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Thermal Decomposition of Ammonium Salts of Transition Metal Oxyacids. I. Thermogravimetric Analysis of Ammonium Paramolybdate

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The decomposition of ammonium paramolybdate (APM) has been investigated by using a quartz spring balance in various ambient pressures. APM is decomposed in four or five stages, including a dehydration procedure, depending on the ambient pressures. However, these results do not agree with those of previous reports. This discrepancy may be attributed to the use of a sensitive quartz spring balance, a small amount of a sample, the application of a slow heating rate, or the utilization of DTG curves in the present study. The control of the ambient pressure was effective in investigating the thermogravimetric change in detail, especially in confirming the dehydration reaction. It is also concluded clearly that, in the course of the decomposition process, there is a final decomposition stage which has never been reported. The kinetics of the thermal decomposition was studied. The activation energies of the decomposition of APM under 760 Torr are 38.6, 194.8, 81.9, and 151.2 kcal·mol^{-1} respectively for the first to the fourth stages.

The thermal decomposition of ammonium paramolybdate tetra-hydrate (APM) has been studied by many investigators, and its decomposition process and the intermediates have been reported.$^{1-9)}$ It was found by thermal analysis that APM decomposes in three stages. However, Rode and Tverdokhlebov reported that it decomposes in four stages, that is, they said there is a dehydration stage of all the hydrated water molecules. They also determined the composition of the intermediates by chemical analysis, by the X-ray diffraction method, *etc.* Their results, however, disagree with each other. Especially, the decomposition temperatures of the first stage and the third stage on their thermogravimetric curves (TGA) and the compositions of the intermediates are not in agreement with each other. This could be due to the differences in the experimental conditions and methods they adopted. Nevertheless, both of them forms a stable substance, $(NH_4)_2O \cdot 4MoO_3$, as a decomposition product up to the second stage.

In the present experiment, the ambient pressure was controlled in order to study the process of the first and third decomposition stages in detail, for about these stages the previous papers were not in agreement. The pressure-control method means to maintain a constant ambient pressure of a desired value during the decomposition.

The gases evolved by decomposition generally diffues slowly from the vicinity of the sample under normal atmospheric pressure, but the diffuse more rapidly when the ambient pressure decreases. As a result, changes in the decomposition process can be expected. If the evolving gases near the sample are continuously eliminated, we can expect to obtain different information.

The experiments were carried out by means of thermogravimetric analysis, using a highly-sensitive quartz spring balance calibrated for thermal agitation, in seven different ambient pressures: 760, 580, 130, 70, 20, 5, and 10^{-3} Torr (*in vacuo*). The final products of decomposition were identified by means of X-ray diffraction.

Experimental

Apparatus and Procedure. The thermogravimetric measurement was carried out by means of the apparatus shown in Fig. 1. A quartz crucible, containing the powdered

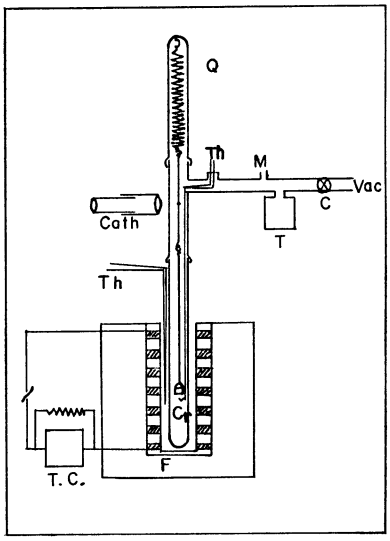

Fig. 1. Apparatus of TGA.

Q: quartz helix
M: to manometer
C: cock
Cath: cathetometer
F: furnace
Th: thermocouple
Vac: to vacuum
T: trap
Cr: crucible
T. C: temp. controller

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1) J. Schibata, This Bulletin, **47**, 242 (1926).

2) T. Dupuis, *C.R. Acad. Sci., Paris*, **228**, 841 (1949).

3) K. Funaki and T. Segawa, *J. Electrochem. Soc. Japan*, **18**, 152 (1950).

4) C. Duval, "Inorganic Thermogravimetric Analysis," Elsevier, Amsterdum, (1953), p. 332.

5) A. J. Hegedüs, K. Sasvari, and J. Neugebaure, *Z. Anorg. Allgem. Chem.*, **293**, 56 (1957).

