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Thermal Decomposition of Calcium Sulfate Dihydrate under Self-generated Atmosphere

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Dehydration of calcium sulfate dihydrate was studied by means of simultaneous TG-DTG-DTA under various sealed atmospheres corresponding to three systems open, completely sealed, and quasi-sealed. Two dehydration steps could be detected under self-generated atmospheres by using 12.3, 18.7, 30.0, and 250 μm tungsten wires. This new method enables us to identify intermediates more easily than any other techniques hitherto adopted. Endothermic DTA peaks appeared earlier, at 129 and 133 °C, than the point of decreasing TG. This technique, resembling the quasi-isothermal and -isobaric thermogravimetry (Q-TG), is superior to Q-TG in that it requires smaller amounts of sample.

By the self-generated atmosphere[1] is meant an atmosphere which is composed of gaseous decomposition products of a reaction and which is in intimate contact with the sample with the aid a sample holder employed. In the case of thermal decompositions producing gases, the equilibrium will be attained for the partial pressure of the gases. It was reported[2] that a thermal decomposition of ammoniumh eptamolybdate(6−) tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, AHM) producing both H_2O and NH_3 was studied by means of simultaneous TG-DTG-DTA from room temperature to 500 °C under static air atmosphere and flow conditions of various gases. This system was also subjected to Q-derivatography (quasi-isothermal and -isobaric thermogravimetry) and home-built quasi-sealed thermogravimetry.[3] The first step of the thermal decomposition of AHM was considered to be associated with two reaction schemes,[4–6] one Funaki's scheme and the other Ma's. Our results proposed a new reaction scheme, and disclosed a new intermediate stage. However, it was difficult to get rid of intermediates out of the apparatus and also more difficult to identify the intermediate because of the uncertainty of element analysis. Until then we had been able to clarify the existence of anhydrous after dehydration and the new intermediate had been confirmed by means of high-temperature oscillating X-ray diffraction with a rotating anode-type large-capacity generator.[7] In the case of thermal decomposition of AHM, our conclusion was that both H_2O and NH_3 are capable of desorbing simultaneously after dehydration. As to the self-generated atmospheres of H_2O and NH_3, the thermal decomposition mechanism was affected by that changeable condition.

Next, we selected calcium sulfate dihydrate ($CaSO_4\cdot 2H_2O$) as a model substance since it produces only H_2O in its thermal decomposition from room temperature to 400 °C which may be followed by TG-DTG-DTA and quasi-sealed TG.

There are various dynamical techniques for thermal analysis which are powerful for studying the thermal decomposition. Instruments have become capable of auto-operation, thus improving both the accuracy and precision of measurements as well as reducing both investigator's time and patience. Advantages of these methods are that extremely small amounts of sample may be required, that operator's time may considerably be saved, and that reaction rate may be determined very easily. But information furnished from various apparatus are different from one another. In order to eliminate the above disadvantages, we will discuss the applicability of the quasi-sealed TG under the condition of self-generated atmosphere.

Experimental

Materials. Calcium sulfate dihydrate of Wako Co. or Nakarai Co. (GR quality) was used in the form of powder. The sample amounts used were from 0.0023 mmol (0.40 mg) to 0.10 mmol (18 mg) and the reference material used for DTA was α-Al_2O_3.

Apparatus. A modified Thermoflex 8002 (Rigaku Denki Co.) was used for simultaneous TG-DTG-DTA measurements. The range of temperature covered was usually from room temperature to 360 °C and the sample was heated, in most cases, at the rate of 1 °C/min (the mean heating rate 1.005 °C/min).

Quasi-sealing. Aluminium small pan and cover (Rigaku Denki Co.) were sealed completely by the sample sealer for liquid materials (Rigaku Denki Co.) (Fig. 1). For the purpose of quasi-sealing, both aluminium pan and the cover and thin tungsten wire (12.3, 18.7, 30.0, 250, or 250 $\mu m\phi \times 2$) were sealed in the same way as illustrated (Fig. 1(a)) and this sealed pan had a small leak along the thin wire. In the case of completely sealed pan, the critical explosion pressure had been determined to be above 3 atm.[8]

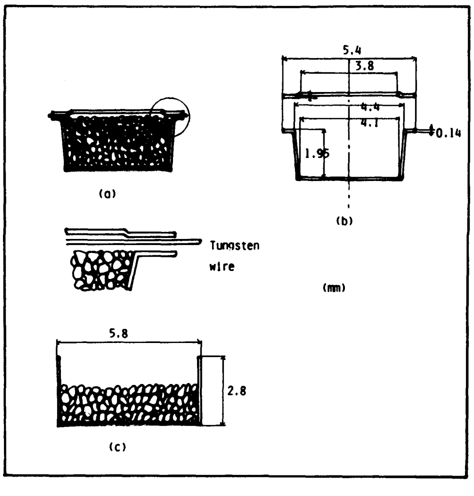

Fig. 1. a) Schematic diagram of a sample cell, aluminum cell. b) Dimension of sample cell. c) Schematic diagram of a sample cell, platinum cell.

