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On the crystallization of sodium nitrate.

By Professor H. A. Miers, D.Sc., F.R.S., and Jacques Chevalier.

[Read January 23, 1906.]

EXPERIMENTS made by Professor Miers and Miss F. Isaac[1] have shown how, by measurements of the refractive index, it is possible to determine for a supersaturated solution the temperature at which it passes from the metastable condition, in which it can only crystallize by inoculation with a crystal of the salt (or of a substance isomorphous with it), to the labile condition, in which it may (and often does) crystallize spontaneously. In a diagram in which concentrations are taken as ordinates and temperatures as abscissae the solubility curve represents the limit between the unsaturated and the metastable state; and the limit between the metastable and the labile state is represented by a similar curve, to which they have given the name 'supersolubility curve'.

When a cooling solution is shaken, the passage to the labile state is

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[1] Journ. Chemical Society, 1906, vol. lxxxix, pp. 413–454.

generally marked by the appearance of a dense cloud of small crystals, but if there be crystals already present clouds may also appear in the metastable solution.

The present experiments were made with the object of ascertaining whether there is any difference in the mode of growth of crystals from a metastable and from a labile solution; what are the particular conditions which cause a labile solution to crystallize; at what parts of such a solution the first crystals appear and why; and how the clouds are produced.

The experiments are of three sorts:—

I. Test-tubes, immersed in a narrow glass trough filled with water at a known temperature, contain solution which is metastable at that temperature, and the growth and behaviour of an immersed crystal is watched by means of a microscope with its tube set horizontal, and the objective against the face of the trough. The tube may be plugged with cotton-wool, or the solution may be covered with a layer of oil at the same temperature, to prevent the access of crystalline germs from the air.

II. Drops of solution of such a strength as to be metastable at the temperature of the room are examined on a glass slide under the microscope until by evaporation, or by cooling, or both, they pass into the labile state. If it be desired to protect it from the air, the drop is enclosed by a cover-glass resting on a ring of Canada balsam, or of vaseline, surrounding the drop.

III. Solutions of known strength contained in sealed tubes are immersed in warm water, and are examined under the microscope while the water cools, in order to study their behaviour while at rest at known temperatures.

Such experiments might be carried on indefinitely, and are required for solutions of all sorts, since previous descriptions have not distinguished between the metastable and labile conditions.

The following experiments relate to sodium nitrate, because that substance has been most fully studied in the memoir referred to above, and because the problem is not complicated by the existence of two crystalline modifications or of salts containing different proportions of water.

I. *Experiments upon solutions in open tubes.*

One objection to the employment of a considerable volume of solution maintained at rest is the fact that, unless a long time be allowed for diffusion, different parts of the solution may be of quite different concentrations.

If, for example, sodium nitrate be dissolved at the bottom of a test-tube, and care be taken not to shake the solution, the lower part of the liquid may be supersaturated while the upper part is unsaturated. The solution may be explored by an immersed crystal of the salt which can be watched under the microscope and seen to grow while in the lower part, but to dissolve while in the upper part of the tube; and sometimes quite a well-defined, oscillating meniscus may be found between the two. It is more than probable that one part of a solution may be in the metastable and another part in the labile state, or that there may be some streams of labile solution in the metastable liquid.

When crystals grow in an ordinary metastable solution they seem to originate either at the top or bottom of the liquid, or at both places; when the solution is uncovered, close examination shows that they probably originate at the surface and are carried to the bottom by their own weight or by the circulating currents. Their origin at the surface may be due to evaporation there, which reduces the solution locally to the labile state. If the liquid is exposed to the air, crystallization is also undoubtedly started in many instances by solid germs falling upon the surface. Attempts were made to prevent evaporation and access of germs by covering the liquid with a layer of oil at the same temperature; but even with this precaution crystals usually appear just below the oil before the solution as a whole passes into the labile state. Crystals so small as to be almost invisible may also be seen to rise in the ascending currents, and to remain at the surface until they have grown so large that they fall by their own weight. In a metastable solution, therefore, crystals always originate at the margin of the solution, and it is just possible that the first crystals may appear at the bottom as well as at the top of the solution.

