CCCXLVII.—*Studies of Precipitated Solids. Part I. Strontium Sulphate.*

By Bertram Lambert and William Hume-Rothery.

In Gmelin and Kraut's "Lehrbuch der Chemie" it is stated that "strontium sulphate is formed as a white powdery precipitate by adding dilute sulphuric acid, or other sulphate, to a dilute solution of a strontium salt . . . or, if concentrated solutions are used, as an amorphous, flocculent precipitate, becoming crystalline." No reference has been found to any detailed or systematic study of the effects of the conditions of precipitation upon the type, nature, and size of the precipitated particles of strontium sulphate. In the present work, the effects of variations in the concentration, temperature, cation, and anion of the precipitating solutions have been investigated within the following limits:

(*a*) Temperature of precipitation, from 0° to 100°.
(*b*) Concentration of solutions, from $0{\cdot}01N$ to $3{\cdot}47N$.
(*c*) Cations of the sulphate solution, $H^{\bullet}$, $Na^{\bullet}$, $Mg^{\bullet\bullet}$, $Al^{\bullet\bullet\bullet}$.
(*d*) Anions of the strontium salt solution, Cl', NO_3', $CH_3{\cdot}CO_2'$.
(*e*) Times of exposure of precipitate to mother-liquor, from shortest possible time up to one week.

All the materials employed were very carefully purified and tested before use, and the concentrations of the solutions checked from time to time; the precipitations were carried out in carefully cleaned and steamed glass vessels; the temperatures of precipitation were controlled to within ± 1°, and great care was taken to prevent alterations in the concentration of the solutions—an important point when working at the higher temperatures.

Owing to the rapid changes undergone by the precipitate, when left in contact with the mother-liquor—in some cases 10 seconds' exposure caused profound alteration—a quick method of filtration had to be used: this was achieved by using "alundum" filtering cones and a rapid-acting filter-pump.

All precipitates were examined microscopically in ordinary and in polarised light, a microscope with a rotating stage being used for measurement of the angles of the crystals. The procedure adopted, and found very satisfactory, for mounting the precipitates prior to examination was as follows: A portion of the washed precipitate was transferred to a watch-glass and stirred with a little pure alcohol (this was definitely proved to have no action on the precipitate); a drop of this suspension was placed on a microscope slide and, after careful evaporation of the alcohol, a cover-glass was adjusted over the precipitate and effectively sealed round the edges with Canada balsam.

I. *Effects of Variations in the Concentration of the Solution, and in the Temperature of Precipitation, upon the Type of the Precipitated Particles.*

Equal volumes of equivalent solutions of strontium chloride and sulphuric acid were used throughout this section of the work, the sulphate solution being added to the strontium salt solution in all cases. The results of more than 350 experiments may be summarised as follows :

(1) *Precipitates obtained with* 3·47N—0·35N-*Solutions.*—At all temperatures from 0° to 100° the *initial* precipitate produced was voluminous and flocculent in appearance, and occupied the whole volume of the solution. This bulky precipitate consisted of fine, needle-shaped crystals, usually too narrow for measurement and of a length dependent upon the conditions of precipitation (see p. 2643). On standing in contact with the mother-liquor, the bulky, flocculent form of precipitate was transformed into a fine, powdery form occupying a small volume and consisting of crystalline particles belonging to the rhombic system. For the present, these two types of precipitated strontium sulphate will be referred to as " needles " and " rhombs," respectively. The rate of change needle$\longrightarrow$rhomb was markedly increased by rise of temperature and, to a less extent, by the increase in the concentration of the mother-liquor (hydrochloric acid). At 100°, the change was complete in 10 seconds. The needle-shaped particles are illustrated (× 200) in Fig. 6.

(2) *Precipitates obtained with* 0·35N—0·125N-*Solutions.*—Between these concentrations the formation of needles was confined to limited ranges of temperature dependent upon the concentration. This may be illustrated by consideration of the results obtained with 0·25*N*-solutions. At 0°, the *initial* precipitate consisted entirely of rhombs and contained no needles; at 50°, slight flocculation was observed in the initial stages of precipitation and needles were found in the mounted precipitate; as the temperature of precipitation was raised, flocculation became more and more marked and a larger proportion of needles was found in the precipitate; at 85°, flocculation abruptly ceased and the initial precipitate formed between this temperature and 100° consisted entirely of rhombs.