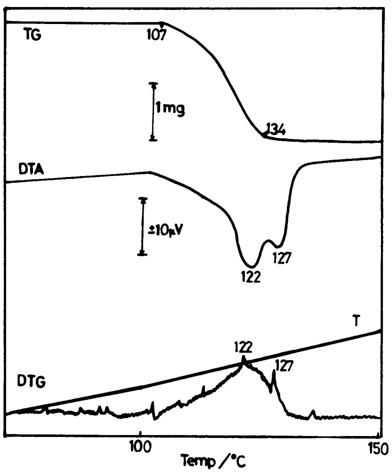

Fig. 2. TG-DTG-DTA of calcium sulfate dihydrate under open system. Sample amount is 0.067 mmol. Reference material is α-Al_2O_3. Cell is platinum. Heating rate is 1 °C/min.

Results and Discussion

Open System. With platinum cells (Fig. 1(c)), sample weights were changed from 0.0289 mmol (4.98 mg) to 0.090 mmol (15.56 mg) and simultaneous TG-DTG-DTA measurements were run. The range of TG used was usually 10 mg, and the ranges of DTA used were both ±100 and ±20 μV (the upper side corresponds to exothermic reaction). Typical results for 0.067 mmol of $CaSO_4 \cdot 2H_2O$ are shown in Fig. 2. The results of TG indicates two different types of descent tendencies and the result of DTG also indicates two peaks but they cannot be seperated from each other completely. If we want to analyse the thermal decomposition by the Freeman-Carroll[9] or Coats-Redfern method,[10] we must discuss these methods.

The endothermic peak of DTA owing to dehydration begins at 102 °C, and the descends of TG and DTG curves begin at 107 and 102 °C, respectively. For the simultaneous technique, the same temperature of 102 °C indicates the coincidence of the thermal and thermogravimetric behaviours of dehydration. But this temperature is not easy to be regarded as the decomposition temperature because the temperature would change if we change some experimental conditions, *e.g.*, the sample amount, heating rate, sensitivity of TG, DTG, and DTA, and signal-to-noise ratio. The DTA peak is divided into two peaks at 122 and 130 °C, and the reaction steps may be considered to be composed of two. With the method described in a previous report[11] it was difficult to seperate reaction steps into two.

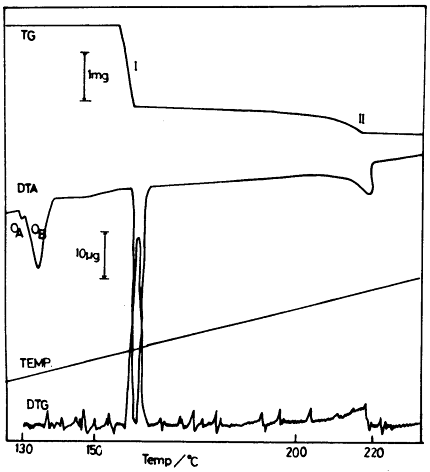

Fig. 3. TG-DTG-DTA of calcium sulfate dihydrate under completely sealed system. Sample amount is 0.0670 mmol. Reference material is α-Al_2O_3. Cell is aluminum. Heating rate is 1 °C/min.

Completely Sealed System. According to the suggestion of Miyazaki,[11] in order to obtain TG-DTA curves in an atmosphere containing much water vapor, TG-DTG-DTA measurements on samples of 0.0136, 0.0293, and 0.0670 mmol were run in the completely sealed system. The results of TG-DTG-DTA for the open system is apparently different from that for the completely sealed system. Figure 3 shows results of the sample of 0.0670 mmol. Concerning the TG results, the first step of TG seems to be a rapid decreasing reaction which corresponds to the dehydration of $\frac{3}{2}H_2O$ to produce $CaSO_4 \cdot \frac{1}{2}H_2O$, from a calculation of weight losses. Concerning the results of DTA, both endothermic peaks of the first and second steps to be at 162 and 219 °C, respectively. At lower temperatures than these, endothermic peaks without decreasing TG appear to be around 129 and 133 °C. These are named the O_A and O_B steps. Such behaviour is observed in 15 cases of sample weights ranging from 0.0030 to 0.0714 mmol. Almost the same temperature is registered for each group of O_A and O_B steps.

