THE MECHANISM OF DEHYDRATION
OF CALCIUM SULFATE HEMIHYDRATE

by

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THE MECHANISM OF DEHYDRATION
OF CALCIUM SULFATE HEMIHYDRATE

The material usually designated hemihydrate of calcium sulfate was discovered by Millon (26). Early investigations by Le Chatelier (24), Potilitzin (30), Lacroix (23), van't Hoff (34), Davis (11), and others led to the belief in four separate forms of calcium sulfate: gypsum, hemihydrate, soluble anhydrite, and anhydrite. Van't Hoff and coworkers studied the vapor pressure relationships between the various forms and reported the equilibrium temperatures with water. Glasenapp (18), Gaudefroy (16), and Grengg (19) studied the dehydration of the hemihydrate crystallographically but failed to find any change in crystal form except the conversion to anhydrite.

The recent series of investigations was started in 1924 by Linck and Jung (25), who studied the dehydration by means of heating curves, isobaric and isothermal dehydration, and variation in density and optical properties with composition. Their isotherm indicated a continuous loss of water throughout the entire range of dehydration. They deduced from this that the compound was of zeolitic nature and interpreted their other results to be in agreement with this conclusion. Both density and optical properties showed a gradual change with loss of water. Jung (21) later made the first x-ray investigation of the problem and reported that the hemihydrate retains its structure on heating until transformed

into anhydrite at high temperatures.

Balarew (1) in 1926 claimed that Linck and Jung did not wait for equilibrium in determining their isotherm. He studied the dehydration isobarically and concluded that the hemihydrate decomposed stepwise, not zeolitically at $97 \pm 2^\circ$ and 23 mm. aqueous vapor pressure.

Chassevent (10) checked the existence of the hemihydrate by measuring electric conductivity and concentration of solutions and liberation of heat during transformation.

In 1927, three papers on the hemihydrate question appeared. Balarew (2) deduced from the standpoint of van't Hoff's vapor pressure work that there must be two soluble forms of anhydrous calcium sulfate. He then obtained data to indicate the existence of these two forms by means of dilatometric studies and heating curves. Parsons (28) failed to find any indication of the hemihydrate on dehydrating gypsum and stated that it could be prepared only by wet methods if it existed. Stumper (33) investigated the gypsum dehydration by means of heating curves and found evidence of the hemihydrate. His results on isobaric dehydration showed no indication of hemihydrate, in agreement with Shuksuke Kôzu and Meich Masuda (32). However, he correctly attributed the absence of a break in the curve to the short equilibrium time.

Partridge and White (29) did not find a soluble anhydrite solid phase in their study of the calcium sulfate-

water equilibrium. Ramsdell and Partridge (31) studied the dehydration by x-ray diffraction methods and reported that the powder photograph for dehydrated hemihydrate was identical with that for hemihydrate.

Balarew (3) in his third paper redetermined the isotherm at 96.5°. He concluded that the hemihydrate dehydrates neither purely hydratically nor purely zeolitically, but as a combination of these two processes. The dehydration is hydratic in that:

- (1) it proceeds from a definite chemical compound
 - (2) the dehydration is monovariant, the pressure-composition curve following parallel to the composition axis.
- The process is zeolitic in that:

- (1) in the region of reversible rehydration no new definite phase is formed--the optical properties change gradually

- (2) the reversible dehydration cannot be carried to completion. At the removal of the last bit of water, there is a spontaneous change of properties.

Balarew also stated that there really exist two soluble forms of anhydrous calcium sulfate--soluble anhydrite and dehydrated hemihydrate, but admitted he was mistaken about the α and β forms of soluble anhydrite previously reported.

The isotherm was reported to be purely zeolitic by Kraus and Jorns (22) in 1930, while Fill (13) in 1931 said microscopic investigations revealed that the decomposition is hydratic.

Gibson and Holt (17), using a differential tensi-meter, obtained a pressure-temperature curve which showed no discontinuity when hemihydrate was being converted into anhydrous salt and concluded that the water was held zeolitically.

