

VIII. Fresh-water Ice. Flame 6 inches from nearest Thermometer.

Temperature of outer air = -37° . January 3, 1876.

Heat applied continuously for two hours.

Time.	Ther. 1.	Ther. 2.	Ther. 3.	Ther. 4.	Tempera- ture of ice house.	Ther. Y.Y.
hours min.						
9 46	-23°	-24°	-21°	-20°	-21°	-23°
10 1	$-22\cdot25$	-24	$-20\cdot75$	-20	$-20\cdot75$	-22
10 16	-21	$-23\cdot5$	$-20\cdot5$	$-19\cdot9$	$-20\cdot5$	-22
10 31	$-20\cdot1$	$-23\cdot25$	$-20\cdot5$	-20	$-20\cdot75$	-22
10 46	$-19\cdot75$	-23	$-20\cdot25$	-20	$-20\cdot5$	$-22\cdot75$
11 1	$-19\cdot25$	-23	$-20\cdot25$	-20	$-20\cdot5$	-23
11 16	$-19\cdot5$	-23	$-20\cdot5$	-20	-21	-23
11 31	$-19\cdot25$	$-23\cdot1$	$-20\cdot5$	$-20\cdot25$	$-20\cdot9$	$-22\cdot5$
11 46	-19	-23	$-20\cdot25$	-20	$-20\cdot75$	$-22\cdot25$
Range in 1 hr.	$3\cdot25$	$1\cdot0$	$0\cdot75$	0	$0\cdot5$	$0\cdot25$
Range in 2 hr.	4	1	$0\cdot75$	0	$0\cdot25$	$0\cdot75$

III. "On the Function of the Sides of the Vessel in maintaining the State of Supersaturation." By CHARLES TOMLINSON, F.R.S. Received February 21, 1878.

Before any consistent theory can be framed of all the phenomena of supersaturated saline solutions, it is necessary to determine whether the sides of the vessel bear any, and what part, in maintaining the state of supersaturation.

It is remarkable that among the multitude of memoirs and papers that have been published on the subject of supersaturation generally, and of special phenomena in particular, my reading should not have made me acquainted with any special experimental researches conducted with the view of determining the point in question.

In 1819, Gay-Lussac* seeing how easily a supersaturated solution of sodic carbonate can be made to solidify, by merely shaking the vessel, expressed his opinion that the state of supersaturation depends, not on a chemical, but a purely mechanical force. "We cannot," he says, "fix the point at which supersaturation ends, since it is entirely accidental in each experiment, depending, as it does, on the nature of the vessel, its polish, its conducting power, and the agitation of the air."

In 1851 Lamy† arrived at the conclusion that the form, thickness, and nature of the vessel, and the quantity of solution contained therein, have no influence on the state of supersaturation.

* Ann. de Ch. et Phys., 2e Serie, xi, 303.

† Comptes Rendus.

Löwel,* whose researches extend over about ten years, namely, from 1848 to 1857, makes frequent reference, in the course of his six memoirs, to the sides of the vessel. He is of opinion that the asperities of the sides exert no action in determining crystallisation; that nothing certain can be affirmed as to the size of the tubes in producing such an effect; that it is not a mechanical action, as Gay-Lussac supposed; that heat deprives the sides of their active, or as he calls it, dynamic power; that even in an open tube the sides are not in a passive state; that nothing is positively decided as to the action of the sides. He also refers to that mysterious unknown force which holds the crystals in an abnormal state; he also speaks of the inner surface of the flasks recovering that particular property of determining crystallisation which heat had deprived it of, the cause of which is unknown; and in his last memoir he supposes that the sides determine the formation of the normal salt by an action of contact.

I have already expressed my opinion† that had Löwel worked with chemically clean flasks and tubes, he would not have encountered so many contradictory results, or have expressed so many uncertain and conflicting opinions as those above quoted.

In 1866 Jeannel‡ threw out an opinion that the state of supersaturation is maintained in closed vessels by reason of the attraction of the sides and the saturation of the interior air.