Reaction scheme for the TG descent may be considered as follows:

$$CaSO_4 \cdot 2H_2O \longrightarrow CaSO_4 \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O, \qquad \text{(I)}$$

hemihydrate (15.70% loss)

$$CaSO_4 \cdot \frac{1}{2}H_2O \longrightarrow CaSO_4 + \frac{1}{2}H_2O. \qquad \text{(II)}$$

nonhydrate (5.23% loss)

The rapid descent of the first step of TG is considered to be in the following sequence. Desorption of H_2O owing to hydration at the O_A and O_B steps and after these steps continue gradually, and the equilibrium vapor pressure is increased greatly by a rise in temperature, until the aluminum pan is caused to explode above the critical pressure. Considering the change in weight of H_2O, 1.812 mg, and the capacity of the sealed cell, 0.029 cm^3, the water vapour pressure is as high as about 6 atm at 159 °C.[9] Then H_2O of 0.0049 mmol is liberated and equilibrated. Over the critical pressure for the aluminium pan, the sealed pan is opened under the vapor pressure of H_2O and the vapor is allowed to escape from the sealed pan through the leak. The equilibrium of Reaction I is disturbed, the self-generated atmosphere is removed from the pan, and the unreacted water of Reaction I begins to be liberated rapidly. The rapid descent for the first decomposition step is caused in such a way that the response rate is slower than the reaction rate or both rates were fast so that the equilibrium is disturbed and the unreacted substance is changed under a superheated condition. We must consider the situation more carefully. However, the temperature of 159 °C is higher than the end temperature of the second reaction illustrated in Fig. 2 (static condition), but it is important that the second reaction is not yet allowed to begin. A summary of the results of TG, DTG, DTA suggests a mechanism for the hydration which is considerably different from that of the first reaction. The results of TG were analyzed by the Coats-Redfern method, the reaction order, n, being determined as follows:

1) In the case of sample weight 15.08 mg and diameter of tungsten wire 12.3 μm:
   I step: 2.0 order reaction.
   II step: 1.0 order reaction.
2) In the case of sample weight 10.00 mg and diameter of tungsten wire 30.0 μm:
   I step: 2.5 order reaction.
   II step: 1.0 order reaction.

According to published results,[11] the first reaction step has been considered to be dehydration of structural water and the second reaction step to be dehydration of mobile water. But this water may come out at relatively high temperatures and the temperature ranges for the two dehydrations are about 60 °C. Until now we couldn't ewplain this behaviour by means of the sealed method or on account of property of mobile water. Moreover, in order to compare the decompositions of $CaSO_4 \cdot \frac{1}{2}H_2O$ and $CaSO_4 \cdot 2H_2O$ by means of the completely sealed TG, measurements were made by TG-DTG-DTA. The same results were obtained except the behavior of the water previously adsorbed (Fig. 4). The second steps of both $CaSO_4 \cdot \frac{1}{2}H_2O$ and $CaSO_4 \cdot 2H_2O$ were almost the same. For this reason the product of the first step of decomposition of $CaSO_4 \cdot 2H_2O$ may be considered to be $CaSO_4 \cdot \frac{1}{2}H_2O$.

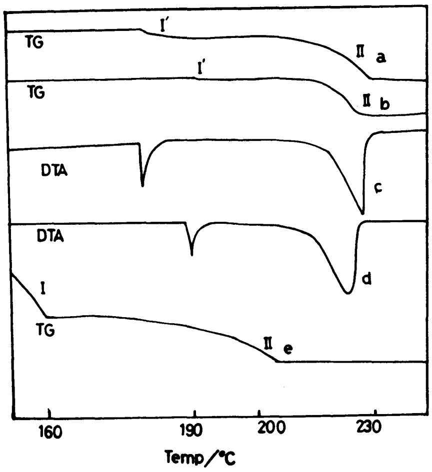

Fig. 4. TG-DTA of $CaSO_4 \cdot \frac{1}{2}H_2O$ under completely sealed method.
a): TG, sample amount is 18.73 mg ($CaSO_4 \cdot \frac{1}{2}H_2O$),
b): TG, sample amount is 15.38 mg ($CaSO_4 \cdot \frac{1}{2}H_2O$),
c): DTA, sample amount is 18.73 mg ($CaSO_4 \cdot \frac{1}{2}H_2O$),
d): DTA, sample amount is 15.38 mg ($CaSO_4 \cdot \frac{1}{2}H_2O$),
e): TG, sample amount is 11.57 mg ($CaSO_4 \cdot 2H_2O$).

