

LIX.—*On the Crystallisation from Supersaturated Solutions of certain Compound Salts.*

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IN a paper published in the Chemical Society's Journal, May, 1879, on "The Action of Isomorphous Salts in producing the Crystallisation of Supersaturated Saline Solutions," I pointed out that if a mixture of dimorphous salts be taken, a separation of the salts may be effected within certain limits by touching the solution with a crystal of one or other of the salts, this separation being limited by and depending on the relative solubilities of the different salts contained in the solution.

The subject of the present paper is a continuation of these observations, employing in this case supersaturated solutions of double salts,

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where it was possible to obtain such, and acting on them with nuclei consisting of one or other of the component salts, in order to find whether any disruption of the compound has taken place by the action of the nucleus. The method of carrying out the experiments was exactly the same as that employed before, and fully described in my first paper, the nucleus being added to the solution to be experimented on by one of two methods: (1) the nucleus being obtained by crystallisation from a supersaturated solution, and in this condition retained in the syphon-tube in the neck of the flask till required for use: or (2) the nucleus being added directly from its mother-liquor in a bulb-tube suspended in a similar manner in the neck of the flask.

In all these experiments, as before, the substances were purified with the greatest care, and the admission of particles from the external air most carefully guarded against.

The first group of salts experimented with consisted of certain of the double chlorides, bromides, and iodides of mercury with the corresponding salts of the alkali-metals. The results obtained with these bodies are detailed in the following table:—

Substance in solution.	Nucleus added.	Result.
HgCl ₂ (NH ₄ Cl) ₂ ,3H ₂ O ..	HgCl ₂ (prismatic)	Active.
„ ..	HgCl ₂ (deposited from hot solution)	Both active and inactive.
„ ..	NH ₄ Cl.....	Inactive.
HgBr ₂ (NH ₄ Cl) ₂ ,3H ₂ O ..	HgBr ₂ (deposited in the cold)	Active.
„ ..	HgBr ₂ (deposited from hot solution)	Both active and inactive.
„ ..	(NH ₄)Br.....	Inactive.
HgI ₂ (KI) ₂	HgI ₂ (needle-shaped crystals)	Active.
„	KI	Inactive.
HgCl ₂ (NH ₄ Cl) ₂ ,3H ₂ O ..	HgBr ₂ (NH ₄ Br) ₂ ,3H ₂ O	Active.
HgBr ₂ (NH ₄ Br) ₂ ,3H ₂ O ..	HgCl ₂ (prismatic).....	Active.
„ ..	NH ₄ Cl.....	Inactive.

It is very difficult to obtain many double salts of the halogen acids in a state of supersaturation, and the field for experiment with them is therefore limited. In the cases described above, however, there are several points to be noticed. With these double salts the salt of the heavy metal invariably caused the crystallisation of the double salt,

whereas the constituent containing the alkali-metal had no action. It was, however, impossible to determine whether the salt causing crystallisation did so by first inducing the deposition of the salt analogous to itself in the solution. Experiments are being carried out to endeavour if possible to determine the primary action which takes place; it is, however, a somewhat difficult one to examine.

It may also be observed that when the mercuric chloride or bromide existed in the nucleus in its true prismatic form, crystallisation at once took place, but that when its deposition from its solution took place at a higher temperature the results were various. On examining this point, I find that the crystalline forms of the mercuric chloride and bromide change when so deposited, which may readily account for the alternation in those cases. The crystalline form also of the double salt is more nearly allied to the form of the heavy metallic salt, than to the constituent containing the alkali-metal.

Finding that a double salt consisting of mercuric cyanide with ammonium chloride ($\text{HgCy}_2, \text{NH}_4\text{Cl}$) existed, forming a good supersaturated solution, I made experiments in order to compare it with the double salts before mentioned; when the following results were obtained:—

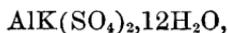
Substance in solution.	Nucleus added.	Result.
$\text{HgCy}_2, \text{NH}_4\text{Cl}$	HgCy_2	Active.
„	NH_4Cl	Active.

In this case there is a distinct difference from the halogen salts employed in the first-mentioned experiments, both components producing the crystallisation of the double salt.

It seems probable, therefore, that the double salts formed from these monobasic acids, although they form good supersaturated solutions, are not so firmly united together as to withstand the disturbing influence of certain of their constituents; but that the disruption produced by them is not sufficient to cause the decomposition of the body, and consequently the double salt is deposited. In the case last mentioned also, of the double cyanide and chloride, both salts are deposited as the final result of the crystallisation.