I had long ago formed an opinion that the adhesion of the solution to the walls of the vessel is an important function in maintaining the state of supersaturation; and it seemed probable if this were so, that any force that could effectually detach the solution from a small portion of the side, below the surface, would cause the whole system to break down.

The most obvious mode of experiment seemed to consist in rubbing the interior surface with a clean wire. About five years ago I obtained a number of results in this way, but did not think them sufficiently important or trustworthy for publication. One source of fallacy soon became obvious. On moving the wire up and down in a nearly vertical direction, a film of the solution is being constantly dragged above the surface, which film, in consequence of rapid evaporation, disengages a molecule of the salt, and this acts as a nucleus to the whole of the solution. Attempts were made to prevent such an effect by tying a piece of linen dipped in hot water loosely round the neck of the tube, and passing the wire through the cloth into the tube, but the result was not satisfactory; for unless the crystals could be seen actually to start from the place rubbed and to spread from this point alone through the solution, no fair conclusion could be formed as to the effect of the rubbing. Friction with platinum, brass and steel wires seemed to

* *Ann. de Ch. et de Phy.*

† *Proc. Roy. Soc.*, xvi, 408.

‡ *Comptes Rendus*, 2nd January.

have little or no effect on solutions of sodic sulphate and sodic acetate. The most satisfactory results were obtained with magnesian sulphate; but with this and other solutions the results varied with the state of the weather as the crystallising force varied, and also with the nature of the rubber, whether a glass rod or the wires just named.

At length it occurred to me to line the tubes with some substance which is not wetted by the solution or imperfectly so. Accordingly, two large tubes (5 oz. and 3 oz.) were made chemically clean, and coated with a solution of amber in chloroform. They were three parts filled with a solution of sodic sulphate (2 to 1), covered over, and left until the next day. A stout platinum wire was taken out of hot water and introduced into each tube, when moderately hard friction was made in a vertical line about one-sixth or one-eighth of an inch in length. A crystalline brush immediately diverged from the part rubbed, and spread all through the solution, the mass of which was sufficient for the eye to note the details, and to convey the assurance that crystallisation set in from the part rubbed and from that only.

The advantage of using amber is that the coating, being transparent, allows the progress of the experiment to be watched. The same advantage may, however, be obtained at less cost and trouble, by means of resin, a small quantity of which, in powder, together with a few drops of spirits of wine, heated in the tube over a spirit lamp, enables the operator easily to spread a coat evenly upon the inner surface by moving the tube about while it is still warm.

A number of one-ounce tubes, coated in this way, were filled with a stronger solution of sodic sulphate (3 to 1) than that before employed. The result was satisfactory: the solutions often became solid in cooling, and always when the inner surface was rubbed with the platinum wire.

The experiment was also made comparative by placing an uncoated by the side of a coated tube, and so leaving them to cool covered with glass capsules, or small beakers. The solution in the coated tube often solidified in cooling, and always remained liquid in the uncoated tube.

The results as obtained with supersaturated solutions of other salts also showed how greatly they depend for their stability on adhesion. The system always broke down when a portion of the solution was detached from the side, by the rubbing action of the wire. The solution of each salt, however, presented those characteristic features of its own, which form one of the principal charms in the study of natural objects. In the ammonia alum solution (1 to 1) the octohedral crystals, under the action of rubbing, seemed to bound forth towards the axis of the tube. In the magnesian sulphate solution (3 to 1) the disengaged crystals were too minute to appear, except as a chalky-white line following the motion of the wire. Zincic sulphate (3 to 1) formed small

woolly-looking crystals after a slight rubbing, and although the wire was rapidly withdrawn as soon as the crystals began to appear, it left behind it a curious kind of trail, consisting of an axis of the form of the wire, repeating its bends and irregularities, while small acicular crystals started out at right angles to this line, and thickly studded it soon after the whole of the solution became solid. Zincic acetate (1 to 1) did not display crystals as soon as the side was rubbed, but slowly, in the course of half-an-hour or so, the part rubbed was occupied by a dense crop of beautiful crystals, the points of which passed beyond the axis of the tube.

