CCCXLVIII.—*Studies of Precipitated Solids. Part II. Calcium Sulphate.*

By Bertram Lambert and Robert John Schaffer.

Text-books on mineralogy describe a microchemical test for calcium involving the precipitation, under the microscope, of "radiating clusters of gypsum." Maschke and Vater (*Z. Kryst. Min.*, 1901, **33**, 57) investigated the form of the crystals which separated from saturated aqueous solutions of gypsum on evaporation at the ordinary temperature; they state that these crystals are prismatic in habit and usually simple in form, clusters being rarely formed and the crystals seldom twinned. Grengg (*Z. anorg. Chem.*, 1914, **90**, 327) described crystals of the hemihydrate $CaSO_4,\frac{1}{2}H_2O$ obtained by heating gypsum with various salt solutions. Copisarow (J., 1923, **123**, 796) described the formation of artificial alabaster by heating sodium sulphate and calcium chloride under pressure. He states that, in the precipitation of gypsum, no state of temporary supersaturation or gelatinisation could be observed, whereas, in the precipitation of calcium carbonate, a definite intermediate gelatinous form was seen. 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 calcium sulphate.

In this work, the effects of varying the conditions of precipitation have been investigated within the following limits :

(*a*) Temperature of precipitation, from 0° to 100°.
(*b*) Concentration of solutions, from 0·125*N* to 2*N*.
(*c*) Cations of the sulphate solutions, $H^{\cdot}$, $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$.
(*d*) Anions of the calcium salt solution, $CH_3{\cdot}CO_2'$, Cl', NO_3', H_2PO_2'.
(*e*) Time of exposure of precipitate to mother-liquor, from shortest time possible up to 7 days.

All the calcium salts were prepared from a quantity of specially selected Iceland spar, these salts and all other materials used being very carefully purified. The method of experiment was substantially the same as that used in Part I (preceding paper). The results are conveniently described under three main headings.

I. *The Chemical Composition of the Precipitated Particles.*

Using equivalent quantities of any one pair of precipitants, it was possible (except in one case) to obtain precipitated calcium sulphate either in the form of the dihydrate ($CaSO_4,2H_2O$) or the hemihydrate ($CaSO_4,\frac{1}{2}H_2O$). Below a certain temperature the precipitate consisted of different forms of the monoclinic dihydrate, whilst, above this temperature, acicular crystals having straight extinction were produced; the latter were shown to be the hemihydrate. There was no evidence for the formation of a crystalline form of the dihydrate with straight extinction (compare Davis, *J. Soc. Chem. Ind.*, 1907, **26**, 726). It was definitely established that the stable phases above and below this temperature were the hemihydrate and dihydrate, respectively; the precipitate could be made to undergo the reversible change, $CaSO_4,2H_2O \rightleftharpoons CaSO_4,\frac{1}{2}H_2O + 1\frac{1}{2}H_2O$, at this temperature, the change from hemihydrate to dihydrate being very rapid in comparison with the reverse change. This transition temperature was not, however, the same for different pairs of solutions, as is shown by Table I.

TABLE I.

Transition Temperature.

(Concentration 2*N*.)	Calcium acetate.	Calcium chloride.	Calcium nitrate.
Sulphuric acid	88°	96°	96°
Sodium sulphate	75	80	80

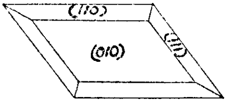
Precipitation with solutions of calcium nitrate and aluminium sulphate was unique in that crystals of the dihydrate were formed at all temperatures up to 100° and no crystals of the hemihydrate could be found in the product even after keeping at 103° for several hours. Crystals of the dihydrate remained unchanged when heated with distilled water at 100° for several hours, although Davis (*loc. cit.*) claims to have brought about the transition in this way. In all the cases examined, with the exception of the above, the transition temperature lay between 75° and 96°.

Changes in the concentration of any given pair of precipitating solutions had little or no effect on the transition temperature; appreciable alterations in the transition point were produced only by changes in the nature of the precipitating solutions.

II. *The Crystalline Character and Size of the Precipitated Particles.*

(a) *The Hemihydrate.*—The hemihydrate was usually precipitated as acicular crystals having straight extinction. On standing in contact with the mother-liquor, these developed sufficiently for their hexagonal form to be observed. With certain precipitants, *e.g.*, calcium acetate and sulphuric acid or sodium sulphate, the crystals were precipitated as hexagonal prisms similar to those produced by Grengg by heating gypsum with various salt solutions (Fig. 1). The length of the crystals varied considerably (8 μ—1000 μ), but no simple relation was found between their size and the conditions of precipitation.

