

THE CRYSTAL FORMS OF CALCIUM SULPHATE

L. S. RAMSDELL* AND E. P. PARTRIDGE.**

ABSTRACT

This paper reviews the work leading up to the statement by Linck and Jung that only three crystal forms of calcium sulphate exist. It describes some new X-ray analyses of gypsum dehydrated to less than 0.3 per cent H_2O which show that this material, commonly called "soluble anhydrite," has a crystal structure identical with that of the hemihydrate, and supports the hypothesis of Linck and Jung that the hemihydrate is zeolitic in nature, losing and regaining its water of hydration without change in crystal structure.

An equilibrium system for the three forms of calcium sulphate in contact with water is described, and some original experiments are recorded which show that gypsum is converted into anhydrite when in contact with water at $100^\circ C$, probably passing through the hemihydrate as an intermediate stage. Similar experiments conducted with anhydrite in contact with water at $11^\circ-15^\circ C$ show that it is slowly converted into gypsum. Photomicrographs of both transitions are included.

IMPORTANT RESEARCHES ON CALCIUM SULPHATE

Until recently it was the generally accepted view that there were four crystal forms of calcium sulphate: gypsum, hemihydrate, "soluble anhydrite," and anhydrite. An extensive and exceedingly contradictory literature has developed concerning the relations between these various forms. The confusion of experimental data is largely the result of three factors: (1) Much of the work reported gives the results from technical investigations concerned less with the production of fundamental data than with the determination of optimum methods for plaster manufacture; (2) There has been a very general failure to differentiate between the concepts of *rate of reaction* and *equilibrium*, short-time tests of a few hours, or even of less than an hour, being accepted as conclusive data on final states; (3) There has been a frequent neglect of the influence of vapor pressure upon the changes between the various forms.

Out of the large number of investigations reported there is an important sequence of researches which lead up to the conclusion that only three crystal forms of calcium sulphate exist, rather than four, and that the material obtained by complete dehydration of gypsum at low temperatures, commonly referred to as "soluble

* Assistant Professor of Mineralogy, University of Michigan.

** Detroit Edison Fellow in Chemical Engineering, University of Michigan, 1925-1928.

anhydrite" is not a separate form, but has a crystal structure identical with that of hemihydrate. This sequence of researches will be briefly listed. Many of the less significant articles containing contributory evidence have necessarily been neglected in giving the general outline.

The hemihydrate was first discovered by Millon (1). Its preparation and properties were extensively investigated by Le Chatelier (2). Both of these investigators found that the hemihydrate lost its water of hydration completely on heating, but Potilitzin (3) was the first to announce that the anhydrous calcium sulphate prepared by complete dehydration of gypsum at temperatures below 200°C. differed greatly from natural anhydrite in its properties. Lacroix (4) studied this difference crystallographically, and noted that the refractive index and double refraction of the material obtained by the dehydration of gypsum at low temperatures were decidedly lower than those of natural anhydrite. He noted the significant fact that anhydrous calcium sulphate prepared at low temperatures was oriented with respect to the original gypsum crystals, while anhydrite prepared by dead-burning gypsum was not oriented at all.

The existence of four forms of calcium sulphate was accepted by van't Hoff and his students (5), who studied extensively the equilibria between these forms in contact with water, obtaining the following transition temperatures:

Transition	Equilibrium Temperature, °C
Gypsum—anhydrite	63.5-66
Gypsum—"soluble anhydrite"	93
Gypsum—hemihydrate	107

The term "soluble anhydrite" was originated by van't Hoff to define the anhydrous form prepared from gypsum at low temperatures. Davis (6) emphasized the extremely rapid rehydration of "soluble anhydrite" in contact with moist air, and criticized van't Hoff's work on this material. Davis further stated that the dehydration of gypsum always took place through the following reversible steps:



and said that hemihydrate and "soluble anhydrite" were both orthorhombic in form. Glasenapp (7), and later Gaudfroy (8),

studied the dehydration of the hemihydrate crystallographically and found no change in crystal form. Gaudefroy emphasized the rapid reversibility of the change between "soluble anhydrite" and hemihydrate, and calculated from density measurements that the molecular volumes of the two forms were identical. Grengg (9) made an extended crystallographic study which confirmed the close relation of these two forms.