6) E. Ya. Rode and V. N. Tverdokhlebov, *Zh. Neorg. Khim.*, **3**, 2343 (1958).

7) W. Romanowski, *Chem. Stosow* **7**(1), 105 (1963).

8) E. Ma, This Bulletin, **37**, 171 (1964).

9) E. Ma, *ibid.*, **37**, 648 (1964).

sample, was hung by means of a fine quartz rod to a quartz spring balance, and the shortening of the helix caused by the decrease in weight was measured by means of a cathetometer. The spring balance had a sensitivity of 0.391 mm/mg with 162 turns, and a maximum load of 1 g, including the weight of the sample crucible (about 0.2 g). The temperature was measured by means of two chromel-alumel thermocouples; one of them was set right under the crucible in the reaction tube in order to measure the decomposition temperature, while the other was set outside of the reaction tube at the same level as the crucible in order to control the heating rate. The control of the ambient pressure was attained by using a liquid nitrogen trap which condensed the evolved gases except a small amount of nitrogen, so that any large change in pressure in the reaction tube was suppressed. The experiments were carried out in a closed system in order to maintain a constant pressure except in the case of 760 Torr.

Samples. The sample was a Merck reagent of an extra pure grade (Germany) and was used without further purification. The sample was powdered to 150—200 mesh. The effect of the particle size on the thermogravimetric change was within the limits of experimental error. Considering the balance sensitivity, the sample weight of 50 mg was used. The final decomposition products in 760 Torr and 10^{-3} Torr were examined by means of the X-ray diffraction method.

Effects of Air Buoyancy and Convection. Before the measurements of the thermogravimetric change, the effects of air buoyancy and convection in the cylindrical decomposition tube must be considered. The temperature change in the spring balance should also be taken into account. Upon a change in temperature the crucible and the crucible with a sample will show an apparent weight change. Therefore, correction is essential in order to obtain an accurate thermogravimetric curve. The factors which cause the apparent weight changes are the air buoyancy, the convection effect in the cylindrical tube, the shape of the crucible, the temperature change in quartz helix, *etc.* In order to determine the above-mentioned correction, the apparent weight change for an inert sample (30 mg) in the crucible in an elevating temperature was measured by means of the apparatus used for the measurement. The correction curves thus obtained are shown in Fig. 2. It may be seen from the figure that the apparent weight increase was observed up to about 200°C regardless of the ambient pressures. The maximum weight increases were found to be about 0.2 mg. Above 200°C, the apparent weight loss was seen up to about 400°C, where the maximum weight loss of about 0.35 mg was observed. The observed weights during the decomposition were thus corrected. Although the corrections are not exact because the weight and volume of the sample change as the decomposition proceeds, the discrepancy is considered to be small and can be disregarded.

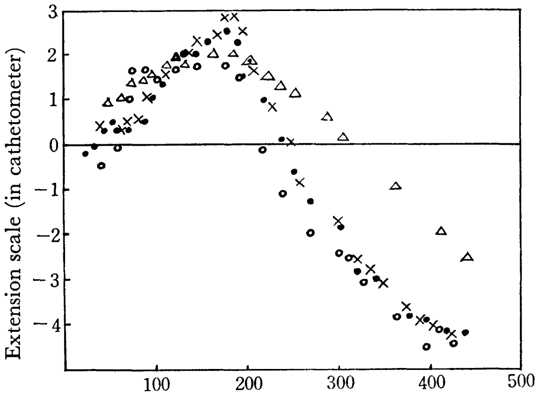

Fig. 2. Apparent weight change of crucible.
●: 760 Torr ×: 580 Torr
○: 130 Torr △: 20 Torr

Corrections of Temperature. Generally, it is difficult to measure directly the temperature of the sample which hangs from the helix during decomposition. The usual way is to measure the temperature in the furnace near the sample. However, this method often introduces a large error in the decomposition temperature. If the furnace temperature is increased at a constant rate, the temperature of the furnace is usually higher than the decomposition temperature. It is said that this thermal lag is about 3 to 14°C, and that it is approximately proportional to the heating rate.[10] The difference was examined by attaching one thermocouple directly to the sample crucible and the other to the outside of the reaction tube near the sample. The results are shown in Fig. 3. It may be seen from the figure that the difference in temperature decreases as the ambient pressure decreases.