Sodic acetate solution does not readily yield to the effort of rubbing, except in certain states of the weather when the crystallizing force is strong; but a case occurred to me some years ago which exactly suits my present purpose. Several flasks containing a highly supersaturated solution of sodic acetate, to which oil had been added without any nuclear effect, were emptied into a small, stout cylindrical glass, where it remained during some weeks without change, the layer of oil on its surface preventing it from absorbing moisture. It was several times stirred with the finger without effect, for this, on being introduced, became coated with oil and so prevented contact. The finger was then pressed against the strong side of the vessel with a considerable amount of force and drawn slowly from the bottom upwards. The solution immediately became solid. I attributed this effect at the time to nuclear action, but I now regard it as an excellent illustration of the point which I am seeking to establish.

A supersaturated solution of sodic carbonate is very sensitive to any interference with its adhesion. A speck of carbon or of ferrous oxide, coming to the surface within the tube, is sufficient, on cooling down the solution, to cause the salt to start from the speck in crystalline lines in all directions, producing immediate solidification.*

In addition to amber and resin some tubes were coated with other substances, such as sulphur, shellac, stearine, and paraffin; but as some of these, in addition to the objection of being opaque, melted when the boiling solution came into contact with them, I need not refer to them any further, except perhaps to paraffin, with which an interesting result was obtained. A large tube was lined with paraffin and passed, telescope fashion, over a smaller tube, containing a nearly boiling solution of sodic sulphate. When cold, the tubes were slowly reversed, so as to pour the solution into the coated tube; but it solidified as soon as it came into contact with the paraffin. If, however, it were poured in while still warm, the solution accommo-

* In the experiments which I had the honour of exhibiting to the Society after the reading of my first paper (28th May, 1868), a case of this kind occurred and was pointed out by my late lamented friend, William Allen Miller, as "a very pretty effect."

dated itself to the new circumstances and remained liquid when cold.

The results of these experiments seem to point to the conclusion that adhesion to the side of the vessel is one of the conditions under which the state of supersaturation is maintained; and that whatever interferes with this adhesion, must prevent supersaturation or destroy it.

This conclusion was tested by another mode of experiment, starting from the idea that if the solution were made to expose an amount of free surface, about equal to the surface of contact with the vessel, the adhesive force would scarcely be sufficient to maintain the state of supersaturation, and the solution in cooling would crystallise as in an open evaporating dish. This is what really did happen in the case of ammonia alum (5 to 3). The solution in three covered shallow vessels deposited massive crystals in cooling, and when cold, the mother liquor was no longer supersaturated. A solution of the same degree of strength was boiled in a flask and the opening plugged with cotton-wool: this deposited no salt in cooling, because the area of adhesion was greatly in excess of that of the free surface. The solution under such conditions will remain unchanged for months. In all cases the re-boiling of the solution in the flask into which it is filtered greatly promotes adhesion, and, consequently, the duration of the solution in the state of supersaturation.

But to return. A similar crystallisation took place in the case of sodic sulphate; but that arose chiefly from the kind of vessel used and the mode of covering it, as will be noticed presently. I must first refer to supersaturated solutions of sodic sulphate (3 to 1) in shallow foot glasses, four inches in diameter and one inch deep in the middle. The boiling solution was poured into these glasses, which were immediately covered with shallow glass vessels, inverted over them so as to fit nicely and rest on their edges, or to fit with friction to the sides. The result was curious and interesting. Instead of crystallising in cooling, the solution relieved itself by throwing down large quantities of the seven-watered salt in finely shaped masses, while the liquid portion remained supersaturated.* Next day these solutions were taken into the open air and uncovered. From a point at the extreme edge of each, crystallisation set in and spread like a fan over the surface and through the solution. This was not a case of nuclear