As the logical outgrowth of the preceding investigations, Linck and Jung (10) proposed in 1924 that "soluble anhydrite" was nothing more than hemihydrate which had zeolitically lost its water of hydration. Their heating curves and eudiotensimeter measurements show a transition of gypsum to hemihydrate at 99°C. followed by a continuous loss of water over the range 120°–190°C. Jung (11) followed up this work by an X-ray analysis of the different forms of calcium sulphate and found but three diffraction patterns. The first was given by gypsum; the second by hemihydrate, by gypsum dehydrated to 1.5 per cent H₂O, and by commercial plaster; the third by gypsum dead-burned at a low red heat, and by natural anhydrite. This work indicated the probable identity of crystal structure of hemihydrate and "soluble anhydrite." Molecular volumes for these two materials calculated by Biltz (12) from the density measurements of Linck and Jung were identical and varied only slightly from the figures of Gaudefroy.

Jolibois and Chassevent (13) (17) have since found that solubilities determined with "soluble anhydrite" give values practically identical with those of hemihydrate. Balarew (14) has been the only one to date to attack the viewpoint expressed by Linck and Jung that there are only three true forms of calcium sulphate. His data should be extended further to be conclusive. To the present writers the hypotheses of three true crystal forms, and of the zeolitic character of hemihydrate represent more accurately the general trend of experimental observations than the hypothesis of four distinct crystal forms. It seemed, however, that the X-ray analysis of Jung based on gypsum dehydrated to a water content of 1.5 per cent should be repeated with more completely dehydrated material, with careful provision against possible rehydration during any part of the process. Some original work was, therefore, carried out which will subsequently be described.

THE DEHYDRATION OF GYPSUM IN CONTACT WITH AIR

It has been previously stated that much conflict in experimental data on dehydration is due to neglect of the effect of vapor pressure. When a hydrate, such as gypsum, is heated in air, it will lose water if the vapor pressure of the hydrate exceeds the partial pressure of the water vapor in the air in contact with it. Hannay (15) emphasized this fact with reference to the dehydration of gypsum in 1877, but it has repeatedly been ignored, even since van't Hoff's measurements of the vapor pressure of calcium sulphate systems as a function of temperature. Under ordinary conditions of experimentation the air is not saturated with water vapor, and the temperature at which dehydration takes place will depend upon the partial pressure of the water vapor in the air. By lowering the partial pressure of water vapor in the air, it is possible to lower the temperature at which dehydration will take place. Thus Shenstone and Cundall (16), and van't Hoff and his students both obtained complete dehydration of gypsum at 70°C. when in contact with air dried over phosphorus pentoxide, and Jolibois (17) states that complete dehydration may be obtained at room temperatures with air dried in this manner, several weeks, however, being required. The lowest possible temperature at which dehydration will occur is indeterminate, for decreasing the temperature decreases the vapor pressure of the hydrate and the time factor becomes indefinitely large because of the small driving force for the reaction.

In the experimental work of the authors it was only desired to obtain complete dehydration of gypsum for the purpose of obtaining samples of "soluble anhydrite" for X-ray analysis. No study of dehydration rates or limiting temperatures was intended. At the temperatures used in these experiments, the vapor pressure of the hydrate was always at least 100 times the partial pressure of the water vapor in the atmosphere, and the time allowed for dehydration varied from one to five days. The material used was either pure selenite gypsum powdered to pass 200-mesh, or a pure precipitated gypsum (Baker's Analyzed C. P.).

The results of the dehydration experiments are expressed for convenience in three series. Series A constituted a check on the dehydration of the materials used, and was carried out in open weighing bottles heated in an electric oven at different tem-

peratures for different periods. The bottles were closed while hot and cooled in a desiccator.

Series B provided the material for the X-ray analysis of "soluble anhydrite." The sample of gypsum was placed in a special tube drawn to a capillary at one end and sealed, and fitted at the other end with a ground glass stopper. The tube was first weighed by itself and again after introduction of a sample of gypsum into the large part. The open tube was heated at the temperatures and for the periods indicated, using an electric oven, and the stopper was then inserted, the tube cooled in a desiccator, and the loss of water determined. Some of the powder was then shaken down into the capillary, which was sealed off and used for X-ray determinations of crystal structure. By this procedure any re-hydration of the material during handling was obviated, and a sample of "soluble anhydrite" containing not more than 0.3 per cent of water was obtained.

Series A and B were both carried out in contact with the laboratory atmosphere. A check on Series B was desired with material prepared in a stream of dry air. In this work, which will be referred to as Series C, an air drying train utilizing first CaCl_2 and then P_2O_5 was used, and no attempt was made to determine the loss of weight of the sample, since the results of Series B indicated that practically complete dehydration was attained at the temperatures used, within the period of the experiment.