Similar results, with different temperature limits, were obtained with 0·15, 0·2, and 0·3*N*-solutions, and it was thought that there might be a definite range of temperature within which a solution of given concentration would give both types of precipitate as the product of *initial* precipitation. Careful experiments showed, however, that this was not so : the upper temperature limit of needle formation altered considerably from time to time, and it was conclusively proved that identical solutions would yield different results in different laboratories owing, it is supposed, to the effect of nuclei of crystals in the air.*

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* Compare Johnson, Mervin, and Williamson (*Amer. J. Sci.*, 1916, **41**, 473), who found that the transition temperature between the calcite and aragonite forms of precipitated calcium carbonate varied from time to time.

(3) *Precipitates obtained with Solutions of Concentration less than* 0·125N.—Under these conditions of concentration the precipitates produced at all temperatures between 0° and 100° consisted entirely of rhombic particles; there was a complete absence of flocculation and no needles were ever observed in the precipitate.

It appears, then, that two definite crystalline types of strontium sulphate are produced by direct precipitation—one consisting of rhombic and the other of needle-shaped particles; the latter type is unstable and undergoes transformation into the more stable rhombic type of particle at speeds dependent upon the concentration of the mother-liquor and, to a greater extent, upon the temperature. The formation of the unstable type of precipitate is confined to solutions of greater concentration than 0·125*N* and is always accompanied by flocculation. Flocculation is completely absent when the initial product of precipitation consists only of rhombic particles, and the particles produced under these conditions are remarkably regular in size. The rhombic particles formed by the transformation of needle-shaped particles are irregular in size and markedly larger except when formed at low temperatures. For instance, with 0·25*N*-solutions the rhombic particles produced by the initial precipitation above 90° were of average size 10 μ and maximum 11·5 μ; those formed by transformation of needle-shaped particles precipitated at about 80° were of average size 15 μ and maximum 25 μ.

FIG. 9.

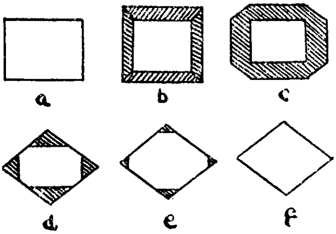
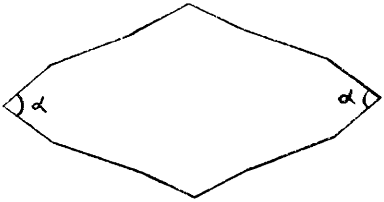


FIG. 10.



The Nature of the Rhombic Particles.—The rhombic particles produced both by direct precipitation and indirectly from the needles varied greatly in form. Examination showed that these variations were not due to the production of essentially different crystalline particles, but to the gradual development of new faces on one and the same fundamental crystalline form, which belonged to the rhombic system and was identical with that of the mineral celestine.

Fig. 9 shows the effect of temperature on the shape of the rhombic

PLATE I

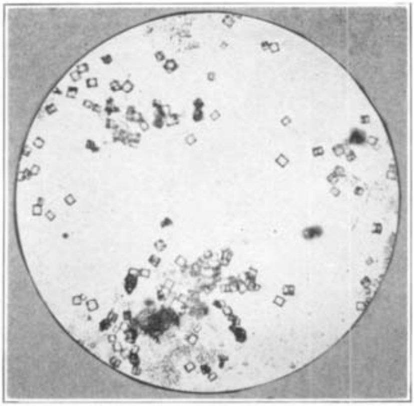


FIG. 1. × 200.

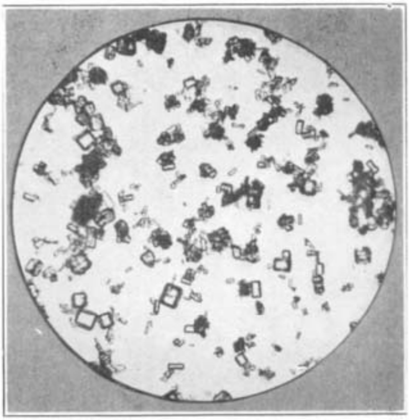


FIG. 2. × 200.

