A Novel Type of Differential Thermogram Revealed in Potassium Molybdate

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(Received January 31, 1966)

Differential thermal analysis experiments have been carried out on anhydrous potassium molybdate, and differential thermograms with novel and interesting features have been obtained. These experiments were conducted in air on a powdered sample packed tightly in a sample cell, by using a new quantitative type apparatus with high sensitivity and resolution.[1] It was previously reported that there are several transition temperatures on anhydrous potassium molybdate;[2-4] 323, 458, 480 and 926°C. In the heating stage, the usual sharp peaks were obtained in our thermograms, as is shown in Fig. 1. The experiments were made up to 500°C; the temperatures and the heats of the transitions were estimated to be 283°C, 8.3±0.1 cal./g. and 457°C, 0.64±0.03 cal./g., respectively, but the third transition, previously reported to occur at 480°C, was not detected. The method of estimating the heats has been described elsewhere.[1]

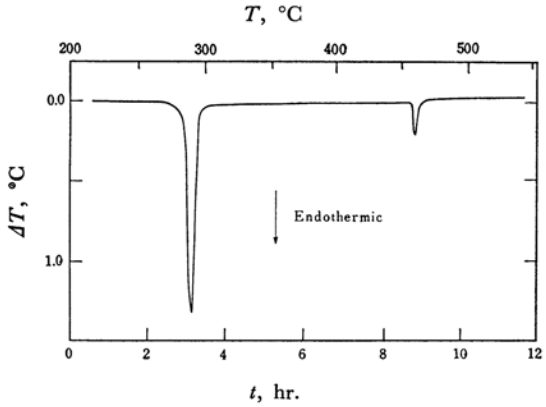

Fig. 1. Differential thermogram of K_2MoO_4 at heating stage in air.
Heating rate, 30°C/hr.

When the sample was heated to about 600°C and then left to be cooled, the transition at 457°C was reversed as a normal peak at the same temperature; however, for the transition at lower temperature, the novel and interesting thermogram which is reproduced in Fig. 2 was obtained. As may be seen in Fig. 2, a saw-tooth-like curve is revealed instead of the usual sharp peak; the transition was supercooled to the temperature range from 152 to 148°C, in comparison with the temperature of the transition, 283°C, in the heating stage. These saw-tooth-like curves are reproducible in nature whenever the sample is cooled after the transition at 283°C, and if one heats the sample up again immediately after the completion of the saw-tooth-like transition, the normal sharp peak is reproduced at 283°C without any change in the peak area. Similar thermograms can be obtained on the same sample by using another type of differential thermal-analysis apparatus with open sample cells.

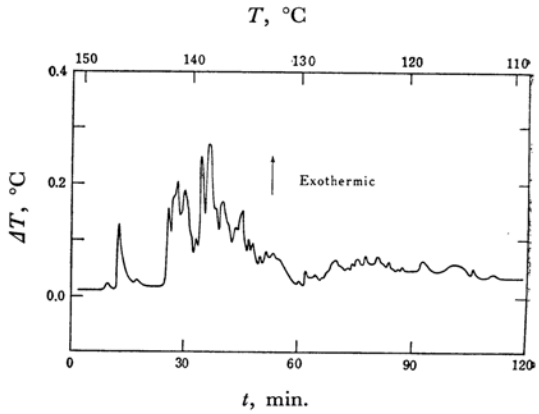

Fig. 2. Differential thermogram of K_2MoO_4 at cooling stage in air.
Cooling rate, about 25°C/hr.

The heats of the transitions in the cooling stage were also estimated. The heat at 457°C was 0.74±0.05 cal./g., somewhat larger than the heats in the heating stage, but the heats of the saw-tooth-like transition were estimated to be about 3.4 cal./g., though the peak area was rather ambiguous and though the recorder did not follow the change exactly because of the long responce time.

Similar thermograms were also obtained in the cooling stage of powdered tin heated to about 450°C. The saw-tooth-like change in the differential temperature began at about 230°C, followed by the usual peak. When the sample was heated again, the usual peak was obtained,

1) T. Ozawa, This Bulletin, **39**, 2071 (1966).
2) F. D. Rossini, *Circular Natl. Bur. Standards*, **C500** (1952).
3) I. M. Kuleshov, *Zhur. Neorg. Khim.*, **1**, 2011 (1956).
4) G. Petit and J. Mireille, *Compt. rend.*, **244**, 1900 (1957).

and the thermogram was reproduced on the same sample at the second cooling. In this case, oxidation seemed to occur; any oxide would have affected the solidification of the tin.

As may be apparent in its great tendency to supercool, the lower transition is difficult to reverse by cooling, and the transformation could not be propagated beyond the crystalline boundary. Hence, any sample particles would be transformed independently, without influencing each other; this behavior might produce a saw-tooth-like curve. If a differential thermal-analysis apparatus with a high resolution and with a micro amount of a sample were constructed, interesting kinetic aspects of transitions such as this would be elucidated.

The apparatus used has been described elsewhere.[1] Briefly, cylindrical sample cells with threaded lids are inserted in ceramic sample holders set in a metal block, and alumel-chromel thermocouples are inserted between the cells and the cell holders. This arrangement makes the quantitative heat measurement possible.[1] The rates of heating are 60°C/hr. and 30°C/hr.; they are controlled with a PI-type program controller and a SCR regulator. The temperature and the differential temperatures are recorded against the time on a six-point recorder. The sample is of a G. R. grade; it is used without further purification, dried at about 120°C for more than 6 hr., and kept in a desiccator above silica gel. The reference material is calcined alumina.