TABLE 1. THE DEHYDRATION OF GYPSUM IN AIR

	Temperature°C	Duration of heating-hrs.	Weight of sample gr.	Loss in weight gr.	%
Series A	120	20	1.5391	0.3143	20.42
	120	68	1.5391	0.3145	20.43
	120	68	1.5795	0.3236	20.48
	143	17	3.0037	0.6007	20.00
	143	60	3.3437	0.6663	19.93
	143	60	2.4479	0.4871	19.90
	150	72	1.8943	0.3820	20.16
	150	72	1.9838	0.4000	20.16
	Series B	150	120	0.2484	0.0512
150		120	0.2382	0.0493	20.70
180		48	0.3633	0.0741	20.39
180		120	0.4127	0.0847	20.52

Series C	150	48	—	—	—
	180	48	—	—	—
	Average % loss for all determinations				20.31
	Theoretical loss for complete dehydration				20.93

The practically anhydrous product secured in the above experiments was distinct from anhydrite, or from dead-burned gypsum, both in its optical properties and in its X-ray diffraction pattern. The patterns found for the samples from Series B and C, carefully guarded from any possible rehydration, were identical with those obtained from material from Series A, which had been allowed to partially rehydrate in contact with the laboratory air, and were also identical with those obtained from plaster-of-Paris. It is, therefore, concluded that the identity of crystal structure of hemihydrate and "soluble anhydrite" is established.

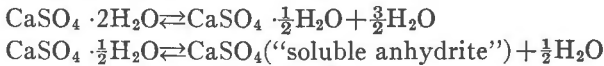
The partial rehydration of "soluble anhydrite" to form hemihydrate was confirmed in the course of the experimental work. The two samples from Series A which had been dehydrated at 150°C. were used, one of them being left covered as a check, and the other being exposed to the air of the laboratory. The gain in weight of the latter sample is indicated in Table 2. The partial pressure of water vapor in the air was approximately equal to the equilibrium vapor pressure for the hemihydrate-gypsum transition.

TABLE 2. REHYDRATION OF COMPLETELY DEHYDRATED GYPSUM

	Weight of Original Gypsum Sample gr.	Loss in Weight on Dehydration %	Duration of Rehydration days	Weight of Sample gr.	Gain in Weight %
Exposed to Air					
	1.9838	20.16	1	1.6348	2.57
			2	1.6943	5.57
			4	1.6979	5.75
			7	1.6962	5.66
			9	1.6943	5.57
Not Exposed to Air					
	1.8943	20.16	1	1.5128	0.03
			2	1.5140	0.11
			3	1.5152	0.16
			4	1.5188	0.40
					Theoretical gain to form hemihydrate
					5.24

During the dehydration experiments there was no suggestion

of the formation of any intermediate product, such as the hemihydrate, which would have a theoretical loss of 15.69 per cent of the original gypsum. This is to be expected at the temperatures used, since the partial pressure of water vapor in the air is far below the vapor pressure of the hemihydrate as well as that of gypsum. The dehydration reaction therefore consists of two simultaneous reactions:



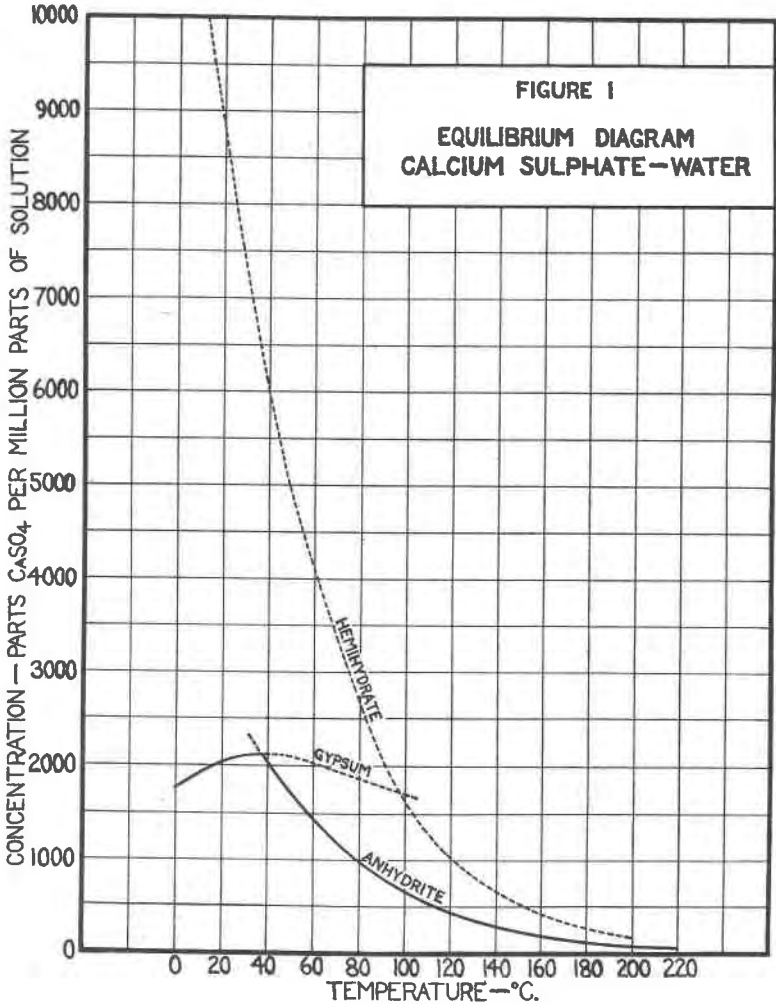
As soon as the hemihydrate is formed, it begins to lose water, and equilibrium is reached only when the vapor pressure of the zeolitic water of hydration of the hemihydrate is equal to the partial pressure of the water vapor in the atmosphere. It should be noted at this point that if the zeolitic nature of the hemihydrate is accepted, it is theoretically impossible to obtain absolutely complete dehydration in contact with an atmosphere containing any water vapor. This would account for the consistent failure of dehydration data to attain to the theoretical per cent loss of 20.93 for the complete dehydration of pure gypsum.