The following is a striking difference between the two sorts of solution. If a crystal of sodium nitrate be immersed into the metastable solution, minute crystals at once form on it, all in parallel position; but if it be immersed into a labile solution the minute crystals which form upon it are in all sorts of positions and are not orientated as the parent crystal (the crystals also appear at the same time upon the sides of the tube and throughout the solution). This appears to indicate that in the labile solution a cloud of minute rhombohedra produced by the introduction of the large crystal attach themselves to it and then continue to grow rapidly, whereas in the metastable solution the centres of growth are only on the surface of the crystal. Precisely the same difference is noticed when a cleavage piece of the isomorphous calcite is employed.

Again, if very minute crystals be quietly introduced into a metastable solution, a few other minute crystals appear in their neighbourhood while they are moving; but in a labile solution they produce a fine shower of crystals.

Clouds of small crystals are, however, not peculiar to labile solutions; they may also be produced, though in a much less degree, in metastable solutions by moving a crystal of sodium nitrate to and fro in the liquid. The moving crystal produces visible streams in its wake, and in these the small crystals make their appearance. When a metastable solution containing a few crystals is violently shaken, a cloud is formed; when a labile solution containing a few crystals is violently shaken, a much more dense cloud is formed and one which consists of much smaller crystals.

When crystals are introduced into the unsaturated solution, they are, of course, partly dissolved and become rounded; and they sometimes remain so when the solution passes into the metastable state, unless shaken. In one such experiment (49 per cent. solution) the rounded crystal was covered with small rhombohedra as soon as the liquid became metastable; but when moved suddenly (at 24°) to another part of the solution it shed a number of small crystals and ceased to grow; it only began to grow again (at its lower end) at 21°. Again, it is sometimes found that the edges and minute protuberances of a crystal introduced into the metastable solution remain unchanged, while the small crystals forming upon its surface in parallel positions are growing rapidly.

The following are the details of two experiments with introduced crystals:—

(1) A 47·6 per cent. solution (which becomes metastable at 24° C. and labile at $13\frac{1}{2}°$), contained in a tube stopped with cotton-wool and immersed in water, was watched through the microscope. The temperature was lowered by the addition, from time to time, of cool water to that in the trough.

The temperature of the water being 24°, a sharp cleavage rhombohedron of sodium nitrate was suspended in the middle of the solution.

$t = 22°$: the crystal appears to be neither growing nor dissolving; a few crystals have formed on the side of the tube just above the edges of the meniscus.

$t = 21°$: a small crystal has formed and is growing upon the top of the immersed rhombohedron.

$t = 20{\cdot}6°$: the small crystal is growing regularly and is now accompanied by a second; the parent crystal may be growing slightly.

$t = 20{\cdot}5°$: fresh crystals are growing on the top of the parent crystal.

$t = 20{\cdot}4°$: fresh crystals are growing on the surfaces of the parent crystal, all in parallel position, and especially along the inequalities of the faces.

$t = 17°$: a small crystal detached from the parent rises to the surface of the liquid; at 16° the streams proceeding from the parent crystal take some of the small crystals to the bottom.

$t = 14°$: the solution has become labile, a shower of small crystals is falling from the top of the solution, from the edges of the tube, and from the parent crystal.

$t = 10°$: the parent crystal is covered with small crystals.

(2) A fresh cleavage piece of sodium nitrate was introduced at 35° into a 50·65 per cent. solution (which becomes metastable at 38°, labile at 29°), and suspended just below the surface. It begins to be slightly dissolved, small particles separate from it and sink to the bottom, and are growing there while the temperature is 34°. The crystal being slightly moved produces visible streams in the liquid, and in these new crystals appear; the parent crystal continues to dissolve; the minute particles which fall from it only become visible a short distance below it; no cloud is produced by gentle shaking of the tube; at 32° the crystal was removed and found to have rounded edges and corners. No cloud was produced by moderate shaking till 28·5°, when the solution had become labile.