In experimenting with mercuric iodide, this substance was introduced by means of a pipette-shaped tube, and the iodide strongly steamed by boiling the flask before it was allowed to cool.

The next double salt examined was ordinary potash-alm



as this salt undergoes supersaturation with very great ease, and may be taken as a good instance of a thoroughly well defined double salt from a bibasic acid. The following results were obtained:—

Substance in solution.	Substance added.	Result.
$\text{AlK}(\text{SO}_4)_2, 12\text{H}_2\text{O} \dots$	$\text{Al}_2\text{S}(\text{SO}_4), 18\text{H}_2\text{O} \dots$	Inactive.
,, 	$\text{K}_2\text{SO}_4 \dots \dots \dots$	Inactive.

showing that neither of the constituents from which the double alum is originally derived, has any action upon its supersaturated solution. This is the more interesting, when it may be remembered that the late Dr. Graham held the view that potash-alum might be split up into its constituents by the process of dialysis. The alum solution used in my experiments was saturated at 90°C .

Other Observations on Supersaturated Alum Solutions.—In connection with the main object of the examination of these solutions, certain other experiments were made which yielded results of sufficient interest to warrant their being mentioned. Cold saturated solutions of potassium and aluminium sulphates at a temperature of 15°C . were mixed together, when it was observed that considerable rise in temperature took place, amounting generally with the mass of substance used to about 15° . At the same time a deposition of crystals took place which on examination were found to be alum, corresponding to the composition $\text{AlK}(\text{SO}_4)_2, 12\text{H}_2\text{O}$. These experiments were repeated many times, the result always being the same.

Some very curious peculiarities were observed with an alum solution saturated at 95° , a temperature slightly higher than that at which the ordinary solutions were prepared. This solution was stoppered with cotton-wool in the ordinary way, and set aside to cool. When it had attained a temperature nearly that of the surrounding air, small opaque crystals began to form in the liquid, and crystallisation gradually proceeded, without, however, the production of heat-currents in the liquid, which is so marked an accompaniment of the more rapid crystallisation from a supersaturated solution. In about four hours the whole contents of the flask, except a thin layer at the bottom, were apparently perfectly solid and the flask quite cold. On touching the solid, however, with a glass rod, and finally stirring the pasty contents of the flask, a great evolution of heat took place, equal to that observed in the ordinary crystallisation of a supersaturated solution of alum. The formation of the crystals in this case was extremely peculiar, and appeared to be accompanied by some contraction causing the mass to creep away from the sides of the flask, which contraction might possibly account for the non-evolution of any large quantity of heat during solidification.

As the same phenomenon was observed with this solution over and over again on its cooling, I determined to examine the crystals deposited by suddenly breaking the flask, and washing its solid contents with ice-cold water. This was accordingly done, and the crystalline

mass, after air-drying, yielded on analysis numbers very closely corresponding with ordinary alum. An examination of the crystalline form of the body deposited showed, however, that the aggregation of the crystals was quite different from the formation deposited from a proper supersaturated solution, the crystals being small, and arranged in tree-like forms like ammonium chloride. It is difficult, however, to examine them accurately, as on touching or moving they are converted into the usual octohedra of alum. From these last-mentioned experiments it would appear that above, say 90° , the limit of supersaturation for alum is passed. There is also some indication of a dimorphous form of alum existing. Another fact with regard to this alum-solution may be mentioned, viz., that after it had solidified, on immersing the *cold* flask in boiling water to remelt the salt, it was observed; first, that the water continued to boil, and, secondly, that the contents of the flask underwent reliquefaction after about ten minutes' immersion; whereas, in ordinary cases, the solution of the same quantity of deposited alum is very gradual, and would take about sixty minutes.

I was anxious to compare the alum experiments with the double sulphates formed from protoxides of the same group, such as the double sulphates of iron and zinc with potassium sulphate, of the general formula $M''K_2(SO_4)_2 \cdot 6H_2O$, but it was found that these sulphates have no tendency to undergo supersaturation—at least to an extent sufficient for our experiments.

I next prepared a supersaturated alum solution by dissolving equivalent quantities of $Al_2(SO_4)_3 \cdot 18Aq$ and K_2SO_4 in a quantity of water exactly corresponding with that which would have been necessary for the solution, had crystallised alum been used instead of the constituents separately. It was found, however, that with the two salts taken separately in the manner described, the quantity of water was not sufficient for their entire solution, and had to be increased by an amount corresponding with nearly one-half of the original quantity taken, before perfect solubility could be obtained. With this solution, however, it was found that neither crystals of $Al_2(SO_4)_3 \cdot 18H_2O$ nor K_2SO_4 were at all active; but the moment it was touched with $AlK(SO_4)_2 \cdot 12H_2O$, the liquid became filled with crystals of alum.