In view of the vapor pressure considerations noted above, the conclusions of Parsons (18) that plaster-of-Paris is not a definite chemical compound, and that gypsum loses all of its water of crystallization in a single stage are not tenable. Jolibois (17) has prepared hemihydrate by heating gypsum to 140°C. in a covered crucible. In this way the water of hydration lost from the gypsum raised the partial pressure of the water vapor in the air within the crucible to the degree necessary to stop the dehydration at the end of the first reaction given above.

THE EQUILIBRIUM SYSTEM FOR THE THREE CRYSTAL FORMS OF CALCIUM SULPHATE IN CONTACT WITH WATER

The foregoing work presents strong evidence of the existence of only three crystal forms of calcium sulphate. If, however, hemihydrate and "soluble anhydrite" are to be considered identical, a revision of the equilibrium diagram for the forms of calcium sulphate in contact with water is necessary. Such a revised diagram has been proposed by Partridge and White (19) as the result of a re-determination of solubility values for calcium sulphate above 100°C. This equilibrium diagram, shown in Figure 1, is based upon the data of a number of investigators. The ex-

cellently concordant values of Raupenstrauch (20a), Hulett and Allen (20b), Melcher (20c), and Cavazzi (20d), have been used to determine the curve for gypsum. It was found that the solubility curve for hemihydrate below 100°C. determined by Chassevent



(20e) was continuous with the curve above 100°C. originally determined by Boyer-Guillon (20f), and commonly referred to as the curve for "soluble anhydrite." Partridge and White re-determined this latter curve and found by optical and X-ray methods that

the solid phase was hemihydrate. The curve for anhydrite is based on the data of Melcher, the minimum values of Hall, Robb, and Coleman (20g), and the data of Partridge and White, for its course above 100°C. Below this temperature there is but one determination available in the literature, that of Haddon and Brown (20h) at 33°C. The curve determined above 100°C. has been extended to pass through this point.

From the curves of Figure 1 the following transition temperatures between the forms of calcium sulphate in contact with water are obtained:

Transition	Equilibrium Temperature °C
Gypsum—anhydrite	38
Gypsum—hemihydrate	98

The hemihydrate curve shows no intersection with the anhydrite curve in the range from 0° to 200°C.

The transition temperature of 38°C. for the change from gypsum to anhydrite in contact with water can only be considered as provisional until extended and accurate measurements of the solubility of anhydrite are made in the range from 0° to 100°C. This provisional transition temperature is appreciably lower than that of 63.5–66°C. given by van't Hoff.

APPARENT ANOMALIES IN THE EQUILIBRIUM DIAGRAM FOR CALCIUM SULPHATE AND WATER

On inspection of Figure 1, it appears that gypsum should be the stable solid phase in contact with water below a temperature of 38°C. and that anhydrite should be the stable solid phase in contact with water above that temperature, while hemihydrate should exist only as an unstable solid phase in contact with water at all temperatures over the range from 0° to 200°C. This general statement is partially contradictory to common experience, for gypsum presents apparent stability in contact with water up to its transition into hemihydrate at 98°C. instead of being transformed into anhydrite at a much lower temperature. This apparent stability of gypsum requires further long-time study. Work is in progress by the authors on this question.