Fig. 1.



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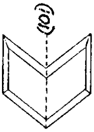

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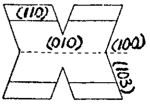

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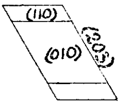

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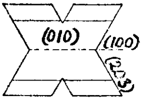

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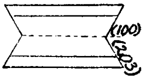

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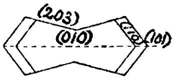

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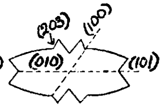

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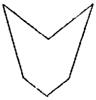

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(b) *The Dihydrate.*—Crystals of the dihydrate could be obtained by direct precipitation below the transition temperature or indirectly from the hemihydrate by precipitation above the transition point and subsequent cooling. The crystals obtained indirectly were always larger and more perfectly developed than those formed by direct precipitation. In either case they always occurred together in both simple and twinned forms [compare Maschke and Vater (*loc. cit.*)]. The size of the particles precipitated directly under any given conditions varied between very wide limits (2μ to $100\,\mu$), and this, together with the simultaneous formation of twinned crystals, made it impossible to trace any simple correlation between the conditions of precipitation and the average size of such particles : increase in the temperature of precipitation and decrease in the concentration of the precipitating solutions led—as appears usually to be the case—to an increase in the average size.

Again, no definite information could be obtained as to the factors influencing the relative numbers of simple and twinned crystals, but it was observed, qualitatively, that rapid precipitation [from reacting solutions of high concentration, or by using salts promoting rapid precipitation (p. 2653)] at the ordinary temperature favoured the formation of simple crystals, and slow precipitation the formation of twinned crystals. The governing factor cannot, however, be simply the velocity of precipitation, since increase in temperature (which increases the velocity of precipitation) favours the formation of twinned and not of simple crystals.

Maschke and Vater (*loc. cit.*) state that the "uninfluenced" form of simple gypsum crystals obtained by evaporation of aqueous solutions of calcium sulphate is (110)(010)(101). The simple crystals obtained by precipitation were not of this form : the faces $(111)(1\bar{1}1)$ were developed and so the crystals have the form (110)(010)(111) (Fig. 2). The twinned crystals were also of the same form. As a rule, the twinned crystals formed by direct precipitation were of the "arrow-head" type, the twin plane being (101) (Fig. 3), but at temperatures immediately below the transition point similar twins on (100) were sometimes observed. Similarly, twinned crystals of the dihydrate formed indirectly were twinned either on (100) or on (101), twins on (100) occurring much more frequently when formed indirectly than when formed directly.

The simple crystals, whether formed directly or indirectly, were always prismatic in the direction (100) and variations in the temperature and concentration of the precipitating solutions had no effect on their habit; but the effect of similar variations on the habit of the twinned crystals was well marked. When precipitated from solutions of calcium chloride or nitrate by means of sulphuric acid at temperatures from 0° to 50°, the twinned crystals were either tabular or somewhat prismatic in the direction of the twin plane (101); at these lower temperatures, their habit was not affected by changes in the concentrations of the precipitating solutions. When precipitated from the same solutions at higher temperatures, the habit of the twinned crystals was definitely affected by the concentration of the precipitating solutions; the crystals were tabular in habit when precipitated from concentrated solutions, but those precipitated from dilute solutions were prismatic in the direction of (100).

When twinned crystals were precipitated from calcium chloride or nitrate solutions by solutions of metallic sulphates, the twins were always tabular in habit.

The above remarks as to the form of the dihydrate crystals refer to precipitation in which the mother-liquor did not contain acetate ions; when this ion was present in any appreciable quantity, several new faces were developed on the crystals. In the presence of free acetic acid (*e.g.*, when equivalent quantities of calcium acetate and sulphuric acid were used), when the concentration of acetate ion was very small, the normal form (110)(010)(111) was precipitated. In the presence of greater quantities of acetate ion—whether added before the precipitation (by using excess of calcium acetate, or by introducing a soluble acetate into the precipitating solutions), or produced as a by-product of the reaction—new forms were obtained in which the faces (203) or (103) replaced (111)($1\bar{1}1$). The face (103) is found in natural crystals of gypsum, but (203) has not hitherto been described.