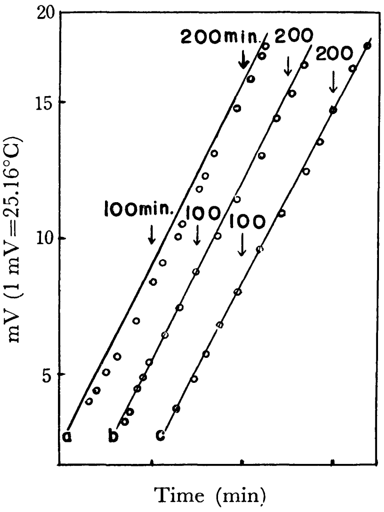

Fig. 3. Temperature correction curve.
○: Sample temp ———: Furnace temp
(a): 760 Torr (b): 130 Torr (c): 20 Torr

X-Ray Analysis. To identify the final products decomposed from APM at 760 Torr and 10^{-3} Torr, the X-ray analysis was carried out using a Schimadzu recording diffractometer with Cu-$K\alpha$ radiation.

Results and Discussion

Thermogravimetric Analysis. The TGA curves obtained by the thermogravimetric measurements in ambient pressures of 760, 580, 130, 70, 20, 5, and 10^{-3} Torr at a heating rate of 2°C/min are shown in Figs. 4 and 5, while the differential thermogravimetric curves (DTG curves) are shown in Figs. 6 and 7. It may clearly be seen from the curves that APM decomposes in four stages under higher pressures and in five stages under the pressures below 130 Torr. Here, the first stage of the decomposition splits into two stages, although the stable range of the intermediate is not very large. This is different from the results reported by other investigators,[1-9] who considered APM to

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[10] A. E. Newkirk, *Anal. Chem.*, **32**, 1558 (1960).

decompose in three stages under 760 Torr. Only Rode reported the decomposition in four stages, but his sample was $5(NH_4)_2O \cdot 12MoO_3 \cdot 12H_2O$.

Funaki and Rode reported that all the molecules of the water of hydration are removed during the first decomposition process (Duval, Hegedüs, and Ma did not show the dehydration step). This suggests that the removal of the water of hydration can occur independently of the removal of ammonia, and that the first decomposition process under pressures of 130 Torr or lower corresponds to a part of the dehydration. As will be described in the next paper, the analysis of the gases evolved by decomposition under low pressures confirms this process.

The DTG curve under 70 Torr shows that the maximum of d*w*/d*t* in the first decomposition process corresponds to 80°C and that the weight loss at the minimum is 23.5%, which approximately corresponds to three water molecules of APM. That is, the first stage in 70 Torr corresponds to the removal of three water molecules of APM, this is also true under 130 Torr. For the cases of 20 and 5 Torr, the elimination of two molecules of water corresponds to the first decomposition stage. By comparing the first minimum on DTG curves under 20 or 5 Torr with those under 130 or 70 Torr, it is seen that the trough of the former

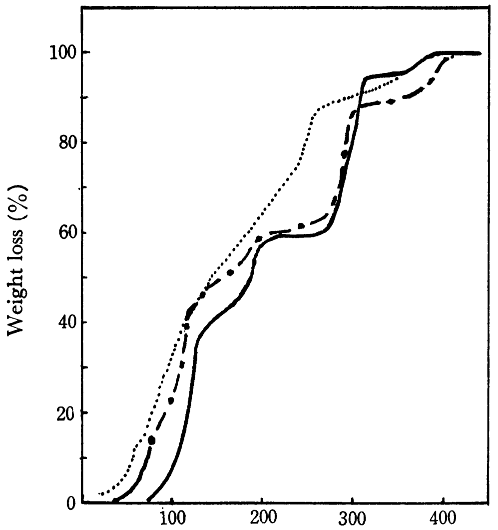

Fig. 4. TGA curve.
———: 760 Torr –·–·–: 130 Torr
------: 20 Torr ·········: 10^{-3} Torr