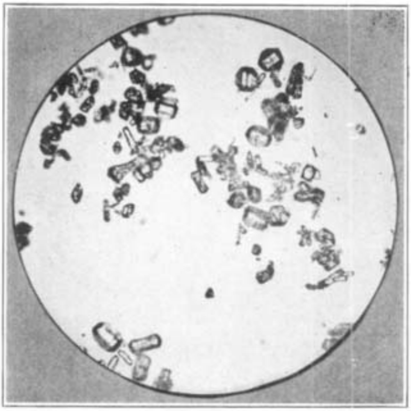


FIG. 3. × 200.

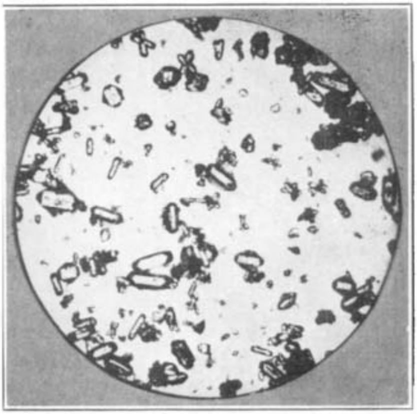


FIG. 4. × 200.

[*To face p.* 2640.]

PLATE II

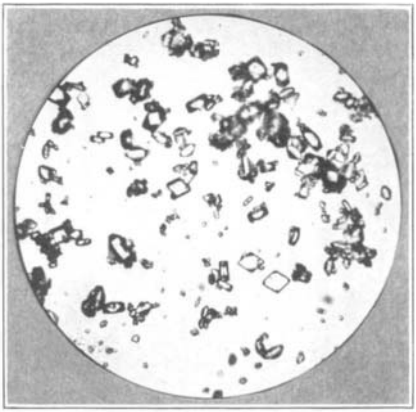


FIG. 5. × 200.

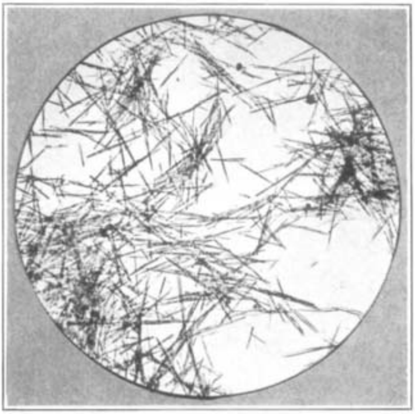


FIG. 6. × 200.

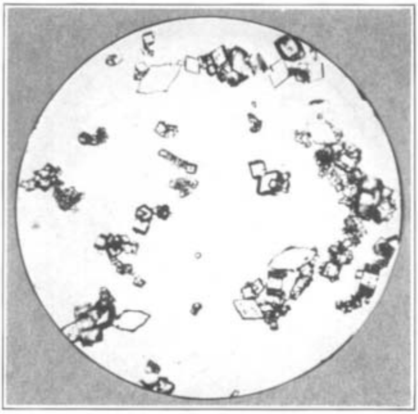


FIG. 7. × 200.

FIG. 8. × 200.

particles produced (indirectly from the needle variety) by precipitation with $3{\cdot}47N$-solutions of strontium chloride and sulphuric acid. At 0°, the particles were strictly rectangular in form, and when viewed through the microscope appeared as in Fig. 9*a*. On raising the temperature of precipitation, a new face began to make its appearance along the edges of the rectangular plate until, at 35°, the particles appeared as in Fig. 9*b*, in which the shaded portion is regarded as sloping downwards from the plane of the paper. At about 50° a new face began to appear along those edges of the plate perpendicular to the plane of the paper as shown in Fig. 9*c*. This face became more and more predominant as the temperature of precipitation was raised from 50° to 100°, the particles passing through the stages shown in Fig. 9*d*, *e*, and *f*, the pure rhombic form making its appearance at about 100°. This series of changes is shown for the $3{\cdot}47N$-solutions in Figs. 1 to 5, which represent the products of precipitation at 0°, 35°, 50°, 75°, and 100°, respectively.*

Alterations in concentration of the precipitating solutions also tended to produce a similar series of changes, increasing dilution favouring the production of the perfect rhombic form, but this effect was not so marked as that of temperature.