An x-ray study of the dehydration was carried out by Feitnecht (12) using copper radiation and a camera 57.3 mm. in diameter. He dehydrated the hemihydrate by heating it in a vacuum over P_2O_5 and took special precautions to prevent rehydration, which he claimed took place in Jung's experiment. He found the stronger lines for the two materials to coincide, but most of the weak lines showed an entirely different spacing. In several cases lines present for one material were absent for the other. He concluded that the structures were different but that the most densely filled planes had the same spacing. He stated that the spacing changed continuously with loss of water, indicating that the water in hemihydrate is zeolitically bound.

Onorato (27) was unable to find any appreciable difference in the diffraction patterns of soluble anhydrite and hemihydrate, and concluded that the structures are identical (monoclinic, 8 molecules per unit cell).

Gallitelli (14) reported that soluble anhydrite prepared through dehydration of hemihydrate has essentially, with exception of a small lattice shrinkage, the same structure as hemihydrate. The hemihydrate is monoclinic, $a_0 = 11.94$, $b_0 = 6.83$, $c_0 = 12.76$ (12 molecules per unit cell). He used

the rotating crystal method to find $a:b:c = 1.7438:1:1.8515$ and $\beta = 90.36^\circ$.

Caspari (9) found the hemihydrate to be hexagonal ($a_0 = 6.76$, $c_0 = 6.24$) and declared the crystals give up water to within 0.1% or less of dehydration without losing form or transparency.

Gaubert (15), in an optical investigation, found evidence that the hemihydrate is hexagonal and not zeolitic.

The most recent paper on the hemihydrate problem is that of Balarew and Koluschewa (4). Isotherms for both dehydration and rehydration were found to be zeolitic and to differ by about 1 mm. Hg. Balarew concluded that the hemihydrate is zeolitic and that van't Hoff's soluble anhydrite is different from the dehydrated hemihydrate of Linck and Jung. Soluble anhydrite can be prepared in HNO_3 of 50° and 40mm. aqueous pressure, while the vapor pressure of dehydrated hemihydrate is about 1 mm. Balarew says that the dehydration of gypsum results in a mixture of soluble anhydrite and dehydrated hemihydrate. On rehydration the soluble anhydrite goes to gypsum and the dehydrated hemihydrate to hemihydrate. This mixture is plaster of Paris. Its composition was proved analytically and microscopically.

The preceding review of the literature demonstrates that the mechanism of dehydration of calcium sulfate hemihydrate and even its existence is open to question. Important work on this question has been carried out by dehydration and x-ray diffraction methods. Linck and Jung (25), Gibson and Holt (17), Balarew (4), and Kraus (22) have reported that plaster of Paris loses its water continuously after the manner of zeolites. On the other hand, Balarew at one time (1) claimed that isobaric dehydration showed the material to be a typical hydrate, and later (3) stated that the water is held in a new manner--"half hydratic and half zeolitic". Parsons (28) failed to find any evidence of a hemihydrate on dehydration of gypsum and concluded that plaster of Paris is not a compound. However, the consensus of opinion seems to be that the so-called hemihydrate is a compound of the zeolitic type.

X-ray investigations, while apparently disagreeing in actual experimental results, have in all cases been interpreted as indicating that calcium sulfate hemihydrate is zeolitic in nature. Thus Jung (21), Ramsdell and Partridge (31), and Caspari (9) reported that the x-ray diffraction-patterns of the hemihydrate and of its dehydration product, dehydrated hemihydrate*, are identical. _ _ _

* It should be pointed out that van't Hoff, Hinrichsen, and Weigert (34) prepared a soluble form of anhydrous calcium sulfate by treating gypsum with nitric acid containing 2.38 mols water per mol nitric acid above 50°C. This material was called "soluble anhydrite" to distinguish it from ordinary anhydrite, and this name has been generally used for the dehydration product of hemihydrate. Balarew (3), however,

Onorato (27) and Gallitelli (14) concluded that the structures of the two materials are identical, but recognized small differences in the diffraction patterns. Feitnecht (12) found definite differences in the powder photographs of the two materials when special care was taken to prevent rehydration, but interpreted his results to indicate that the material is zeolitic.