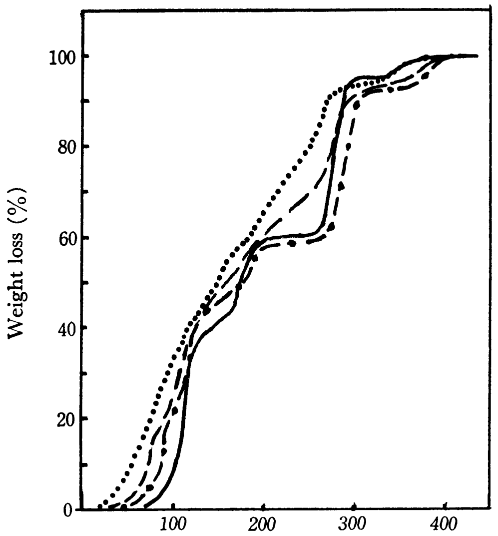

Fig. 5. TGA curve.
——: 580 Torr –·–·: 70 Torr ······: 5 Torr

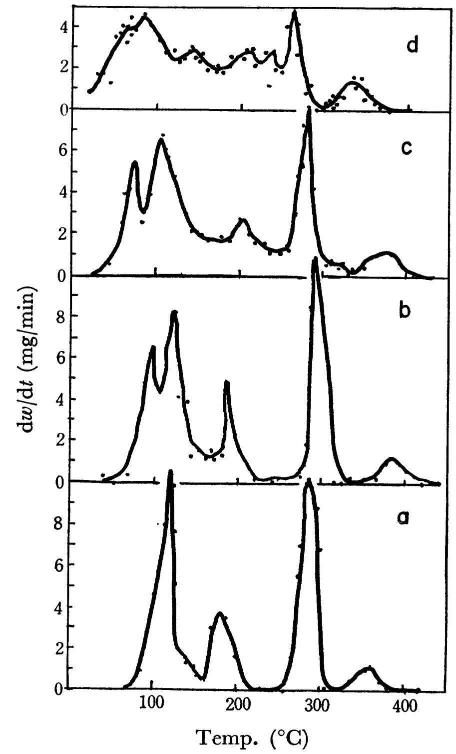

Fig. 6. DTG curve.
a: 760 Torr b: 130 Torr c: 20 Torr d: 10^{-3} Torr

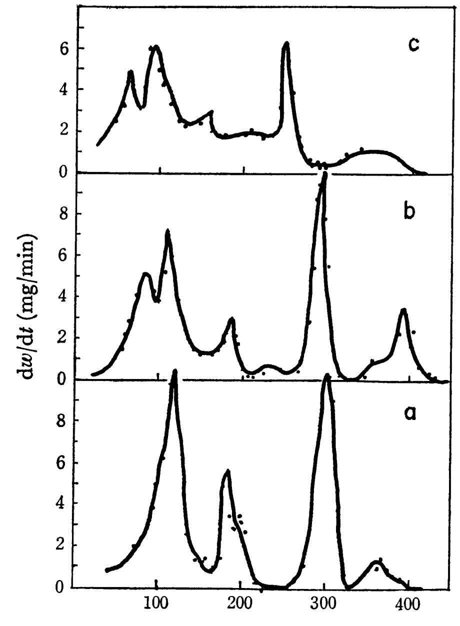

Fig. 7. DTG curve.
a: 580 Torr b: 70 Torr c: 5 Torr

is deeper than that of the latter. The depth of the trough on the DTG curve is considered to be related to the stability of the intermediate; that is, the height of the trough above the base line indicates the instability of the intermediate. The higher trough means that the intermediate is more unstable, and that two continuous reactions overlap considerably. Accordingly, by comparing Figs. 6 and 7 we can find that the intermediates under 20 or 5 Torr are more stable than those under 130 or 70 Torr. Therefore, it is not unreasonable to suppose that, also under 760 or 580 Torr, the dehydration reaction occurs prior to the removal of ammonium oxide, but the overlap of the two succeeding reactions is so large that the processes can not be observed separately, as they can under lower pressures. Judging from the tendency for the number of removed water molecules to decrease with a decrease in the ambient pressure, it will be expected that more than three water molecules can be removed in the first decomposition stage under 760 or 580 Torr and less than two under 10^{-3} Torr. Ma reported that, under 760 Torr APM begins to evolve ammonia at the temperature of about 120°C. The dehydration becomes rapid at around 115°C, and it is almost complete at 130°C. He concluded that, in the first stage in 760 Torr, four molecules of water are removed at first, and that then some ammonia is removed, without being any step resulting in $2(NH_4)_2O\cdot 5MoO_3$ at about 130°C. Lindqvist[11] showed, by crystallographic investigations, that the four hydrates were not included in the crystal structure of the discrete hepta-molybdate ion, $Mo_7O_{24}{}^{6-}$. This indicates that the water molecules of hydration exist independently in crystal lattice and that they are bonded with a weak bonding strength. Therefore, they can easily break away with a decrease in the atmospheric pressure before ammonium oxide evolves.