The rhombic crystals shown in Fig. 5 were identified with the celestine system by measurements of index of refraction (1·62—1·63), optical behaviour in polarised light, and measurements of their angles ($75° \pm 1°$ as compared with 75° 50′ for celestine). The 75° rhombs were also found to be anhydrous; in their various modifications, they were produced as the sole constituent of the final precipitate with solutions of strontium chloride and sulphuric acid of concentrations between the following limits: $0{\cdot}01N$ to $0{\cdot}05N$ at high temperatures, and $0{\cdot}35N$ to $3{\cdot}47N$ at all temperatures.

Between the limits $0{\cdot}35N$ to $0{\cdot}05N$, however, a second series of rhombic particles made its appearance, having an angle $55° \pm 1°$, whilst in experiments with other cations and anions (see later) a third series, having an angle $43{\cdot}5 \pm 1°$, was observed. These were all identified as further examples of the celestine series on the following grounds:

(1) Their index of refraction and optical properties agreed with those of celestine, and they were all anhydrous.

(2) If all three series belong to the same crystal system, a simple relation should exist between $\tan \frac{1}{2}(75°)$, $\tan \frac{1}{2}(55°)$, and $\tan \frac{1}{2}(43{\cdot}5°)$. The actual values are 0·767 : 0·520 : 0·399 or 3 : 2 : 1·5 approximately.

(3) In certain cases in which both 75° and 55° rhombs were

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* These rhombic particles were of course formed indirectly from the needles, but the same effect was observed for the rhombs produced by direct precipitation in the more dilute solutions.

produced, a number of exceptionally interesting crystals were formed which appeared to be a " transition form " between the two types. The shape of the crystals is shown in Fig. 10, the angles denoted by α being approximately 75°, indicating the connexion with the celestine form. Fig. 7 contains three clear examples of these interesting crystals, which are rarely met with.

A corresponding transition form was found for the 43·5° rhombs and is shown in Fig. 8, the angle α again being approximately 75°.

These facts indicated that the 75°, 55°, and 43·5° rhombs all belonged to the celestine system, and this was confirmed by the fact that the 55° and 43·5° rhombs underwent the process of modification shown in Fig. 9. In these cases, the rectangular forms were not observed, but forms corresponding to Fig. 9*c*, *d*, *e*, and *f* were observed for the 43·5° and 55° rhombs just as with the 75° rhombs. On the other hand, some of the 55° rhombs, and particularly the modified 55° rhombs, became opaque after keeping for some time on the micro-slides, indicating that they were unstable. This fact was not satisfactorily accounted for, but it is possible that there were really two series of rhombs of approximately the same angle.

The Nature of the Needle-shaped Crystals.—The needle-shaped crystals were identified as a new hydrated form of strontium sulphate on the following grounds :

(1) They were more strongly doubly-refracting than the celestine rhombs.

(2) The index of refraction of the needles (estimated by observing their appearance when immersed in standard oils) was 1·55 approximately; the interference colours showed that the index of refraction in the direction of their length was greater than that at right angles to the length, but the exact values could not be determined.

(3) The needles were decomposed on keeping over sulphuric acid and also on exposure to air.

Attempts were made to analyse the needles, but these were unsuccessful because it was impossible to dry the specimen without causing some dehydration.

II. *Effects of Variation in* (1) *the Cation of the Sulphate Solution and* (2) *the Anion of the Strontium Salt Solution on the Type of the Precipitated Particles.*

Numerous experiments were carried out over ranges of concentration from 0·1 to 1·0*N* and over ranges of temperature from 0° to 100°. The following is a summary of the points established.