Several experiments were made in which a metastable solution, covered with oil, was stirred by means of a glass rod, which had been immersed in it for a long time while the solution was cooling from a high temperature: this usually produced a cloud, but it is impossible to prove that it may *not* be due to crystals already forming at the surface of the liquid and set in motion by the rod, or forming upon the rod just above the part immersed.

Scratching the side of the tube with a rod produces crystallization along the line of the scratch in a labile, and perhaps also in a metastable, solution; but if the tube be scratched before the cooling solution has attained the metastable state no crystals appear upon the scratch. Is it not possible that the effect is due to crystalline material which the rod has picked up on its entry through the surface? It may be mentioned here in this connexion that crystals do not seem to form in sealed tubes at the points where they have been rubbed by enclosed fragments of glass.

When a number of crystals appear in a metastable solution they seem to be propagated from one another by means of the concentration streams proceeding from each crystal, and it may be because these carry away the minute individuals which form upon the surface of the parent crystal. In a labile solution the streams are more active, and more general, and rapidly give rise to crystals of considerable size or to long needles.

Some attempts were made to introduce drops of labile liquid into a metastable solution, and in these experiments crystals seemed to be produced by the contact of the two liquids: but in all such experiments it is difficult to make sure that germs of solid crystals are not introduced at the same time, and it is possible that the crystallization is really due to these.

The whole process of crystallization and the formation of clouds may be beautifully shown by projection upon a screen, which renders it possible to watch the growth of individual crystals as they move through the liquid. By projection through crossed nicols the observations are made both more beautiful and more intelligible, owing to the polarization tints exhibited by the most minute crystals of sodium nitrate, which allow one to trace the increase in thickness of each rhombohedron as it rises or sinks through the liquid. A very common feature of this substance when growing in an agitated solution is the appearance, beside the ordinary rhombohedra, of fine hair-like crystals or rods. Projection upon the screen shows that these are only elongated rhombohedra growing rapidly in a vertical direction in the slender vertical streams of ascending or descending (perhaps labile) solution.

II. *Experiments with drops.*

When a crystal of sodium nitrate is introduced into a drop of the metastable solution it generally causes a few crystals to make their appearance at once in its immediate neighbourhood; the drops very often divide into two, and the portion which contains no crystals may remain without crystallizing until it reaches the labile state. When a crystal of sodium nitrate is introduced into a drop of the labile solution it causes the sudden appearance of crystals throughout the whole drop; if a portion separates, it also crystallizes at once.

In both cases a cleavage fragment of calcite produced exactly the same effect as a crystal of sodium nitrate.

The experiments are best performed by placing the drops on a slide close to the crystal, enclosing both with a ring of balsam or vaseline, and covering with a thin cover-glass. The drop is allowed to stand for a considerable time; the absence of crystals proves that it has not been contaminated by inoculation from the air, and the loose crystal may then be pushed in by means of a needle passed through the balsam.

If a drop be left to itself without the introduction of a crystal it will not crystallize until it passes into the labile state, when a number of crystals make their appearance and continue to grow rapidly.

When a drop is free to evaporate the crystals appear first in a ring round the edge. No doubt the drop is locally reduced to the labile state at the edge.

A curious feature in the metastable drop into which a crystal has been introduced, and one which is not in accordance with the statements generally made, is that the small crystals produced in the immediate neighbourhood of the large parent crystal may proceed to grow rapidly while the parent crystal itself does not increase in size.

III. *Experiments with sealed tubes.*

The tubes employed were about 10 cm. in length and about 1·4 cm. in internal diameter, and were two-thirds filled with solutions of known strength.