It is seen that both the first minimum under 760 and 580 Torr and the second minimum below 130 Torr on the DTG curve occur at the same temperature of about 160°C. However, the intermediates have different compositions and are comparatively unstable, with no horizontal portions being observed on the TGA curves. Different compositions for the intermediate have been reported by different investigators. Funaki and Rode decided it was a product of mere dehydration. On the other hand, Ma and others obtained the $2(NH_4)_2O\cdot 5MoO_3$ formula, but their TGA curves also suggest a lack of stability. Accordingly, it can be presumed that the intermediates in this region are so unstable that the compositions vary depending on the decomposition conditions.

From the TGA and DTG curves, it may be seen clearly that a stable intermediate, $(NH_4)_2O\cdot 4MoO_3$, is produced under any conditions except under pressures below 20 Torr. This is in good agreement with the conclusions described in the literature. However, even this stable compound could not be recognized in an ambient pressure below 20 Torr. This means that the two succesive reactions overlap very much and that the effect of the ambient pressure is large in the low-pressure range. The temperature range for the existence of this stable compound was around 220—260°C, which is in good agreement with the results reported by other workers.

It is of interest to note that a new intermediate was found at the third decomposition stage under 760 and 580 Torr and at the fourth decomposition stage under below 130 Torr. This stage exists between the stable compounds, $(NH_4)_2O\cdot 4MoO_3$, and the final product, MoO_3, and seems to be fairly stable. It may be seen from the DTG curves that the stable intermediate exists in the temperature range of 315—330°C under any conditions. From the weight loss data, the mole ratios, $(NH_4)_2O/MoO_3$ of this intermediate lie approximately in the range from 0.04 to 0.06. It converts into a final product, MoO_3, through another decomposition stage. According to Ma, the catalytic decomposition of ammonia to hydrogen and nitrogen by MoO_3 occurs at this stage. However, the reaction is not a catalytic decomposition but the oxidation of ammonia by Mo(VI) oxide, for no hydrogen was detected. The TGA data indicates that the weight loss percentage increases as the ambient pressure decreases. In the pressure below 70 Torr, the total weight loss was greater than the theoretical value. For example, under 10^{-3} Torr, the total weight loss percentage was 19.04%, this was 0.57% larger than the theoretical value, and the composition calculated from this value was approximately $MoO_{2.98}$ It seems to be reasonable to assume that the loss of oxygen was mainly due to the oxidation of ammonia. Moreover, the oxygen deficiency of MoO_3 was not observed upon decomposition under pressures above 130 Torr because of the reoxidation by the oxygen in the surrounding atmosphere. This conclusion will be confirmed by the analysis of the evolved gases in the succeeding paper.

From the above discussion, the following can be said to be the processes of the thermal decomposition in 760, 130, and 20 Torr:

760 Torr;

The color of the final product was a deep greenish gray.

$$3(NH_4)_2O\cdot 7MoO_3\cdot 4H_2O \xrightarrow{90\text{—}130^\circ\text{C}} \underset{7.8\text{—}7.9\%(7.8\%)^{\text{a)}}}{5(NH_4)_2O\cdot 14MoO_3}$$

$$\xrightarrow{175\text{—}210^\circ\text{C}} \underset{11.1\%(11.1\%)}{(NH_4)_2O\cdot 4MoO_3} \xrightarrow{285\text{—}315^\circ\text{C}} \underset{17.6\%(17.5\%)}{(NH_4)_2O\cdot 28MoO_3}$$

$$\xrightarrow{360\text{—}395^\circ\text{C}} \underset{18.45\%(18.47\%)}{7MoO_3}$$

130 Torr;

The color of the final product was a grayish green.

$$3(NH_4)_2O\cdot 7MoO_3\cdot 4H_2O \xrightarrow{65\text{—}105^\circ\text{C}}$$

$$\underset{4.3\%(4.4\%)}{3(NH_4)_2O\cdot 7MoO_3\cdot H_2O} \xrightarrow{105\text{—}145^\circ\text{C}} \underset{8.5\text{—}9.2\%(9.0\%)}{9(NH_4)_2O\cdot 28MoO_3}$$

$$\xrightarrow{180\text{—}210^\circ\text{C}} \underset{11.0\text{—}11.1\%(11.1\%)}{(NH_4)_2O\cdot 4MoO_3} \xrightarrow{275\text{—}305^\circ\text{C}} \underset{16.6\%(16.5\%)}{(NH_4)_2O\cdot 15MoO_3}$$

$$\xrightarrow{360\text{—}400^\circ\text{C}} \underset{18.56\%(18.47\%)}{7MoO_3}$$

a) The value of the observed weight-loss percentage, with the theoretical value in parentheses.