(1) Using solutions of the sulphates of sodium, magnesium, and

aluminium (to study the effects of uni-, bi-, and ter-valent cations), the strontium salt solution being the chloride :

(*a*) Needles (with flocculation) were produced at lower concentrations with sodium and magnesium sulphates than with sulphuric acid. Aluminium sulphate more closely resembled sulphuric acid.

(*b*) The limits of concentration and temperature within which the different types of rhombs appeared were different in each case, but no generalisations could be made. In all cases, however, the various types of rhombs underwent the transformation shown in Fig. 9—rise of temperature and decrease in concentration favouring the formation of the perfect rhombic particle : this appears to be a general rule for all the rhombic particles of strontium sulphate.

(2) Using solutions of strontium chloride, nitrate, or acetate, and sulphuric acid :

(*a*) Under comparable conditions of temperature and concentration the nitrate behaved, in general, like the chloride.

(*b*) With strontium acetate solution the formation of needles (with flocculation) took place in solutions as dilute as 0·1*N*. At 100°, rhombs alone were produced as the initial product of precipitation at all concentrations.

III. *Effects of Variations in Concentration, Temperature, Anion and Cation on the Size of the Precipitated Particles.*

Nearly 500 experiments were performed in this section, and the following summarises the conclusions which have been drawn, all remarks applying only to the particles of the initial precipitate and not to those formed by a secondary change.

(1) *Temperature Effects.*—(*a*) Under conditions when needles are formed, rise of temperature favours the production of longer and thicker needles, the effect being most marked at high concentrations. Thus, with 3·47*N*-solutions of strontium chloride and sulphuric acid the average needle length was 5, 5·5, 8, 13, and 15 μ at 0°, 25°, 50°, 75°, and 100°, respectively.

(*b*) Under conditions when rhombs are formed by direct precipitation, increase of temperature up to about 75° causes an increase in the size of the particle; but above 75° the effect is sometimes reversed. Thus with 0·1*N*-strontium nitrate and sulphuric acid solutions, the average size of the rhombs was 3, 6·5, 10, 11, and 7·5 μ at 0°, 25°, 50°, 75°, and 100°, respectively.

(2) *Concentration Effects.*—(*a*) Under conditions when needles are formed, increase of concentration causes the formation of a smaller needle, the effect being more pronounced at low than at high temperatures. Thus, at 0° the needle length was 15 μ and

5 μ for 0·5*N*- and 3·467*N*-solutions, but at 100° the lengths were 22 μ and 15 μ, respectively.

(*b*) Under conditions when rhombs are formed by direct precipitation, decreasing concentration leads to the formation of larger sized rhombs, but a limiting dilution is reached beyond which the effect is reversed. Thus at 100°, using 0·10, 0·05, 0·03, 0·025, 0·02, and 0·01*N*-solutions of strontium chloride, the sizes of the rhombs were 4, 6, 10, 8, 6, and 4 μ, respectively. As the temperature was lowered this limiting dilution moved towards higher concentration; thus, at 50° the maximum-sized rhomb was formed with 0·075*N*-solutions as compared with 0·03*N* at 100°.

(3) *Anion and Cation Effects.*—Under conditions when needles were formed, it was definitely established that the use of strontium acetate caused the formation of a much smaller needle than strontium nitrate or chloride under comparable conditions of temperature and concentration. A similar but much less pronounced effect was caused by substituting a metallic sulphate for sulphuric acid. The fact that three types of rhombs were produced makes it impossible to draw any definite conclusions about cation and anion effects when rhombs were formed.

IV. *The Effects of Variations in the Anion and Cation of the Precipitating Solutions on the Velocity of Precipitation.*

It was of interest, in connexion with the theory of precipitation, to study the effects of variation in the conditions of precipitation upon the time which elapses before the precipitate becomes visible, since strontium sulphate is one of the few substances suitable for such an examination.

