

CHEMICAL REACTIONS UNDER ULTRA HIGH PRESSURE. DEHYDRATION OF SALT HYDRATES.

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Introduction.

It is already reported^{(1),(2)} that the molecules were destroyed and chemical reactions were caused by the mechanical force accompanied with the pressure applied to the solid sample at room temperature. For example, under pressure of 5,000 kg/cm², ammonium carbonate was converted to urea by the dehydrating reaction, and also from egg-albumin the water contained was separated. In order to confirm whether salt hydrate powder is dehydrated or not by the mechanical force, this experiment is performed, calcium sulphate and cupric sulphate being used as samples.

E. S. Larsen and P. W. Bridgman already reported⁽³⁾ that, on the shearing experiment which was attempted to form the so-called "stress mineral" under high pressure at room temperature, the dehydration of gypsum occurred. According to them, applying the shearing stress of 10,000 ~ 15,000 kg/cm² under pressure of 50,000 kg/cm², gypsum loses water and is definitely changed. From the results of X-ray examination, when the powdered sample is compressed, the central part of sheared gypsum still consists of gypsum. Its outer part does not resemble the pattern of anhydride nor that of plaster of paris. It must be either the monohydrate or soluble anhydride.

In general it is known^{(4),(5)} that, when salt hydrate is together with a small quantity of hydrate of lower grade, the rate of dehydration is accelerated because the latter becomes the nucleus of reaction and a auto-catalytic reaction occurs. Therefore, if the lower hydrate would be formed even in a small quantity by applying pressure, it might be expected that the dehydration is accelerated. Then, in this paper, after the solid sample itself is directly compressed by means of a piston without the pressure transmitting fluid up to any desired pressure, the dehydration curves are determined. From these results it seems plausible that the crystal water of salt hydrates become unstable by applying pressure.

Experimentals.

(1) The sample.

(i) Calcium sulphate.

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- (1) R. Kiyama and T. Yanagimoto, *This Journal*, 21, 32 (1951)
 - (2) R. Kiyama and T. Yanagimoto, *ibid.*, 21, 41 (1951)
 - (3) E. S. Larsen and P. W. Bridgman, *Amer. J. Sci.*, 36, 81 (1938)
 - (4) W. E. Garner and M. G. Tanner, *J. Chem. Soc.*, 47 (1930)
 - (5) W. N. Rae, *J. Chem. Soc.*, 109, 1229 (1916)

(a) Calcium sulphate dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

It is prepared by the double decomposition of calcium chloride and sodium sulphate. The quantity of crystal water is 20.93 %.

(b) Calcium sulphate hemihydrate (plaster of paris) $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.

It is prepared by heating the dihydrate at 110°C .

(c) Soluble calcium sulphate anhydride CaSO_4 .

It is prepared by heating the dihydrate at 200°C for a long time.

(d) Insoluble calcium sulphate anhydride CaSO_4 .

It is prepared by igniting the dihydrate at $700 \sim 800^\circ\text{C}$.

(ii) Cupric sulphate.

Commercial cupric sulphate pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is recrystallized from its aqueous solution and the 250 mesh fine powder obtained is used as the sample. Cupric sulphate monohydrate $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is prepared by heating the pentahydrate at 115°C .

(iii) Sodium chloride.

NaCl guaranteed for analysis is used.

(2) The high pressure apparatus and procedure.

The high pressure apparatus used for the present experiment has been already reported⁽¹⁾.

After calcium sulphate has been subjected to any pressure at room temperature, this sample is kept in an air-thermostat at 60°C , being compared with the original one (pressure not applied), and the dehydration curves are determined by measuring the decrease of weight.

For cupric sulphate, the same operation is carried out in a desiccator with CaCl_2 at room temperature ($0 \sim 7^\circ\text{C}$).

Experimental Results.

(A) Calcium sulphate.

(1) Dehydration curves of the dihydrate.

To compare the samples to which pressure has been applied with those not applied, the dehydration curves of calcium sulphate dihydrate alone or a mixture of dihydrate and a small quantity of either hemihydrate or soluble anhydride or insoluble anhydride, are determined. As shown in Fig. 1, the crystal water does not yet decrease in duration of the measurement, excepting for a small quantity of soluble anhydride with the dihydrate.

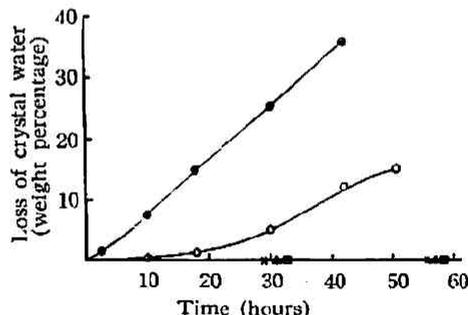


Fig. 1 Dehydration curves of the dihydrate at 60°C .