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11) I. Lindqvist, *Ark. Kemi*, **2**, 325, 349 (1950).

20 Torr;

The color of the final product was a grayish green.

$$3(NH_4)_2O\cdot 7MoO_3\cdot 4H_2O \xrightarrow{50-85^\circ C}$$

$$\underset{3.0-3.2\%(2.9\%)}{3(NH_4)_2O\cdot 7MoO_3\cdot 2H_2O} \xrightarrow{85-140^\circ C} \underset{9.7-10.4\%(10.0\%)}{2(NH_4)_2O\cdot 7MoO_3}$$

$$\xrightarrow{190-210^\circ C} \underset{12.9-13.4\%(13.2\%)}{5(NH_4)_2O\cdot 28MoO_3} \xrightarrow{265-290^\circ C}$$

$$\underset{17.3-17.5\%(17.2\%)}{(NH_4)_2O\cdot 15MoO_3} \xrightarrow{360-390^\circ C} \underset{18.73\%(18.47\%)}{7MoO_3}$$

The final product decomposed under 760 Torr was a light greenish gray. In the 10^{-3} Torr sample the color changed during decomposition; it was light green at 200°C, a light greenish gray at 250°C, and violet black at the final decomposition temperature.

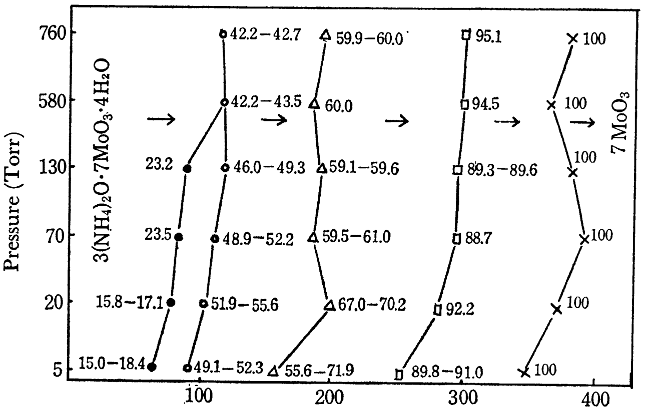

Fig. 8. Relationship between pressure and maximum decomposition temperature and percentage of decomposition.

Figure 8 shows the general relationship between the maximum temperatures of decomposition (corresponding to the peaks of the DTG curves) in various ambient pressures and the weight-loss percentage. The X-ray patterns of the final products (composition, MoO_3) obtained by decomposition are given in Table 1. They show a reasonable agreement with the X-ray patterns for MoO_3 reported in the literature,[12] but the present author could not enough investigate for the lower Mo(VI) oxides with the oxygen-deficient structure.

Table 1. X-Ray analysis of the final products prepared by decomposition of APM under 760 Torr (a) and 10 Torr (b) pressures

(a)		(b)	
d(Å)	I/I_0	d(Å)	I/I_0
6.97	0.1	3.80	0.70
3.79	0.57	3.44	0.38
3.44	0.43	3.24	1.00
3.25	1.00	2.54	0.38
2.54	0.13	2.30	0.325
2.30	0.37	1.84	0.375
1.97	0.17	1.656	0.25
1.95	0.21	1.625	0.225
1.84	0.28		
1.73	0.20		
1.66	0.19		
1.63	0.19		

Reaction Kinetics. The advantages of studying the reaction kinetics from the data obtained under a rising sample temperature are that considerably less experimental data are required than in the isothermal method, and that the kinetics can be continuously probed over the entire temperature range. However, it is necessary to measure the temperature accurately and also to avoid any change in the heating rate by an *endo*- or *exo*-thermic reaction. The latter effect can be avoided fairly well by suing a small amount of the sample. The reaction kinetics using the TGA data has been investigated by a number of workers. Freeman and Carroll[13] obtained the following equation applicable to the sample under heating and examined its applicability:

$$\frac{-\Delta E^*/2.3\boldsymbol{R}\Delta(1/T)}{\Delta \log W_r} = -x + \frac{\Delta \log \mathrm{d}w/\mathrm{d}t}{\Delta \log W_r}$$

E^*: energy of activation.
$\boldsymbol{R}$: gas constant.
T: absolute temperature.
x: the order of reaction.
$W_r = W_c - W$
W: total weight loss up to the time t.
W_c: weight loss at the completion of the reaction.