When the tubes were placed in a horizontal position, the first minute crystals generally made their appearance, shortly after the labile condition was attained, at the bottom of the tube, and almost at the same time (but usually a little later) upon the surface of the liquid. The crystals which floated on the surface united themselves in a chain parallel to the length of the tube. When the tube is in a vertical position, isolated crystals can be seen beginning to form almost simultaneously at the top and bottom of the liquid, and others may be seen falling near the sides of the tube.

In general it appears that the first crystals which form upon the surface appear at or near the edges of the liquid, and that those which float gravitate to the lowest part of the meniscus, thus forming a chain when the tube is horizontal. It is possible that most of the crystals which appear at the bottom of the tube have fallen thither from the surface, but perhaps before they are large enough to be visible. It is, however, certain that some of those which grow on the surface have been taken there from below by ascending currents. The weaker the solution the larger and less numerous are the crystals which form; with stronger solutions they are smaller and more numerous, and form more rapidly.

Unless the salt be completely dissolved crystals will, of course, appear as soon as the solution falls to the saturation temperature. They sometimes appear although there is no visible solid in the solution; but this is always due to the fact that the tubes have not been heated for a sufficiently long time or have been inadequately shaken while heating.

It requires prolonged heating and constant shaking to dissolve the last traces of salt.

On the other hand, if the tubes are kept at rest there is no reason why crystals should appear at the exact temperature at which the solution passes into the labile state. It is true that if the temperature be reduced very gradually the first crystals generally appear as soon as that state is attained if the tube be shaken, and give rise to a copious cloud. But if the tube be suddenly chilled it may be taken to a far lower temperature without crystallizing, and even then only a few crystals may appear, and may grow quietly unless the tube be shaken. Since in such experiments crystals do not usually appear unless either the tube contains some foreign substance, or has been warmed and shaken again while cooling, it is possible that the sudden chilling has only had the effect of reducing portions of the liquid to the labile state.

In general, if a solution be kept quiet, it is very difficult to distinguish between the metastable and labile states. For isolated crystals, which may appear spontaneously or have been introduced, may continue to grow independently in a uniform manner in either solution. It is only when the tube is shaken that a distinction can be observed. If the tube contains no crystals a cloud appears in a labile, but not in a metastable, solution. In a labile solution it is possible, by slightly moving a tube containing a crystal, to produce a fine cloud at a distance from the crystal: with a metastable solution this is not possible. If there be crystals present, the cloud produced by shaking a metastable solution is quite different in character from that of a labile solution. The former is thin and consists of comparatively few nuclei; the latter is dense. We distinguish them as a 'metastable cloud' and a 'labile cloud'.

In the production of these clouds the initial temperature seems to be an important factor: if the solution be reduced by sudden cooling from the metastable to the labile temperature, and then shaken, a dense labile cloud is produced: but if it be reduced to the labile temperature by sudden cooling from a higher temperature, and then shaken, a metastable cloud is produced. In these experiments, again, it is possible that though the solution is, in part at least, reduced to the labile temperature, it is not completely reduced to the labile state; for the process of crystallization resembles that in a metastable solution into which a few crystals have been introduced.

A number of experiments were made with tubes containing other substances in addition to the solution of sodium nitrate. In all these it was found that a piece of calcite (either a cleavage fragment or a crystal) produces exactly the same effect as a crystal of sodium nitrate. It is, of course, impossible to introduce a crystal of sodium nitrate in the same way as one can an insoluble substance like calcite: but with care it is possible to leave a small crystal adhering to the top of the tube while the rest is completely dissolved in the lower part. As soon as the solution passes into the metastable state crystals begin to grow in parallel position on the calcite: if other substances appear to relieve the supersaturation like calcite, it is only because the sodium nitrate has not been completely dissolved, and their presence renders solution a little more difficult. If the solution has been complete, calcite is the only substance which has this power, as we have proved by comparative experiments on tubes of the same solution containing different mineral substances, examined side by side. Calcite appears to act even more energetically than sodium nitrate itself: for example, with a tube of 50 per cent. solution containing a piece of calcite in the liquid and crystals of sodium nitrate out of it, crystals began to appear on and near the calcite at 35°; when the liquid was brought into contact with the sodium nitrate the crystals produced in their neighbourhood did not grow so rapidly, and were not so numerous as those close to the calcite.

