether is deposited outside the silken boundary, this immediately becomes reduced in size, but expands again as the cold produced by evaporation augments the contractile force of the exterior portion"[14].

Now, supposing a drop of the ethereal solution of oil to spread on the surface of a supersaturated solution of GLAUBER'S salt, the first effect would be, according to my view, to lower the surface-tension of the solution, and in the absence of the ether to spread out the oil-film with nuclear action; but the presence of the ether (especially in so large a proportion as 20 to 1) prevents this; for it immediately begins to evaporate, and in doing so restores the surface-tension of the solution, so much so, that by the time the oil-film is released from its ethereal chain, the surface is in a condition to resist adhesion.

In the case of a drop of oil free from ether being deposited on the surface, it is the superior tractive force of the surface surrounding the drop that spreads it into a film, and in the very act of doing so degrades its own contractile force to that of the oil; in the case of the ethereal solution the oil is not in contact with the surface, but when the oil is spread by the surface itself it is: the distance in the one case, as compared with that of the other, may be less than the millionth of an inch, but it is not the less real.

(5) *Are we to understand that the minute microscopic particles floating in the air act as nuclei, not of themselves, but in consequence of some film of other matter with which they are contaminated?*—Such is my view; for if the fine dust gathered from the floor or from shelves or the tops of books &c., which is powerfully nuclear, be washed in a weak solution of caustic alkali and dried out of contact with air, it is no longer nuclear. Flasks containing supersaturated saline solutions may be kept uncovered during a long time in an open space in the country, in calm weather, without any separation of salt;

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[13] *Sur la Tension superficielle des Liquides. Mémoires Couronnés de l'Acad. Roy. des Sciences de Belgique,* 1869. An abstract of this paper is given in the Phil. Mag. for Dec. 1869 and Jan. 1870.

[14] Phil. Mag. Dec. 1869, § 32. See also another remarkable example in Phil. Mag. Jan. 1870, § 22.

but when crystallization does take place it will be found that a small fly, a speck of soot, &c. has entered the flask and acted as a nucleus. The finger, if cleaned in caustic alkali or alcohol, or by drawing it through the flame of a spirit-lamp, may be held in a supersaturated saline solution for some time without inducing crystallization; but if the finger while in this condition be drawn along the side of the glass so as to produce a smear, such smear is immediately active, the skin supplying the matter of the active film.

(6) *Is it true that a fully hydrated salt, chemically clean, is not a nucleus to its supersaturated solution?*—In my first paper on Supersaturated Saline Solutions[15] it was shown that a crystal is not *necessarily* a nucleus to a saturated saline solution of its own kind. For example, a supersaturated solution of GLAUBER'S salt, by long keeping, parts with a portion of its water by evaporation through the cotton-wool plug, and crystals are formed on the glass above the solution; on washing these down they do not act as nuclei: so also a cold supersaturated solution of magnesic sulphate *in vacuo* over sulphuric acid forms, also by evaporation, crystalline crusts on the surface, and these crusts are not nuclear. Cases of other salts have been urged where such a crystal becomes a nucleus, and the old fact has been restated that a salt of a lower degree of hydration is not a nucleus to a supersaturated solution of a salt of a higher degree of hydration. What is wanted is to show that the sodic sulphate and the magnesic sulphate, formed as above described, are not the normal salts, but salts of a lower degree of hydration; and this has not yet been done.

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[15] Philosophical Transactions, for 1868, p. 665.