By using a plot of $(\Delta\log \mathrm{d}w/\mathrm{d}t)/(\Delta\log W_r)$ *vs.* $(\Delta 1/T)/(\Delta\log W_r)$ for each reaction, the activation energy can be calculated. For the purpose of this plot, dw and W_r were determined directly from the TGA values. The straight lines in Figs. 9 and 10 show the decomposition reaction from the first to the fourth stage under 760 Torr. From the slopes of these lines, the activation energies of the decomposition of APM

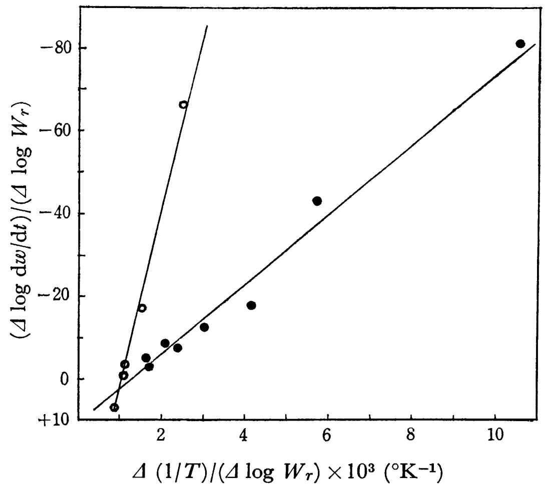

Fig. 9. Kinetics of 1st and 2nd decomposition.
●: First decomp. step
○: Second decomp. step

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[12] A. Magnéle, G. Anderson, B. Blomberg, and L. Kihlborg, *Anal. Chem.*, **24**, 1998 (1952).

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

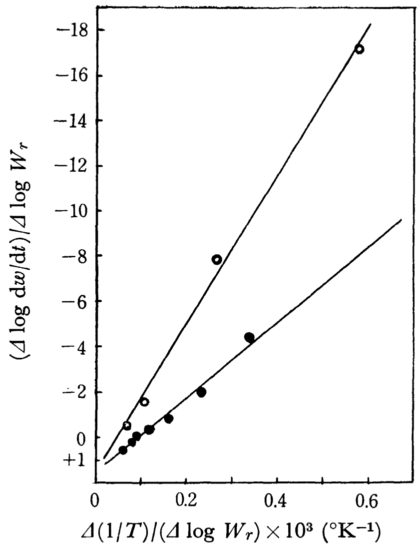

Fig. 10. Kinetics of 3rd and 4th decomposition.
●: Third decomp. step
○: Fourth decomp. step

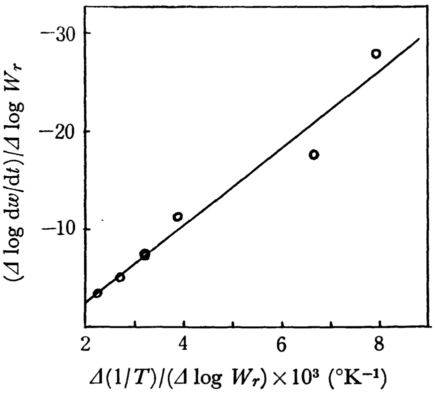

Fig. 11. Kinetics of water loss.

in 760 Torr were found to be 38.6, 194.8, 81.9, and 151.2 kcal·mol^{-1} respectively from the first to the fourth stage. As has previously been described, there is a dehydration reaction stage in the decomposition process under the pressures below 130 Torr. By using the data obtained from the dehydration reaction, the activation energy was claculated for the dehydration process. Figure 11 shows the plot of $\Delta(1/T)/(\Delta \log W_r)$ *vs.* $(\Delta \log dw/dt)/(\Delta \log W_r)$ for the case of 70 Torr. The activation energy was found from its slope to be 17.3 kcal·mol^{-1}.

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