A considerable number of experiments were carried out with 0·25*N*- and 0·10*N*-solutions. The results may be summarised as follows :

(1) *Cation Effects.*—Strontium chloride solutions were used and sulphates with the cations $H^{\cdot}$, $Na^{\cdot}$, $Mg^{\cdot\cdot}$, and $Al^{\cdot\cdot\cdot}$. At 25°, 50°, 75°, and 100°, the times before appearance of the precipitate definitely increased with variations in the cations in the order $Na^{\cdot} < Mg^{\cdot\cdot} < Al^{\cdot\cdot\cdot} < H^{\cdot}$ when 0·25*N*-solutions were used. At 0°, the order was the same except that aluminium sulphate precipitated more slowly than sulphuric acid. With 0·10*N*-solutions, the order of increase in the times of appearance of the precipitate was the same at temperatures above 75°, but, at lower temperatures, $H^{\cdot}$ caused more rapid precipitation than any of the other cations.

(2) *Anion Effects.*—Sulphuric acid solutions were used and strontium salts with the anions Cl', NO_3', $CH_3{\cdot}CO_2'$. At all tem-

peratures the times before appearance of the precipitate definitely increased with variations in the anion in the order $CH_3{\cdot}CO_2' < Cl' < NO_3'$, using 0·25*N*-solutions. With 0·10*N*-solutions, the order of increase in the times of appearance of the precipitate was the same at temperatures above 50°, but was less definite below this temperature.

The theoretical significance of these results is discussed below.

Discussion.

The mechanism of precipitation of solids is very far from being a simple process, but it would seem that some light can be thrown on the subject by a consideration of the results obtained in this work. Von Weimarn (*Kolloid Z.*, 1909, **5**, 221) has shown that there is considerable evidence for the existence of an intermediate colloid stage in the formation of precipitates, and the results obtained from the study of the precipitates of strontium and calcium sulphates (the latter is considered in the following paper) afford strong support for this theory.

If von Weimarn's conception is valid, we may reasonably assume that the process of precipitation from solution takes place in the following stages: (1) Collisions of ions to form molecules of the insoluble substance; (2) aggregation of these molecules to form a disperse system (colloidal solution); (3) precipitation of the colloid (from sol to gel in some cases)—effected and affected by the remaining ions in the mother-liquor; (4) further aggregation of the colloid particles to form visible particles of solid; (5) changes of the solid particles owing to contact with the mother-liquor (formation of more stable forms, crystal growth, etc.).

The interpretation of experimental results will generally offer difficulties, since alteration in the conditions of precipitation may affect the velocity of any one or all of these stages. If, under a given set of conditions, any one of these stages is the predominant factor in the process of precipitation, the results obtained within such a range of experiment may throw some clear light on the subject. In this connexion, let us consider stage (3) of the process of precipitation.

It is known that barium sulphate forms a positively charged colloid (Kato, *Mem. Coll. Sci. and Eng. Kyōtō*, 1909—1910, **2**, 187; Feilman, *Trans. Faraday Soc.*, 1909, **4**, 176; Recoura, *Compt. rend.*, 1908, **146**, 1274) and it might reasonably be assumed that the analogous strontium sulphate, in the colloidal state, will have the same kind of charge. With a given anion, therefore, it is to be expected that the time taken for stage (3) of the precipitation will depend upon the protective power of the cation for a positive colloid.

In Section IV we have seen that, using 0·25*N*-solutions of strontium chloride and precipitating with equivalent solutions of sodium, magnesium, aluminium, and hydrogen sulphates (in this order) at temperatures from 25° to 100°, a definitely increasing time was required for the appearance of the precipitate. Now this same order—$Na^{\cdot} < Mg^{\cdot\cdot} < Al^{\cdot\cdot\cdot} < H^{\cdot}$—is the order of increasing protective power of these cations for a positive colloid. It would seem, then, that at this concentration and within this temperature range, stage (3) is the predominant factor in the precipitation.

Similar experiments with 0·10*N*-solutions gave the same order when precipitation was carried out above 75°, but, at lower temperatures, the hydrogen ion appeared to be less protective in its action than the other cations and it would seem that stage (3) had ceased to be the predominant factor. In this connexion, it may be noted that the viscosities of salt solutions are generally greater than those of equivalent solutions of their acids, and this may be the reason that sulphuric acid precipitated faster than metallic sulphates in these dilute solutions in which the particles have to travel a comparatively great distance.