The crystals precipitated in the presence of acetate ion were, therefore, either (110)(010)(103) or (110)(010)(203); the former were always produced as cruciform twins, twinned on (100) as shown in Fig. 4, whilst the latter frequently occurred as simple crystals prismatic in the direction of (100) or (203) as shown in Fig. 5, as well as in a variety of twinned crystals depicted in Figs. 6, 7, 8, and 9.

When calcium hypophosphite solutions were used, equivalent quantities of the precipitants gave the normal type of dihydrate crystals, but a large excess of the hypophosphite gave similar results to those given by a low concentration of the acetate (Fig. 9). Apart from these two salts, however, the form of the dihydrate crystals was not affected by excess of any one of the precipitants.

It would seem as though the acetate ion has the power of exerting an orienting force sufficiently strong to determine the form of the precipitated crystals of calcium sulphate. The possibility that intramolecular forces play some part in determining crystal form is now being recognised, and Tutton ("Crystallography and Practical Crystal Measurement," 1922, p. 1417) has suggested that such forces may ultimately be traced to the electrons—probably those in the outer ring.

A study of the effects of leaving the precipitated dihydrate particles in contact with the mother-liquor led to some interesting observations and conclusions about crystal growth. It was observed, qualitatively, that larger and more regularly developed crystals generally resulted from such treatment, but no simple generalisation could be deduced as to how far this rate of growth depended upon the temperature, concentration, and composition of the mother-liquor.

Two interesting relevant points were (*a*) the development of solution faces and (*b*) the development of " arrow-head " twins.

(*a*) Whenever crystals were precipitated directly in a sufficiently developed state, the angle between (101) and (100) was clearly defined as a sharp point, but when the crystals were left in contact with the mother-liquor this sharp angle became rounded and, after a time, the faces $(\bar{1}11)(1\bar{1}1)$ were developed. In cases where the crystals under observation were too small for the pyramidal faces to be distinguished, the trace of $(\bar{1}01)$ was observed and the presence of $(\bar{1}11)(\bar{1}\bar{1}1)$ inferred by analogy with the larger crystals. This confirms the hypothesis that the rounded and water-worn faces $(\bar{1}11)(\bar{1}\bar{1}1)$—pyramidal faces on (101)—found on natural gypsum crystals are due to solvent action.

(*b*) The arrow-head twins were shown to be twinned on (101) and, since the simple crystals are holohedral, the edges of the twins should be parallel (Fig. 3). When first precipitated, this was not the case. Crystals of the form shown in Fig. 10 were produced, but on standing in contact with the mother-liquor the crystals grew until, ultimately, the edges were parallel. More than 250 measurements were made of the acute angle of the twinned crystals obtained at different temperatures and concentrations, both immediately after precipitation and after they had been left in contact with the mother-liquor for varying times. The figures obtained could be divided into five groups of 21°, 26°, 36°, 44°, and 52·5°, corresponding to the possible crystal faces (401), (301), (201), (302), and (101), respectively, the last being the normal face which was favoured by high temperature and low concentration of the precipitating solutions. A similar phenomenon was observed when simple crystals of sufficient size for measurement were precipitated at low temperatures. At high temperatures, the normal face was developed on the initial crystals.

We thus have a direct proof that gypsum crystals grow in stages, with the development of a possible crystal face at each stage, and that the generally accepted view that crystal growth takes place by the deposition of parallel layers is not always true.

III. *The Effect of Variations in the Anion and Cation of the Precipitating Solutions on the Velocity of Precipitation.*

The velocity of precipitation, measured by the time which elapsed between the mixing of the precipitants and the first visible appearance of the precipitate, varied not only with the temperature and concentration of the solution, but also with the anion and cation of the precipitants. The latter variations are of interest as affording evidence of the existence of an intermediate colloidal form of calcium sulphate which is precipitated or protected by ions present in the mother-liquor. Tables II and III show typical results, the order of the velocity of precipitation being the same at other temperatures and concentrations examined.

TABLE II.