The crystals which form in a sealed tube at rest almost invariably exhibit a minute triangular speck on one face; and when crystals growing on the surface of the solution are watched from the time of their first appearance, this spot is seen to occupy the position of the original nucleus; it may be a cavity (hopper-structure) on the upper surface of the crystal, produced by the presence of solution round the crystal and absence of solution above it, as generally happens with floating crystals. This suggests that all these crystals have originated in the surface of the liquid.

IV. *General conclusions.*

We would not venture to draw any general conclusions from the preceding rather fragmentary experiments, were it not that the experiments upon sodium nitrate are, in general, confirmed by those upon other substances, although we have in the present communication confined ourselves to sodium nitrate.

The experiments show that the process of crystallization enables us to distinguish between the metastable and labile states, and so confirm the distinction which has been already established by means of the refractive index.

An aqueous solution, either by cooling without serious change of concentration, or by evaporation of the solvent without serious change of temperature, or by both, becomes supersaturated and passes first into the metastable state (in which it will only crystallize by inoculation with a crystal of the solute or of an isomorphous substance) and then quite suddenly into the labile state (in which it may crystallize spontaneously). Spontaneous crystallization in the latter is generally induced by shaking or by friction, but in any case it is started by introduction of a crystal of the solute or of an isomorphous substance; whereas the introduction of such a crystal into the metastable solution only produces a few crystals in its immediate neighbourhood.

In a metastable solution centres of growth are only on the surface of a crystal already present, in a labile solution they may be anywhere.

When a labile solution containing a crystal is shaken, a dense cloud of new crystals is produced, both by the contact of the crystal with fresh portions of the solution, and by the creation of fresh centres of growth at a distance from itself owing to the mere motion of the liquid.

The cloud which is produced when a metastable solution containing a crystal is shaken is not so easy to explain: but it is certain that a number of minute crystals grow on the surface of the parent crystal as soon as it is introduced: it is probable, therefore, that many of these get loose and become new centres of growth when the crystal is moved through the liquid; and even when the parent crystal is still, they may be swept away from it by the concentration streams.

We were at first inclined to think that a crystal can only grow in contact with a labile solution; that when a crystal is growing in a metastable solution this is only due to the liquid in contact with it being so concentrated as to be really labile; and that therefore the cloud produced by moving a crystal in a metastable solution is due to droplets of this enveloping halo of labile liquid getting loose, and becoming new centres of growth. Experiments made by one of us[1] upon the strength of the solution in contact with a growing crystal of sodium nitrate have, however, shown that this liquid is not labile but metastable. We are therefore led to the conclusion that the cloud is produced by the liberation, not of liquid, but of solid particles from the parent crystal: and that these solid particles exist has been proved above by direct observations.

The fact that the liquid in contact with the growing crystal is not labile, but metastable, explains another curious feature of the experiments. It seems strange that in a labile solution a crystal which has made its

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[1] H. A. Miers, Phil. Trans., 1903, Ser. A, vol. ccii, p. 515.

appearance should continue to grow quietly, and that crystallization should not spread through the whole liquid which is *ex hypothesi* ripe for it. But this is prevented by the halo of metastable solution which surrounds the growing crystal and protects the labile solution from contact with the solid. The experiments seem to indicate that this is only true of a crystal which has appeared spontaneously in the solution, whereas a crystal *introduced* into a fully labile liquid starts crystallization throughout the liquid.

If this be true, then a crystal growing in a labile solution is surrounded by a halo of liquid less concentrated than the main mass; but a crystal growing in a weakly supersaturated metastable solution may be surrounded by a halo of more concentrated solution.