When considering the precipitating effect of anions on positive colloids, we should expect $CH_3{\cdot}CO_2'$, because of the known abnormally high precipitating power of organic anions, to cause more rapid precipitation than Cl' or NO_3', and this is in agreement with our experiments. The order of the velocity of precipitation of strontium sulphate in the presence of the anions $CH_3{\cdot}CO_2'$, Cl', and NO_3' is the order in which these anions occur in the lyophile series. It is claimed that these results afford substantial evidence of the validity of von Weimarn's conception.

In the interpretation of the results of our experiments on the factors which influence the size of the precipitated particle, we are faced with some difficult problems. It has been definitely established that increasing dilution of the precipitating solutions leads to the production of a progressively larger solid particle until a critical dilution has been reached beyond which further dilution has precisely the opposite effect [see III, (2), (*b*)]. At first sight, it might appear that the effect of concentration was a simple result of the alteration in the velocity of precipitation, since rapid crystallisation is known to favour the formation of smaller crystals; but this simple conception is clearly not in accordance with the results obtained at great dilution. Further, increasing the temperature of precipitation undoubtedly increases the velocity of precipitation and should, on the same reasoning, lead to the formation of smaller particles; but there is no doubt that, in general, increasing temperature tends towards the precipitation of a larger and not a smaller particle [see III, (1)].

Owing to surface energy effects the particles of a precipitate will tend to be as large as possible, but it is reasonable to suppose that there may be two main factors influencing their size : (*a*) Velocity of precipitation—increase of which favours a smaller precipitated particle; (*b*) facilities for diffusion—increase of which favours a larger particle. The facilities for diffusion must be connected with the viscosity of the solutions and particularly of the mother-liquor.

Increase of temperature will cause an increase in (*a*) and (*b*), but the predominating effect would seem, in most cases, to concern (*b*). Increase in the concentration of the precipitating solution results in more rapid precipitation without, apparently, any marked compensating effect on the facilities for diffusion, and leads to the formation of smaller particles [see III, (2), (*a*)]. The apparent anomaly at extreme dilution can be explained by assuming that there is a limiting dilution at which the decrease in (*b*) overcomes the effect due to slower precipitation, owing to the fact that the molecules will have to diffuse a comparatively long distance to form a larger particle. Since rise of temperature favours diffusion, we should expect the limiting concentrations to become more dilute as the temperature rises, in agreement with our results [see III, (2), (*b*)].

Variations in the anions and cations will clearly affect (*a*) and (*b*), but, in general, stage (3) of the precipitation, as affected by the influence of the anions and cations on the positive colloid, appears to predominate.

Summary.

The effect of conditions of precipitation upon the form and nature of the precipitated particles of strontium sulphate has been examined. It has been shown that under certain conditions the initial precipitate consists of fine needle-shaped crystals of a hitherto unknown hydrated form of strontium sulphate, to which, however, it has not been possible to assign a formula. On standing in contact with the mother-liquor, the needles are transformed into stable rhombic crystals of anhydrous strontium sulphate (celestine), which are also sometimes formed as the initial product of the precipitation.

The examination of the anhydrous rhombic particles has yielded interesting crystallographic information, a regular series of changes in form taking place with changes in the temperature and concentration of the precipitants.

Observations on the times which elapsed before the appearance of the precipitate when different salts were used have led to the conclusion that the precipitation takes place through the medium of a colloidal form carrying a positive charge, the colloid being precipitated more or less rapidly according to the protective or precipitative effects of the other ions present. This conception accounts completely for the relative velocities of precipitation in the more concentrated solutions, but in dilute solutions other effects, such as viscosity, play an increasingly important part in determining the relative times of appearance of the precipitate.

The sizes of the particles produced by direct precipitation have been shown to depend on two main factors : (1) the velocity of precipitation, increase of which leads to a smaller particle, and (2) the facilities for rapid diffusion, which favour a larger particle.

Our thanks are due to Dr. T. V. Barker for his help and interest in the crystallographic part of this work, and we wish also to express our thanks to the Government Grant Committee of the Royal Society for a grant which covered part of the cost of the work.

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