The purpose of the present investigation is to check the existence of a hemihydrate of calcium sulfate and to study the mechanism of its dehydration. Experiments carried out by x-ray diffraction and vapor pressure methods show that calcium sulfate hemihydrate is a definite chemical compound that decomposes stepwise in typical hydrate fashion to give another compound, dehydrated hemihydrate, which has an x-ray diffraction pattern distinct from those of the hemihydrate and anhydrite.

has stated that the "soluble anhydrite" of van't Hoff is different from the material obtained by dehydration of hemihydrate. Both Balarew (3) and Partridge (31) prefer to apply the term dehydrated hemihydrate to the dehydration product, and this terminology will be adhered to in this paper.

Experimental

Isobaric Dehydration. The gypsum used for these experiments was transparent selenite which was ground in an agate mortar. Isobaric dehydration of this material was carried out in an apparatus that had been previously used for this purpose (35). Samples were kept in weighing bottles in an electric oven. The temperature was maintained constant within $\pm 1^\circ$ for short periods of time and to within $\pm 2^\circ$ for longer periods. A constant aqueous vapor pressure of 23.6 mm. was maintained by passing air through water at 25°C . This air was then preheated by passing it through a 15 foot glass coil in the oven. All samples used weighed approximately 0.2 gram.

A complete dehydration-rehydration isobar was run for one sample. The results are given in Table 1 and Figure 1. Dehydration of four additional samples was studied for the hemihydrate portion of the curve. The results of this investigation are given in Table 2 and Figure 2. The points on the curve represent the average deviation of less than 0.01 mol. The samples were held at the various temperatures for extremely long periods of time and weighed at intervals until equilibrium was reached. In some cases over 500 hours were allowed to insure equilibrium.

Table 1
 Isobaric Dehydration-Rehydration Data
 Dehydration

Temperature °C	Composition Mols H ₂ O/Mol CaSO ₄
40	2.00
49	1.98
55	1.90
60	1.58
75	0.52
80	0.52
89	0.51
105	0.04
115	0.03
140	0.02

Rehydration

Temperature °C	Composition Mols H ₂ O/Mol CaSO ₄
105	0.03
100	0.04
95	0.47
91	0.47
85	0.48
80	0.48

Figure 1
Dehydration-Rehydration Isober

Table 2

Isobaric Dehydration Data

Temperature °C	Composition Mols H ₂ O/Mol CaSO ₄			
	1	2	3	4
25	2.00	1.98	2.00	1.99
70	0.52	0.54	0.55	0.54
75	0.52	0.53	0.55	0.54
80	0.52	0.52	0.53	0.52
89	0.52	0.52	0.53	0.53
95	0.51	0.52	0.52	0.52
100	0.08	0.08	0.10	0.10
105	0.05	0.05	0.07	0.07
163	0.01	0.02		
185	0.01	0.02		
210	0.01	0.02		

Figure 2

Dehydration Isotherm of Calcium Sulfate Hemihydrate
(Each point represents the average value for four separate
samples)

X-ray Diffraction Examination. A preliminary study of the x-ray diffraction patterns of (a) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, selenite; (b) hemihydrate prepared by heating (a) to 95° at a vapor pressure of 23.6 mm.; (c) dehydrated hemihydrate prepared by heating (a) at 145° in a vacuum; and (d) anhydrite prepared by heating (a) at over 400° was made by means of a General Electric x-ray diffraction outfit with K_α Mo radiation. Films were standardized by means of pure sodium chloride. As the dehydrated material is highly hygroscopic (5), (20), it was found necessary to exercise great care in obtaining samples. The sample tubes were filled with dehydrated hemihydrate in the oven before the vacuum dehydration. After 24 hours heating in a vacuum, dry air was allowed to enter through a U-tube filled with magnesium perchlorate and the sample tubes sealed off immediately inside the oven. The seals were examined microscopically for imperfections. The results of this preliminary investigation are given in Figure 3. From the diagram it is apparent that there are four distinct crystal forms of calcium sulfate. Although the hemihydrate and dehydrated hemihydrate patterns are similar, they are not identical. Samples were also prepared by heating gypsum 24 hours in a vacuum at 134° , 159° , 180° , and 219° . The patterns obtained were identical with that for dehydrated hemihydrate in all cases, showing that the samples were free from anhydrite and undecomposed hemihydrate. Analysis of material dehydrated