* A three-ounce flask was coated with resin, and into it was poured a boiling solution of magnesia sulphate (3 to 1). The flask was covered with a small beaker and set on the window ledge to cool. A fine display of crystals of the modified salt sprang from the bottom nearly to the surface of the solution, which remained supersaturated. Here again, as in the case of sodic sulphate, the solution relieved itself by this deposit and there was sufficient adhesion on the part of the remaining liquid to maintain a moderate degree of supersaturation.

action derived from the atmosphere (rain having fallen during some hours and having scarcely ceased) but was due to another force. Last summer, as noticed in my former paper,* drops of sodic acetate exposed on glass always started the crystallisation from the edge. So, in these wide shallow glasses in the open air, crystallisation set in from the edge, or capillary curve, where the solution is most drawn out and attenuated. Now, supposing evaporation to be active all over the surface, this thin portion, becoming thinner by the process, would be the first to detach a molecule of the salt, and this, once set free, would act as a powerful nucleus to the whole. Lines, or rather thin planes of crystals, diverge from the point, and this so quickly as not to afford time for the molecules to arrange themselves into crystalline forms.

On one occasion the mass of seven-watered salt rose so near the surface, that the solution resting on it was scarcely more than a film. This, by evaporation, also disengaged a minute portion of the normal salt, which acted as a centre of crystallisation.

Solutions containing two parts of salt to one of water behaved much in the same way as the stronger ones. A weaker solution, containing only one of salt to one of water, accommodated itself to the conditions under which it was placed. It did not deposit any modified salt, and on being uncovered in the open air, crystallised from the edge.

In the case before referred to, where the solution crystallised in cooling, as in an open evaporating dish, namely, in the form of large prisms of the normal salt, the vessel was a shallow dessert dish with a scalloped edge, so that the protecting cover did not confine the air over the surface of the solution, but allowed it to circulate; hence, in cooling down, the molecules were also in a condition to circulate and gradually to arrange themselves into groups, ready to assume the crystalline form when the temperature had sufficiently declined. Whereas, in closely covered vessels, the strong adhesion to the side prevents this circulation and re-arrangement, the adhesion holding the molecules in a forced state, bearing some kind of analogy to the glass in Prince Rupert's drops and the Bologna phial.

It must also be noted, that in the last case also, there was no nuclear action; for, had there been, the solution would have cooled down to a certain point, and then have suddenly crystallised in closely packed planes; whereas, in the case now referred to, the crystals were large and of the usual shape, while the mother liquor was no longer supersaturated.

Solutions of zincic sulphate and of magnesian sulphate (3 to 1 each) in these covered shallow vessels, also threw down a good deal of the modified salt, in the case of the zinc solution the monohydrated salt

in long clustered cylinders, but being left undisturbed for a day or so, the remaining supersaturated liquor in both cases became solid, the normal salt being formed. Sodid acetate solution (6 to $1\frac{1}{2}$) poured boiling into these large shallow vessels and covered over did not change during twenty-four hours. On being taken into the open air and uncovered, the solutions remained some time in the liquid state, but on touching the bottom of the vessel with the finger, they immediately became solid.

The alum solution, before referred to, deposited the normal salt in large crystals, while the solution was still warm. It could not relieve itself in any other way, because by its constitution it cannot form a salt of a lower degree of hydration than the normal, that is, with 12 aq., and the throwing down of that in considerable masses, so as to get rid of the state of supersaturation altogether, forcibly illustrates the dependence of that state on the adhesion of the solution to the sides of the vessel.

The weather was mild while these experiments were in progress. At lower temperatures the solutions would doubtless have been even more sensitive.

The result of these experiments satisfies me that the state of supersaturation is dependent on the adhesion of the solution to the sides of the vessel, coupled with the tension of the surface. This tension may be lowered, so as to throw more work upon the other force, which it may be able to bear; but anything that effectually detaches a portion of the solution from contact with the sides of the vessel, produces the sudden crystallisation of the solution.

If this view be correct, many of the phenomena of supersaturation are accounted for, and the whole subject is far advanced towards that obedience to law, which can alone invest it with dignity.