- dihydrate
 △ dihydrate + hemihydrate (weight ratio 50:1)
 × dihydrate + insol. anhydride (" ")
 ○ dihydrate + sol. anhydride (trace)
 ⊙ dihydrate + sol. anhydride (weight ratio 50:1)

(2) Dehydration curves of the pressure applied dihydrate.

(i) In an experiment of the dihydrate alone, the dehydration curve of the 5000 kg/cm^2 pressure applied, as shown in Fig. 2,

resembles that of the original mixture of dihydrate and a trace of soluble anhydride.

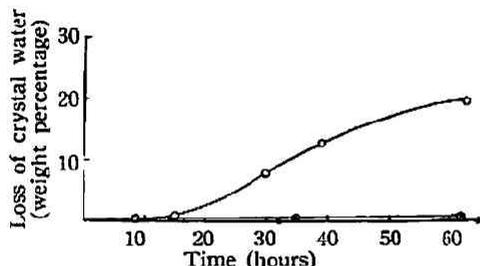


Fig. 2 Dehydration curves of the pressure applied dihydrate at 60°C.

- × atmospheric (on the time axis)
- 500 kg/cm² applied
- 5,000 kg/cm² applied

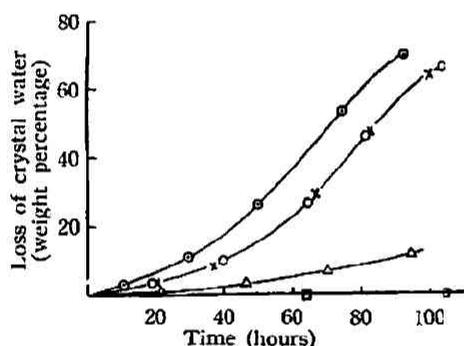


Fig. 3 Dehydration curves of mixtures of dihydrate and sodium chloride (equi. weight) at 60°C.

- | | | |
|---|----------------------------------|--------|
| □ | atmospheric (on the time axis) | 0 hr. |
| △ | 1,000 kg/cm ² applied | 0 hr. |
| ○ | 5,000 kg/cm ² applied | 0 hr. |
| × | 5,000 kg/cm ² applied | 2 hrs. |
| ● | 6,300 kg/cm ² applied | 0 hr. |

in Fig. 4, the adherent water is lost without delay to 2 mols crystal water.

(iv) In case of compressing hydrostatically the sample to pressure of 5,000 kg/cm² using an air as pressure transmitting medium, as already reported^{(2), (6)}, the dehydration curve is the same as that of the original.

(3) Others.

After the dihydrate was compressed to pressure of 5,000 kg/cm², the change of crystal water is measured from weight by igniting, but it is not changed.

(ii) In case of compressing a mixture of dihydrate and sodium chloride which was used as a catalyst in the previous work⁽¹⁾, as shown in Fig. 3, it is known that the increase of dehydrating velocity is greater than that of the pressure applied to dihydrate alone and when higher pressure is applied, the dehydrating velocity increases.

The influence of duration of the pressure applied for the rate of dehydration can not be recognized, as shown the curves of 5,000 kg/cm² pressure applied in Fig. 3. But, prolonging the hour to apply the pressure, it is observed, makes the sample semitransparent and hardened.

(iii) After a pressure of 5,000 kg/cm² is applied to the dihydrate, the sample is exposed in the air at room temperature during a definite hour. In this case, if the lower hydrate has been formed by compression, it will return to the dihydrate by absorbing the moisture in the air. When the dehydration curves of such samples are measured, as shown

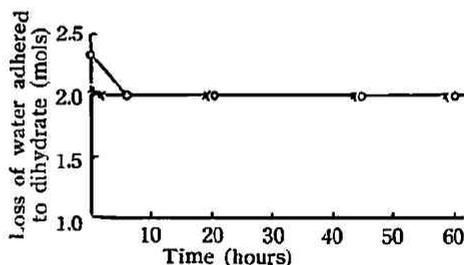


Fig. 4 Dehydration curves (at 60°C) of the exposed sample of the pressure applied.
 × dihydrate
 5,000 kg/cm² applied, 0.5 hrs. exposed.
 ○ dihydrate+sodium chloride (equi. weight)
 5,000 kg/cm² applied, 2.5 hrs. exposed.

From the results of X-ray examination the difference between the samples of 5,000 kg/cm² pressure applied and not applied can not be recognized.