Being unable to obtain good supersaturated solutions of the double sulphates represented by the general formulæ $M''K_2(SO_4)_2 \cdot 6H_2O$ and $M''M''K_4(SO_4)_4 \cdot 12H_2O$, which have been described by Vohl (*Annalen*, 95), I determined to try some experiments with a double sulphate of zinc and copper, known as Lefort's salt, the composition of which, according to that author, is $Zn_3Cu(SO_4)_4 \cdot H_2O$, and which will undergo recrystallisation without decomposition.

Quantities of this salt were dissolved in rather less than half their

weight of water, zinc sulphate ($\text{ZnSO}_4, 7\text{H}_2\text{O}$) and copper sulphate ($\text{CuSO}_4, 5\text{H}_2\text{O}$) being employed as the nuclei.

In these cases both the constituents were active in causing crystallisation, that from the zinc sulphate nucleus being more rapid than that from the copper sulphate nucleus. An examination of the crystals deposited showed that they were crystals of the double salt, and their deposition presented some very peculiar phenomena. When the zinc sulphate was employed, the crystals of the double salt are formed first in long shaped needles, closely resembling those of $\text{ZnSO}_4, 7\text{H}_2\text{O}$; this form is retained till the crystallisation is very nearly at an end, but shortly afterwards the crystals gradually begin to change, and break up into truncated needles exactly similar to Lefort's salt.

In the case of the copper sulphate nucleus, the deposition of the salt was slower, and the crystals, though not doubly oblique like $\text{CuSO}_4, 5\text{H}_2\text{O}$, were truncated needles, and never came down in long needles as in the first mentioned case. The deposit here was also found to be the double salt.

From these experiments it will be seen that the nucleus in certain cases exercises a determining influence on the crystals of the body deposited, in a manner similar to some other cases mentioned in my first paper.

This I think may be due, at least in the case of the zinc sulphate, to the nucleus of that salt beginning the action by separating first $\text{ZnSO}_4, 7\text{H}_2\text{O}$ crystals; but the forms of both the constituents being to a certain extent similar, it gradually induces the crystallisation of the copper salt as well, and the double salt is deposited.

Some curious phenomena were to be observed in the deposition of the crystals from these solutions, when the nucleus became detached from the introducing tube and fell to the bottom of the flask. In such cases when the nucleus was moved along the bottom of the flask by slightly inclining it, crystallisation was observed to take place, first along the line upon which the nucleus had travelled, and it was some little time before crystallisation extended in other directions throughout, showing that crystalline activity had been induced directly by the nucleus.

Experiments with Microcosmic Salt, $\text{Na}(\text{NH}_4)\text{HPO}_4, 4\text{Aq}$.

The experiments on solutions of this body were made in the same way as on the other substances, the nuclei being added both with the syphon-tube and with the bulb-tube.

Substance in solution.	Nucleus added.	Result.
$\text{NaNH}_4\text{HPO}_4, 4\text{H}_2\text{O}$..	$\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$..	Inactive.
.. ..	$(\text{NH}_4)_2\text{HPO}_4$
.. ..	$(\text{NH}_4)\text{H}_2\text{PO}_4$
.. ..	$\text{Na}_4\text{P}_2\text{O}_7$

It was found extremely difficult to obtain the ammonium phosphates free from sodium, many weeks being taken up in preparing good samples. They were finally obtained by neutralising perfectly pure phosphoric acid by ammonium carbonate. There are also several points with regard to the composition of the ammonium phosphates, which require further investigation.

In the case of microcosmic salt, on attempting to form it from cold saturated solutions of the disodic and diammonic phosphates, the same result was observed as in the case of alum, the solution when brought in contact undergoing a considerable rise in temperature, and crystals of microcosmic salt being deposited. The rise in temperature in these cases was less than in the alum experiments, being generally an increase of from 10° to 12° .

In connection with these double phosphate experiments, others were made with the double arsenate of sodium and ammonium, with the following results:—

Substance in solution.	Nucleus added.	Result.
$\text{NaNH}_4\text{HASO}_4 \cdot 4\text{H}_2\text{O} \dots$	$\text{Na}_2\text{HASO}_4 \cdot 12\text{H}_2\text{O} \dots$	Inactive.
„ ..	$(\text{NH}_4)_2\text{HASO}_4 \cdot 4\text{Aq}_2 \dots$	„

In these cases both constituents were inactive to the double salt, as in the case of the alum and the phosphates.