H_2SO_4 and	Temp.	2*N*.	1*N*.	*N*/2.	*N*/4.
$CaAc_2$.*	0°	20 secs.	30 secs.	135 secs.	—
	16	10 ,,	20 ,,	90 ,,	25 mins.
	50	2 ,,	5 ,,	20 ,,	3 ,,
	75	Immediate.	Immediate.	10 ,,	35 secs.
	100	,,	,,	3 ,,	5 ,,
$CaCl_2$.	0	45 secs.	4 mins.	—	—
	16	25 ,,	2·25 ,,	30 mins.	7—8 hours.
	50	10 ,,	60 secs.	3 ,,	20 mins.
	75	6 ,,	45 ,,	2 ,,	10 ,,
	100	5 ,,	30 ,,	1 ,,	7 ,,
$Ca(NO_3)_2$.	0	65 secs.	8 mins.	—	—
	16	40 ,,	5 ,,	45 mins.	7—8 hours.
	50	15 ,,	80 secs.	10 ,,	25 mins.
	75	10 ,,	60 ,,	6 ,,	10 ,,
	100	8 ,,	45 ,,	4 ,,	7·5 ,,

* In *N*/8-solutions the times for 16°, 50°, 75°, and 100° are 60, 7, and 4 mins. and 27 secs. respectively.

TABLE III.

(Temp. : 16°.)		Na_2SO_4.	$MgSO_4$.	$Al_2(SO_4)_3$.	H_2SO_4.
$CaAc_2$.	*N*/2	30 mins.	1 hour.	2 mins.	90 secs.
	1*N*	10 ,,	30 mins.	90 secs.	20 ,,
$CaCl_2$.	*N*/2	2·25 mins.	8 mins.	20 mins.	30 mins.
	1*N*	1·25 ,,	1·5 ,,	2 ,,	2·25 ,,
$Ca(NO_3)_2$.	*N*/2	5 mins.	20 mins.	25 mins.	45 mins.
	1*N*	2 ,,	4 ,,	5 ,,	5 ,,

As in the case of strontium sulphate, the effect of variation in the anion and cation of the precipitating solutions indicates that calcium sulphate forms a positive colloid. The anions $CH_3{\cdot}CO_2'$, Cl', and NO_3' caused a decrease, in this order, in the velocity of precipitation, and this is the order of the precipitating power of these ions for a positively charged colloid. With solutions of the nitrate and chloride of calcium, the cations $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and $H^{\cdot}$ caused a decrease, in this order, in the velocity of precipitation, and this is the order of the increasing protective power of these cations for a positively charged colloid.

When calcium acetate solutions were used, the cation effect was not the same and the order of decreasing precipitating power was $H^{\cdot}$, $Al^{\cdot\cdot\cdot}$, $Na^{\cdot}$, $Mg^{\cdot\cdot}$. This is the order to be expected, since in the case of $H^{\cdot}$ and $Al^{\cdot\cdot\cdot}$ the protecting ions are withdrawn as acetic acid and aluminium hydroxide respectively.

Summary.

1. From a given pair of precipitants, calcium sulphate can be precipitated directly either as the dihydrate or the hemihydrate. The determining condition is temperature and there is, for each pair of precipitants, a fairly definite transition point above which the hemihydrate and below which the dihydrate is stable.
2. The normal form of the precipitated dihydrate crystals is (110)(010)(111), which differs from the form (110)(010)(101) obtained by Maschke and Vater by crystallisation from aqueous solutions.
3. The presence of acetate ion has a marked effect on the form of the precipitated dihydrate crystals and gives rise to the forms (110)(010)(103) and (110)(010)(203), of which the latter has not hitherto been described. These forms have been observed to crystallise in a variety of twins, the type of twin being determined by the concentration of acetate ion.
4. Direct evidence has been obtained that the faces $(\bar{1}11)(\bar{1}\bar{1}1)$—pyramidal faces on $(\bar{1}01)$—usually found rounded and water-worn on actual gypsum crystals owe their appearance to solvent action.
5. It has been shown that crystal growth does not always take place by deposition in parallel layers and that gypsum crystals grow in stages with the development of a possible crystal face at each stage.
6. The velocity of precipitation of calcium sulphate is affected by variations in the anions and cations of the precipitants in agreement with the hypothesis that it passes through a colloidal stage in which the colloid is protected or precipitated by the ions present in the mother-liquor.

We wish to express our thanks to Dr. T. V. Barker for valuable help and criticism and to the Royal Society for a grant which has covered part of the cost of this investigation.

UNIVERSITY MUSEUM, OXFORD.

[*Received, July* 17*th*, 1926.]