Figure 3

Diagram of X-ray Diffraction Patterns for Selenite, Hemihydrate,
Dehydrated Hemihydrate, and Anhydrite
(G.E. apparatus, K_{α} Mo radiation)

simultaneously with these samples showed that they contained ± 0.01 mols water per mol calcium sulfate. The tube containing the 154° dehydrated hemihydrate was opened and the material allowed to rehydrate over night in the atmosphere. The diffraction pattern of this rehydrated material corresponded to that of hemihydrate. Rehydration of samples dehydrated at 159° and 219° resulted in compositions of 0.63 and 0.60 mols H_2O per mol $CaSO_4$, respectively.

A more exact determination of the differences between the x-ray diffraction diagrams for the hemihydrate and dehydrated hemihydrate was carried out by means of a Seemann crystal analysis unit with $Cu K_\alpha$ radiation filtered through nickel foil. A precision Debye-Scherrer camera with a diameter of 115.3 mm. was used. Long exposures were required because of the low symmetry of the material, the small primary particle size, the large size aperture of the camera, and the necessity for obtaining a large number of lines. The exposure time was 30 to 35 hours at 60 m. a. and 40 k. v. The samples were placed in Lindemann glass tubes and extreme care used to prevent rehydration as described above.

Pure nickel oxide for use as a standard was prepared by recrystallizing nickel nitrate three times and igniting in a current of nitrogen. The lattice constant of this nickel oxide (8) was taken as $4.1684\text{\AA}$ in calculating the camera radius. This value of the radius

was checked by redetermining the lattice constants of copper and nickel oxide on separate films. These values were obtained by the method of Bradley and Jay (6), but were not corrected for film shrinkage.

Nickel oxide was also used in order to correct the calcium sulfate patterns for possible errors due to film shrinkage, eccentricity of sample, and absorption in the sample. This material was mixed with the samples in a ratio of about 1 part nickel oxide to 12 parts calcium sulfate. The values of $\sin \theta$ for the various reflections of nickel oxide were determined from the observed spacings on the film. These values were then compared to those calculated assuming $a_0 = 4.1684 \text{ \AA}$. A curve obtained by plotting corrections against $\sin \theta$ was used to determine the corrections for the various reflections from calcium sulfate. The results are given in chart form in Figure 4, while some of the negatives are reproduced in Figure 5. The corrected data for purpose of comparison is given in Table 3. The interplanar spacings in Angstroms are denoted by d_{hkl} and the estimated relative intensities by I . The pattern for a sample obtained at 164° in a vapor pressure of 23 mm. was identical with that obtained by dehydrating the hemihydrate 24 hours in a vacuum at 145° .

Figure 4

Diagram of X-ray Diffraction Patterns for Hemihydrate
and Dehydrated Hemihydrate
(Seemann apparatus, K_{α} Cu radiation)

Figure 5

X-ray Diffraction Patterns of Hemihydrate and Dehydrated
Hemihydrate

Table 3
X-ray Diffraction Data

Hemihydrate $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$		Dehydrated Hemihydrate CaSO_4	
d_{hkl}	I	d_{hkl}	I
6.000	10	6.000	10
3.468	9	3.468	7
3.002	10	3.012	10
2.898	1		
2.797	10	2.793	10
2.703	3	2.711	3
(N10) 2.407	7	(N10) 2.407	7
2.337	2	2.335	3
2.272	1		
2.131	2	2.138	1
(N10) 2.084	9	(N10) 2.084	9
2.002	1	1.995	1
1.905	3	1.870	4
1.848	10	1.844	7
1.792	1		
1.732	3	1.741	3
1.692	7	1.692	5
1.662	4		
1.602	1		
1.527	1	1.506	1
(N10) 1.474	10	(N10) 1.474	10
1.441	1	1.432	1
1.394	1		
1.353	1	1.349	1
1.296	4	1.292	4
(N10) 1.257	5	(N10) 1.257	5
1.238	4	1.237	4
(N10) 1.203	5	(N10) 1.203	5
1.167	1	1.161	1
1.153	2	1.142	3
1.122	1		
1.079	1	1.090	1
1.068	2	1.065	1
1.056	2		
(N10) 1.042	3	(N10) 1.042	3
1.011	1	1.026	2
0.9969	1	1.009	2
(N10) 0.9563	4	(N10) 0.9918	2
0.9418	1	(N10) 0.9563	4
(N10) 0.9321	4	0.9441	1
		(N10) 0.9321	4