The general statement given above is in accord with common experience concerning the instability of hemihydrate. Hemihydrate has never been reported in a natural occurrence with the

exception of one possible case noted by Sworykin (21). In contact with water below 98°C. it rehydrates to form gypsum, while in contact with water above this point it changes gradually to anhydrite.

From the equilibrium diagram it is evident that between 38° and 98°C. gypsum in contact with water should change into anhydrite without passing through the intermediate stage of the hemihydrate, while below 38°C. hemihydrate in contact with water should change into gypsum through anhydrite as an intermediate stage. Further work is necessary to clear up these unusual relations implied by the course of the solubility curves.

The relative stability of gypsum and anhydrite above 98° and below 38°C. has been tested by the authors in some original work which will be described in the following section.

THE DEHYDRATION OF GYPSUM AND REHYDRATION OF ANHYDRITE IN CONTACT WITH WATER

Davis (6) has stated that minute gypsum crystals are converted into hemihydrate within a few hours when in contact with water at the atmospheric boiling point, and Farnsworth (22) has observed a slower transition of gypsum to hemihydrate in contact with water at 110°C. These observations are in accord with the equilibrium diagram of Figure 1, since at 100°C. gypsum represents a solid phase unstable with respect to hemihydrate. Hemihydrate, however, is also unstable with respect to anhydrite, and it would be expected that gypsum should ultimately be replaced by anhydrite, with hemihydrate as an intermediate stage.

The change of anhydrite to gypsum when in contact with water at ordinary atmospheric temperatures is a well-known geological phenomenon, and has been noted in the laboratory by Gill (45)(23), but only after an extremely long period. Both this change, and that from gypsum to hemihydrate at 100°C. are analogous to the setting of plaster-of-Paris in that a more soluble form goes into solution with subsequent recrystallization of a less soluble form.

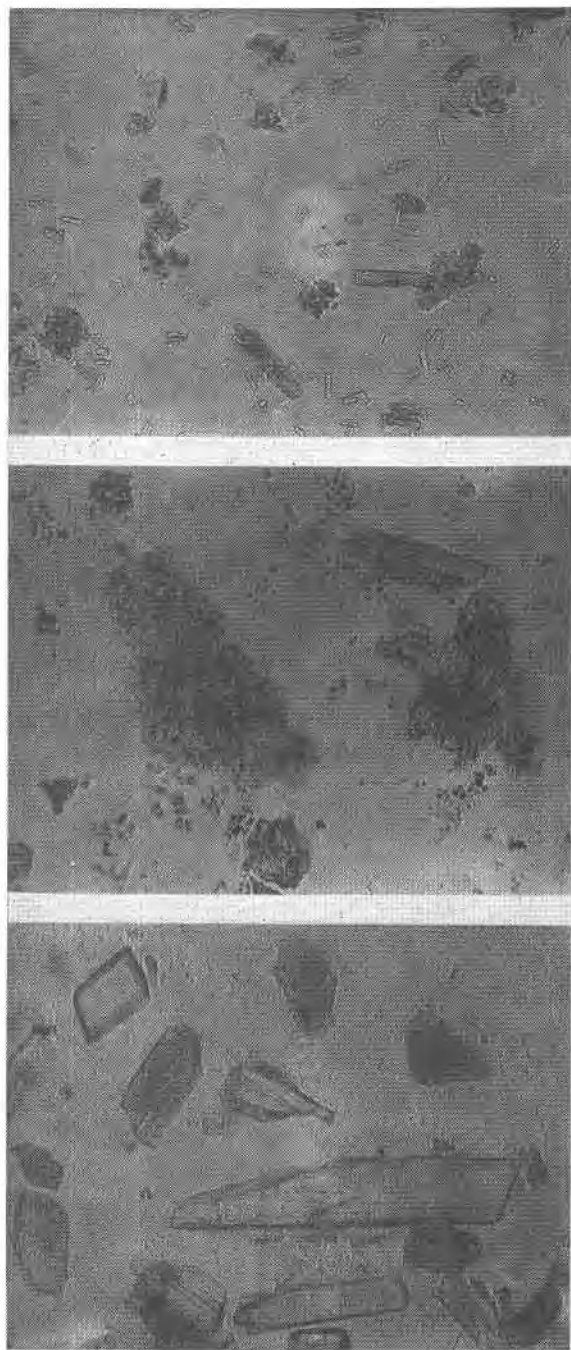
Some original experiments were made by the authors at 100°C. and at 11°-15°C. to determine accurately the dehydration of gypsum at the former temperature and the rehydration of anhydrite at the latter temperature. These will be referred to, respectively, as Series D and Series E.