With respect to these O_A and O_B peaks, Table 1 and Fig. 5 show figures and behaviour of O_A and O_B, when the amount was changed from 0.00302 to 0.0714 mmol. Peak temperatures are consistent with each other within the experimental error. The difference in temperature of the O_A and O_B peaks is about 4 °C on the average, in dependent of sample amount. Two possible explanations are applicable to these results: one is that there are two binding states of water which may be seperated from each other in the process of dehydration; the other is that in the case of complete sealing, a part of H_2O is caused to come out in an endothermic reaction. Moreover, when the system temperature is increased

Table 1. Peak temperatures of DTA of O_A step (T_{O_A}) and O_B step (T_{O_B}) under completely sealed system

W/mmol[a]	T_{O_A}/°C	T_{O_B}/°C
3.02×10^{-3}	127	135
5.98×10^{-3}	127	135
5.98×10^{-3}	127	135
1.36×10^{-2}	133	135
2.93×10^{-2}	131	134
2.93×10^{-2}	132	134
2.94×10^{-2}	130	133
2.94×10^{-2}	131	133
2.97×10^{-2}	130	133
2.99×10^{-2}	130	133
5.78×10^{-2}	127	130
6.63×10^{-2}	129	131
6.70×10^{-2}	130	134
6.72×10^{-2}	128	133
7.14×10^{-2}	127	131
Average	129.3 ± 2.0	133.3 ± 1.6

a) W is sample weight.

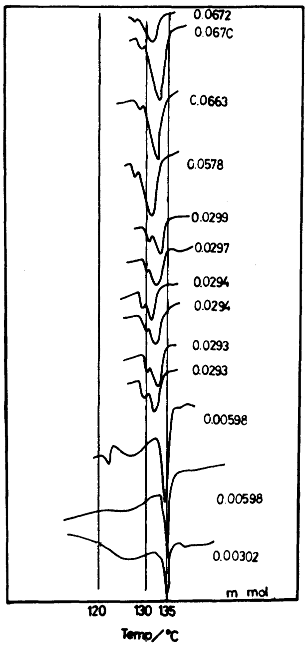

Fig. 5. Temperatures of endothermic DTA peaks, O_A and O_B. Sensitivity is aribitary.

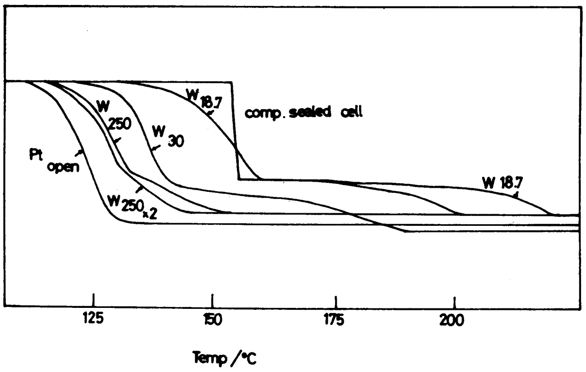

Fig. 6. TG results of quasi-sealed system (and those of open system and completely sealed system).

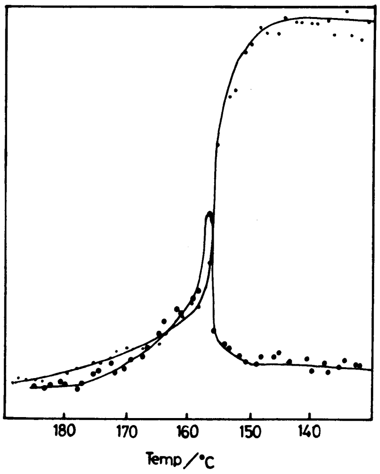

Fig. 7. High temperature oscillating X-ray diffraction pattern of $CaSO_4 \cdot 2H_2O$.
Heating rate, 2 °C/min. Chart speed, 0.5 cm/min. X-Ray source, Cu *Kα* 120 mA, 50 kV.

several degrees, the decomposition process is resumed and the amount of the water coming out from the sample is increased. If the sample amount is made to decrease, the O_A peak of DTA becomes broader and the effect of diffusion in the sealed cell comes to play an important role. In addition, the descent for the second step of TG is caused slowly in raising temperature and it is better to consider that the leak is in operation.