Action of the Constituents on Supersaturated Solutions of Double Tartrates and Citrates.

It is not easy to find double salts of organic acids which will undergo supersaturation without passing into a gummy consistency which precludes experiment. The substances, however, which we have been able to employ are the double tartrate of sodium and potassium or Rochelle salt ($\text{KNaH}_4\text{C}_4\text{O}_6 \cdot 4\text{Aq}$); the double potassium and sodium citrate, $\text{K}_3\text{Na}_3(\text{H}_5\text{C}_6\text{O}_7)_2$; and the double magnesium and sodium citrate, $\text{MgNaH}_5\text{C}_6\text{O}_7$. The methods of adding the nuclei were similar to those employed in the other cases, as the constituents undergo supersaturation with great readiness.

With Rochelle salt the following results were obtained:—

$\text{KNaH}_4\text{C}_4\text{O}_6 \cdot 4\text{Aq} \dots$	$\text{K}_2\text{H}_4\text{C}_4\text{O}_6 \dots$	Inactive.
„ ..	$\text{Na}_2\text{H}_4\text{C}_4\text{O}_6 \dots$	Active.

The sodium tartrate was specially made and perfectly purified. In all these cases crystallisation from the sodium tartrate took place, but never from the potassium tartrate. It now became important to examine if possible the composition of the crystals which were gradually deposited from the nucleus. For this purpose experiments

were carefully performed in flasks containing the Rochelle salt, to which the nuclei of neutral sodium tartrate were added by means of the syphon-tubes. The crystals gradually and slowly formed from the point of the syphon-tube, and were allowed to grow till a considerable cluster had formed, and a great part of the salt had been thus removed from the solution in the flask. The deposit adhering to the syphon-tube was withdrawn from the mother-liquor removed from the flask, washed with ice-cold water, pressed between blotting-paper, air-dried, and analysed. On analysis the deposit gave numbers closely agreeing with the composition of Rochelle salt.

Now it is to be observed that the crystals forming the deposit here in no wise resemble those of Rochelle salt, but closely resemble those of sodium tartrate, giving us evidence of the probable dimorphism of Rochelle salt. We have also to note that if the crystals formed by the nucleus of sodium tartrate are allowed to grow till the contents of flask are nearly solid, and then rinsed from the mother-liquor, this mass being then stirred, a sudden and considerable amount of heat is evolved, as in the case of the alum solution before mentioned. After stirring the mass and examining the crystals by the microscope, they present the appearance of ordinary Rochelle salt.

At present it is difficult to see why the sodium tartrate should be active and the potassium salt inactive, but it may be remarked that the solubility of the sodium salt is less than that of the potassium salt, which may perhaps account for its activity. A corresponding result has been observed with the citrate of potassium and sodium, in which the sodium citrate has always proved active, whilst the potassium salt is inactive. Here also the solubility of the potassium salt is greater than that of the corresponding sodium salt.

In the case, however, of the double magnesium and sodium citrates, the results were different, both of the constituent salts proving inactive to the double salt.

From these experiments it will be seen that the double salts of monobasic acids apparently suffer disruption more easily than the salts from acids of higher basicity like sulphuric and phosphoric acids; but that in the case of the first of these two latter acids, salts may exist, like Lefort's salt, which is acted upon by the constituents.

It will be observed, however, that such salts indicate more of molecular than of atomic grouping in their constitution, whereas in the true alum and double phosphate we have a firmer union of the salts. This is also, I think, to be observed in the salts from the organic acids. By its mode of formation and its composition, the double sodium and potassium citrate appears more like a molecular grouping of the constituent salts, and both constituents are capable of causing disruption, whereas in Rochelle salt and the magnesio-sodic

citrate, there is evidence of a closer binding of the component salts. In the case of Rochelle salt, only one constituent produces disruption, and in the case of the magnesio-sodic citrate, neither constituent has any action. It is to be hoped that further experiments carried out on these solutions may assist in the examination of the condition of such salts when in a state of solution.

I am at present engaged on certain experiments with regard to the amount of heat evolved in the crystallisation of these compound salts, and comparing the numbers obtained in the different groups of salts. These experiments take much time to carry out, but I hope soon to be in a position to lay the results before the Society.