In comparison with the external appearance of two pressure-applied samples, dihydrate and anhydride, the former by compressing to 5,000 kg/cm² becomes glassy semitransparent block as if it were melted, on the other hand, the latter is only an assembly of white powder cake even though compressed to the same degree.

(B) Cupric sulphate.

In case of cupric sulphate is obtained much the same results with calcium sulphate. As shown in Fig. 5, from the dehydration curve the following is known.

(i) In case of the pressure not applied, a trace of monohydrate being mixed with the pentahydrate, the decrease of weight occurs, and not in case of pentahydrate alone.

(ii) In case of the pressure applied, the crystal water decreases in amount, but after the pressure-applied sample was exposed in the air, it does not decrease.

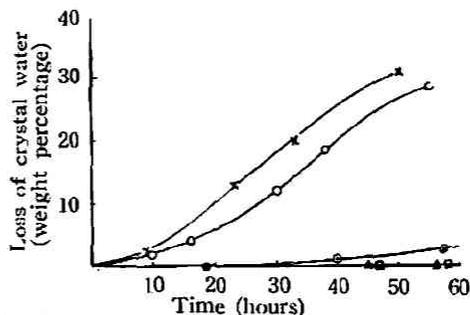


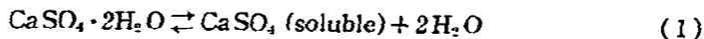
Fig. 5 Dehydration curves of the pentahydrate at 0~7°C.

Pentahydrate alone
 □ atmospheric (on the time axis)
 ○ 500 kg/cm² applied
 ○ 4,500 kg/cm² applied
 △ 4,500 kg/cm² applied (2.5hrs. exposed)
 pentahydrate+monohydrate (weight ratio 20:1)
 × atmospheric

Considerations.

(A) Calcium sulphate.

From the dehydration curves it is known that the pressure-applied dihydrate is more easily dehydrated than that not applied at 60°C. It seems, from Figs. 1 and 2, because a small quantity of soluble anhydride is formed by compression as shown in the following equation and it acts as a core of reaction.



However, from the dehydration curve of the pressure-applied sample exposed for a certain hour in the air, and from the results of the measurement of a quantity of crystal water by igniting and the examination of X-ray, the dehydration of dihydrate does not occur. It is because that the difference between compressed and uncompressed samples can not be recognized by their methods since all or the greater part of soluble anhydride formed returns to dihydrate at once by absorbing the moisture in the air.

Considering the volume change of equation (1), at atmospheric pressure the volume of the right side is greater than that of the left. If this relation is kept until a pressure of 5,000 kg/cm², the dehydration may not occur seeing from the thermodynamic standpoint. And moreover, the pressure-applied sample does not

differ from the original when a pressure applied to the dihydrate hydrostatically using the air and the duration of pressure applied does not effect the dehydration curve, but it is known that the crystal grains are broken and teared out by the shearing stress caused by the compression and part of the reaction system is under a condition as shown in equation (1). Then, taking out the sample from the pressure vessel the reaction tends to the left side of equation (1), but, in consequence of losing the water accidentally during the operation, a small quantity of soluble anhydride, which can not be recognized by X-ray examination or weighing, is produced. Therefore, it is considered that the dehydration process corresponds to that of the uncompressed dihydrate with a small quantity of soluble anhydride.

Although the promotion of dehydration may be expected from the change of grain size caused by the compression, and not from the formation of soluble anhydride, yet it is denied from the following reasons. The difference in grain size between the pressure-applied dihydrate and that not applied, can not be recognized on the dehydrating curves (Exp. results 2 (iii), 1). Therefore, the promotion of dehydration in this experiment depends upon not so much the change of grain size as a small quantity of soluble anhydride in the dihydrate. In addition, as it is known⁽⁷⁾ that the surface area decreases on account of being compact when the powdered solids are compressed, the rate of dehydration may decrease.

As for the effect of sodium chloride, P. P. Budnikoff and L. A. Schtschukareva already reported⁽⁸⁾ that it retards the dehydration of gypsum in atmospheric pressure, but it is contrary to this high pressure experiment.

The effect of temperature in compression need not be considered since the difference between the effect of adiabatic compression and isothermal one is not recognized.

Comparing these results with E. S. Larsen's and P. W. Bridgman's⁽⁴⁾, although they maintain that gypsum loses water and changes to soluble anhydride or monohydrate, yet the existence of the latter is denied in general, and then the former is only the expected one and is agreed with the expectation from this experiment. But, in this experiment it is known that the crystal water become unstable at lower pressures than those they used.

(B) Cupric sulphate.

The result of cupric sulphate is quite analogous with the results in calcium sulphate and supports the above considerations.

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