Quasi-sealed Method. A TG-DTG-DTA curve was recorded for the quasi-sealed system and is shown in Fig. 6, which induces the results for both the open and completely sealed systems for comparison; a selection has been made so that all the sample weights may fall in the range 11.54—12.60 mg. As the radius of tungsten wire is increased, results become similar to those of the open system. Onset temperatures of reaction are 111, 113, and 114 °C in the case of open system, two pieces of 250 μm tungsten wire, and a piece of 250 μm tungsten wire, respectively. But the turning point of TG presents itself more clearly and the peaks of DTA can be seperated more easily. The results of both the 30 and 18.7 μm tungsten wires indicate that the decreasing temperatures are 125 and 127 °C and appear with more enhanced separation. These results are what we have expected. In the case of quasi-sealed system, dehydration first occurs after some inner pressure of water vapor had been reached, making a TG decreasing recognizable. If we want to get the stable state of $CaSO_4 \cdot \frac{1}{2}H_2O$, we must use a tungsten wire 30 μm or less in radius.

A precise measurement of high-temperature oscillating X-ray diffraction of calcium sulfate dihydrate was done at a heating rate of 2 °C/min. The result could identify the stable $CaSO_4 \cdot \frac{1}{2}H_2O$ (Fig. 7).

In connection with the above-mentioned experimental results, the following conclusions may be drawn:

(1) According to the experimental results of Miyazaki,[11] it is difficult to separate the first and the second steps of $CaSO_4 \cdot 2H_2O$ decomposition. However, he succeeded only in first making non-hydrate $CaSO_4$ followed by making $CaSO_4 \cdot \frac{1}{2}H_2O$ under the saturated vapor pressure of water. But in our cases, we could easily seperate two steps under a quasi-sealed condition using 12.3, 18.7, and 30.0 μm tungsten wires.

(2) This method enables one to seperate dehydrations of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $CaSO_4 \cdot 2H_2O$, *etc.*, so that we can easily get intermediates. The advantage of this method is that it requires smaller amounts of sample than the Q-TG method. By smaller amounts of sample it is meant that there are narrower ranges of temperature distribution and that there may be many applications available to other fields, for example, biochemistry.

(3) In the process of dynamic heating, the temperature distribution caused by endo- and exothermic behaviour is relatively small so that the quasi-equilibrium condition may be established easily.

(4) With the completely sealed system, two types of reactions, O_A and O_B occur without decreasing TG. But this phenomenon cannot be explained in terms of different stages of binding or influence of the self-generated condition.

Simple inorganic salts containing water have been studied by means of simultaneous TG-DTG-DTA. Since it seemed most important to investigate first self-generated atmospheres, we planned to study those in the vacuum condition as well as in the gas-flowing condition; thus in the present report, we have studied the self-generated atmosphere.

This study will be applied to various dehydration systems, especially those for which it is said to be difficult to remove intermediates. Now we are planning to apply this method to various decompositions involving gases such as CO_2, H_2S, and NH_3. We are also planning to invent a micro-quasi-isothermal and -isobaric thermogravimetry.

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References

1) W. W. M. Wendlandt, "Thermal Method of Analysis," 2nd ed, John Wiley and Sons, New York (1973), p. 37.

2) K. Isa, Y. Hirai, and H. Ishimura, *Proc. of the 5th Int. Conf. on Thermal Analysis*, Kyoto, Sept. 1977, p. 348.

3) K. Isa, S. Fukuo, H. Kondo, and H. Ishimura, 15th Calorimetry Conference in Japan (1979), p. 130.

4) K. Funaki and T. Segawa, *J. Electrochem. Soc. Jpn.*, **1950**, 152.

5) E. Ma, *Bull. Chem. Soc. Jpn.*, **37**, 649 (1964).

6) Funaki's scheme:

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O \longrightarrow (NH_4)_6Mo_7O_{24} \longrightarrow (NH_4)_4Mo_8O_{26} \longrightarrow MoO_3.$

Ma's scheme:

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O \longrightarrow (NH_4)_5Mo_5O_{17} \longrightarrow (NH_4)_4Mo_8O_{26} \longrightarrow MoO_3.$

7) K. Isa and H. Ishimura, *Bull. Chem. Soc. Jpn.*, **54**, 3628 (1981).

8) Private communication.

9) E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).

10) A. W. Coats and J. P. Redfern, *Nature*, **201**, 68 (1968).

11) H. Miyazaki, *Kogyo Kagaku Zasshi*, **70**, 261 (1967).