Discussion

Isobaric dehydration of gypsum results first in the formation of the hemihydrate, which adsorbs a small amount of water. Upon further heating, the hemihydrate decomposes stepwise into the highly hydrous dehydrated hemihydrate. This material which is a very strong dessicant (5), (20) does not lose all of its water until heated at temperatures much greater than the hemihydrate decomposition temperature. The dehydration isobars for hemihydrate, both on dehydration and rehydration, are clearly typical of hydratic decomposition of a hydrous material into a material that adsorbs water, and show no indication of a continuous, zeolitic loss of water. These results are in agreement with the isobar of Linck and Jung (25) and that first obtained by Balarew (1). The isotherms of Balarew (4) seem to indicate the hemihydrate loses most of its water at the same vapor pressure although it shows an apparent gradual decrease in vapor pressure with the loss of approximately the last 0.1 mol. It appears likely that this final continuous part of the isotherm is due to the loss of adsorbed water. The conflicting results obtained by Linck and Jung and others must be attributed to the failure to obtain equilibrium.

X-ray diffraction studies show that there are four separate crystal forms of calcium sulfate: gypsum, hemihydrate, dehydrated hemihydrate, and anhydrite.

The powder diffraction pattern for dehydrated hemihydrate, while very similar to that of hemihydrate, has distinct characteristic differences. The close agreement between the principal reflections of the two materials shows that the type of lattice and size of the unit cell are similar. However, the pronounced changes in the hemihydrate pattern on dehydration indicate that the water molecules occupy definite fixed positions in the lattice. The hemihydrate of calcium sulfate, therefore, cannot be classed among the compounds of zeolitic type, which show no change in crystal structure on dehydration.

Jung (21), Ramsdell and Partridge (31), and Caspari (9) reported that powder photographs of the two materials are the same, while Onorato (27), and Gallitelli (14) stated that the structures are identical, but recognize small differences in the patterns. It appears that the latter investigators did not realize the significance of the small differences involved. This case is not unique; e. g., Bradley and Roussin (7) have reported the existence of a range of aluminosilicate compounds, the mullites, which likewise show small, but distinct, differences in x-ray powder photographs. The failure of other investigators to recognize the change in the hemihydrate pattern on dehydration was probably due to the use of small size cameras, use of molybdenum radiation in some cases, the failure to use a reference material to standardize films, and the failure to prevent rehydration of dehydrated material.

However, using a large camera, standardizing material, copper radiation, and taking care to prevent rehydration, the differences obtained are unquestionable. These differences agree qualitatively with those of Feitnecht, but exact comparison is impossible because this investigator published his results only in rough chart form.

Summary

1. Contrary to the results of Balarew, Linck and Jung, Gibson and Holt, and others, calcium sulfate hemihydrate on dehydration does not lose its water continuously after the manner of zeolites. Careful isobaric dehydration results in a univariant step curve of the typical hydrate type.

2. Contrary to the conclusions of Jung, Ramsdell and Partridge, Caspari, Onorato, and Gallitelli, the structure of dehydrated hemihydrate is not identical with that of hemihydrate as would be expected for a zeolitic type compound. While the structures are analogous, x-ray diffraction diagrams obtained by precision methods show distinct differences between the two materials. The water molecules form an essential part of the lattice and their removal causes a small, but definite rearrangement of the unit cell. These results are in accord with those obtained by vapor pressure methods which show that calcium sulfate hemihydrate is a definite chemical compound of the ordinary hydrate type.

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