For the experiments of Series D a pure sample of selenite gypsum

was powdered and screened, and the portion which passed a 100-mesh screen and was retained on a 150-mesh screen was used. Samples of this material of approximately 0.2 gram each were placed in small test tubes with 5 cc. of distilled water. The tubes were heated to 100°C. in a water bath and were sealed off and then were suspended in distilled water boiling under atmospheric pressure. After various periods of time, tubes were removed and the contents were immediately filtered and washed with alcohol and with ether on a suction filter, after which they were examined optically.

The original material consisted chiefly of clear angular cleavage fragments, with low double refraction and inclined extinction. Some of the grains seemed to have been shattered by the powdering and appeared as fine-grained aggregates. After ten days in contact with water at 100°C a sample was examined and it was found that the shattered gypsum grains had disappeared and the cleavage fragments were distinctly corroded. A sample taken after twenty days showed further disintegration of the gypsum. In both of these samples there appeared a new product which consisted essentially of radiating clusters of very minute doubly refracting prisms embedded in an isotropic material. No satisfactory identification of this material could be made by optical methods, and the X-ray results were likewise inconclusive. Due to the small change between the 10-day and 20-day samples, the next sample was not taken until 46 days had elapsed. In this sample the gypsum had entirely disappeared, the intermediate phase had partially disappeared, and a large number of rectangular crystals of anhydrite had appeared. These gave the characteristic refractive indices, high double refraction, and parallel extinction of anhydrite and this determination was checked by X-ray analysis which gave the characteristic diffraction pattern for this form of calcium sulphate. The earlier samples showed only the characteristic lines of gypsum on X-ray analysis. Judging from the solubility curves, and from the work of Davis and of Farnsworth, hemihydrate would be expected as an intermediate product. This was not proved in the present experiment. The intermediate phase described above may have been hemihydrate, but the amount in any one sample was insufficient to produce an X-ray pattern. Figure 2 shows photomicrographs of the original gypsum, the intermediate phase, and the new crystals of anhydrite.

FIG. 2.—The Conversion of Gypsum to Anhydrite in Contact with Water at 100°C.



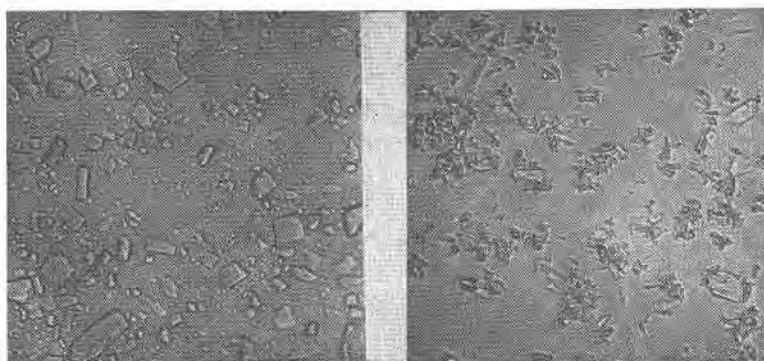
A
Original Gypsum Fragments. $\times 70$.

B
Intermediate Phase and Corroded Gypsum
Fragments after 10 days in water at 100°C.
 $\times 90$.

C
Anhydrite and Residual Intermediate
Phase after 46 days in water at 100°C. $\times 70$.

For the experiments of Series E powdered anhydrite and dead-burned gypsum were used. Several samples of each were sealed in glass tubes containing distilled water, and these tubes were held between 11° and 15°C. in a water bath. After 45 days the dead-burned gypsum had entirely disappeared and was replaced by gypsum crystals, of a short prismatic type and untwinned. The natural anhydrite changed much more slowly, and after 120 days still showed a few unchanged grains of anhydrite. The greater portion, however, was in the form of small gypsum crystals, either short untwinned prisms, or needles showing the characteristic swallow-tail twinning. Figure 3 shows photomicrographs of the original anhydrite used in this experiment and of the product after 120 days contact with water at 11°–15°C.

FIG. 3.—The Conversion of Anhydrite to Gypsum in Contact with Water at 11°–15°C.



A
Original Anhydrite Fragments. $\times 95$.

B
Gypsum Crystals and Residual Anhydrite Fragments after 120 days in water at 11°–15°C. $\times 95$.

A third series of experiments at a temperature of 50°C. is still in progress. Gypsum was used as the initial solid phase in tubes containing water as before. These were sealed off at 50°C. and were maintained at that temperature in an electric oven. After 120 days there was no evidence of any change. The crystals showed no sign of solution, and there was no new product formed. This either indicates that gypsum is less soluble than anhydrite at this temperature and is therefore the stable phase, and that therefore the intersection of the solubility curves for gypsum and anhydrite

should lie above 50°C., or else it indicates that this temperature is so near the point of intersection that the rate of reaction is extremely slow. This experiment cannot be regarded as furnishing any definite information at the present time and is being continued.

The analogy of the solution of plaster-of-Paris with subsequent recrystallization of gypsum to the change from gypsum to anhydrite at 100°C. and the change from anhydrite to gypsum at 11°–15°C. is emphasized by the fact that in both of the series of experiments a distinct setting of the samples was observed. On the other hand, a sample of hemihydrate added to water maintained at 100°C. did not set at all during a period of three days. This was to be expected, since the hemihydrate is less soluble than gypsum at 100°C. and therefore would not be expected to rehydrate, while the conversion to anhydrite is such a slow reaction that no setting from this cause was apparent during the time of the experiment.

CONCLUSIONS

(1) Three crystal forms of calcium sulphate exist, rather than four. These are gypsum, hemihydrate, and anhydrite. "Soluble anhydrite" is identical in crystal structure with hemihydrate, the latter apparently belonging to the zeolitic class of substances which lose and regain water of hydration without change in crystal structure. The term "hemihydrate" should, therefore, be interpreted not as referring to a compound with a definite water content, but as referring to a compound which gives a certain definite X-ray diffraction pattern. The term "soluble anhydrite" is a misnomer, and should be replaced by the term "dehydrated hemihydrate" which more nearly expresses the true relationship of the hemihydrate and the material obtained by complete dehydration at low temperatures.

(2) The transition temperature for the change from gypsum to anhydrite when in contact with water is provisionally placed at 38°C.; for the change from gypsum to hemihydrate, when in contact with water, is more definitely placed at 98°C.

(3) Anhydrite has been obtained experimentally from gypsum in contact with water at 100°C., with evidence of setting similar to that of plaster-of-Paris.

(4) Gypsum has been obtained from anhydrite in contact with water at 11°–15°C., with evidence of setting similar to that of plaster-of-Paris.

(5) The conversion of gypsum to anhydrite at 100°C. and of anhydrite to gypsum at 11°–15°C. are analogous to the conversion of hemihydrate to gypsum noted in the setting of plaster. In each case a more soluble unstable solid phase dissolves in water, with subsequent crystallization of a less soluble stable phase from the solution which is supersaturated with respect to it.

REFERENCES

- (1) Millon, E. Remarks on Some Examples of Chemical Affinity, *Ann. Chim. Phys.*, (3) **19**, 222–230 (1847).
- (2) Le Chatelier, H. Experimental Researches on the Constitution of Hydraulic Mortars. *Paris* (1887); Concerning the Setting of Plaster, *Compt. Rend.*, **96**, 1668–1671 (1883).
- (3) Potilitzin, A. Concerning the Solubility of Anhydrous Gypsum, *J. Russ. Phys. Chem. Ges.*, **26**, 170 (1894); **26**, 221–229 (1894); **27**, 265–270 (1895); *Berichte*, **27** (4), 613–616 (1894); *Chem. Zentr.*, (1894), 515, 609.
- (4) Lacroix, A. On Anhydrous Calcium Sulphate Produced by the Complete Dehydration of Gypsum, *Compt. Rend.*, **126**, 360–362 (1898).
On the Formation of Anhydrite by the Calcination of Gypsum at a High Temperature, *Compt. Rend.*, **126**, 553–554 (1898).
- (5) van't Hoff, J. H.; Armstrong, E. F.; Hinrichsen, W.; Weigert, F.; Just, G. Gypsum and Anhydrite, *Z. Phys. Chem.*, **45**, 257–306 (1903).
van't Hoff, J. H.; Hinrichsen, W.; Weigert, F. *Sitzber. Akad., Berlin* (1901) 570.
van't Hoff, J. H.; Weigert, F. *Sitzber. Akad., Berlin* (1901) 1140.
van't Hoff, J. H.; Armstrong, E. F. *Sitzber. Akad., Berlin* (1900) 563.
van't Hoff, J. H.; Just, G. *Sitzber. Akad., Berlin* (1903) 249.
- (6) Davis, W. A. The Nature of the Changes Involved in the Production and Setting of Plaster-of-Paris, *J. Soc. Chem. Ind.*, **26**, 727–738 (1907).
- (7) Glasenapp, M. Studies on Plaster of Paris, Dead-Burned Gypsum, and Estrichgyps. *Tonind. Z.*, **32**, 1148–1152 (1908).
- (8) Gaudefroy, C. On the Dehydration of Gypsum, *Compt. Rend.*, **158**, 2006–2007 (1914); **159**, 263–264 (1914).
- (9) Grengg, R. The Dehydration Products of Gypsum, *Z. Anorg. Chem.*, **90**, 327–360 (1914).
- (10) Linck, G., and Jung, H. Concerning the Dehydration and Rehydration of Gypsum, *Z. Anorg. Allgem. Chem.*, **137**, 407–417 (1924).
- (11) Jung, H. X-Ray Investigations of the Dehydration Products of Gypsum, *Z. Anorg. Allgem. Chem.*, **142**, 73–79 (1925).
- (12) Biltz, W. Note Concerning the Volume of Water in the Hydrates of Calcium Sulphate. *Z. Anorg. Chem.*, **143**, 231–232 (1925).
- (13) Jolibois, P., and Chassevent, L. On the Setting of Plaster, *Compt. Rend.*, **177**, 113–116 (1923).
- (14) Balarew, D. Concerning the Dehydration of Gypsum, *Z. Anorg. Chem.*, **156**, 258–260 (1926).
Concerning the Equilibrium between the Hydrates of Calcium Sulphate. *Z. Anorg. Chem.*, **163**, 137–140 (1927).

- (15) Hannay, J. B. Examination of Substances by the Time Method, *J. Chem. Soc.*, **32**, 381-395 (1877).
- (16) Shenstone, W. A., and Cundall, J. T. The Influence of Temperature on the Composition and Solubility of Hydrated Calcium Sulphate and of Calcium Hydroxide, *J. Chem. Soc.*, **53**, 544-550 (1888).
- (17) Jolibois, P. Plaster, *Bull. Soc. Chim.*, **41**, 117-135 (1927).
- (18) Parsons, A. L. *Contributions to Canadian Mineralogy, 1927, University of Toronto Studies No. 24*, pp. 24-27.
- (19) Partridge, E. P., and White, A. H. The Solubility of Calcium Sulphate from 0° to 200°C. *J. Am. Chem. Soc.*, **51**, — (1929). (Not yet published at time of printing).
- (20a) Raupenstrauch, G. A. Concerning the Measurement of the Solubility of Some Salts in Water at Different Temperatures, *Monatshefte für Chemie*, **6**, 563-591 (1885).
- (20b) Hulett, G. A., and Allen, L. E. The Solubility of Gypsum, *J. Am. Chem. Soc.*, **24**, 667-669 (1902).
- (20c) Melcher, A. C. The Solubility of Silver Chloride, Barium Sulphate, and Calcium Sulphate at High Temperatures, *J. Am. Chem. Soc.*, **32**, 50-66 (1908).
- (20d) Cavazzi, A. The Solubility, Supersaturation, and Setting of Gypsum, *L'Industria Chimica*, **6**, 366-368 (1904); *Chem. Zentr.*, (5) **9**, 1693-1694 (1905).
- (20e) Chassevent, L. Researches on Calcium Sulphate. I. Action of Water on Calcium Sulphate, *Ann. Chim.*, (10) **6**, 244-294 (1926).
- Researches on Plaster, *Bull. Soc. Encour. Ind. Nat.*, 789-803, (1926).
- (20f) Boyer-Guillon, A. Study of the Solubility of Calcium Sulphate, *Ann. Conserv. Arts et Metiers*, (3) **2**, 187-211 (1900).
- (20g) Hall, R. E.; Robb, J. A., and Coleman, C. E. The Solubility of Calcium Sulphate at Boiler-Water Temperatures, *J. Am. Chem. Soc.*, **48**, 927-938 (1926).
- (20h) Haddon, C. L., and Brown, M. A. W. Calcium Sulphate Cement, *J. Soc. Chem. Ind.*, **43**, 11-16T (1924).
- (21) Sworykin, A. J. Concerning the Question of the Solubility of the Natural Hemihydrate of Gypsum after its Heating at Different Temperatures, *Z. Anorg. Chem.*, **163**, 178-184 (1927).
- (22) Farnsworth, M. The Hydration of Anhydrite, *Ind. Eng. Chem.*, **17**, 967-970 (1925).
- (23) Gill, A. C. The Hydration of Anhydrite and Dead-Burned Gypsum, *J. Am. Ceram. Soc.*, **1**, 65-71 (1918).