

On the Calculation of Rate Parameters of Solid-state Reactions by Thermogravimetric Analysis*

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Rate parameters of solid-state reactions have been evaluated from the decomposition of equal amounts of calcium oxalate monohydrate of different but controlled particle size at different rates of heating.

Recently Freeman and Carroll¹ proposed a method for calculating the rate parameters of solid-state reactions from thermogravimetric curves. They calculated the activation energy and the 'order of the reaction' for various reactions taking place during the heating up to 900° of calcium oxalate monohydrate. Since then values of these parameters have been reported for other oxalates by different authors^{2,3}.

Many variables, such as, particle size, heating rate, atmosphere of the furnace, the balance design, and air buoyancy, however, affect the shape of the thermogravimetric curves, but how these affect the finally calculated parameters is not known. Of these factors, the balance design and furnace atmosphere are not taken into account as only one type of balance and air atmosphere are considered. Also for the balance used, air buoyancy was found not to contribute very significantly in the temperature range studied.

Hence decomposition of equal amounts of calcium oxalate monohydrate of different but controlled particle size at different rates of heating has been studied in order to evaluate the applicability of the method.[†]

EXPERIMENTAL

Calcium oxalate monohydrate was prepared from E. Merck G. R. quality CaCO_3 by first converting it to the chloride by treatment with pure 1*N*-HCl and then precipitating it with pure 0.1*N*- $\text{H}_2\text{C}_2\text{O}_4$. The precipitate was filtered, washed, and dried at 80°. It

*Paper No. 13, read at the Symposium on 'Rate Processes', held in Bombay on January 1, 1960, under the auspices of the Indian Chemical Society.

1. Freeman and Carroll, *J. Phys. Chem.*, 1958, **62**, 394.

2. Padmanabhan *et al.*, Paper No. 14 of the Symposium, since published in *J. Inorg. Nucl. Chem.*, 1960, **12**, 356.

3. Agarwala and Naik, Personal communication, since published in *Anal. Chim. Acta*, 1961, **24**, 128.

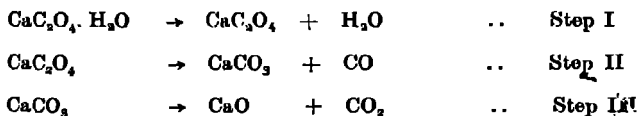
†At the Symposium on Thermal Methods of Analysis, held by the Division of Analytical Chemistry, 137th Meeting of the American Chemical Society, Cleveland, Ohio U. S. A., April 1960, the effects of the balance atmosphere, air buoyancy, heating rate, etc. were discussed [*Anal. Chem.*, 1960, **32**, 1558]. The findings reported there are in substantial agreement with the results obtained and reported in this paper.

was ground and sieved through standard sieves to provide three fractions: (1) 100-125, (2) 200-240, (3) 300-325 mesh B. S. S. The sieved portions were stored in tightly closed bottles.

Thermogravimetric Curves.—The thermogravimetric curves were recorded on a Stanton 'High-temperature' model thermobalance of 1 mg. sensitivity with a standard heating rate of $6^{\circ}/\text{min}$. Slower and faster heating rates were obtained by disconnecting the furnace from the built-in programmer and manually controlling the heating by means of a variac. Five runs were made for each sized sample at one heating rate in order to check reproducibility of the equipment. The results recorded in Table I represent the mean of the five runs. In these duplicate runs equal weight of the material was packed to equal height in recrystallised alumina crucibles. The temperature was continuously recorded on the thermobalance and also measured on a potentiometer, using a separate couple.

DISCUSSION

Calcium oxalate monohydrate undergoes three decomposition reactions before final conversion to CaO at about 900° . The reactions are:



In any true evaluation of the kinetics of decomposition, the partial pressures of the gaseous component should be taken into consideration as well as the composition and partial pressures of the gases constituting the environment which in most cases is air.* No attempt has been made in the present study to evaluate these effects, as these are planned to be studied separately. Attention has been focussed only on those physical parameters (viz., particle size and heating rates) which would affect the shape of the thermogravimetric curves in all cases.

Heating Rates

In a closed system the decomposition of any salt is truly an equilibrium phenomenon and it should be studied only under equilibrium conditions, i.e., isothermally. Therefore methods, like thermogravimetric analysis, which are essentially dynamic methods, can at best yield only approximately correct values of reaction parameters. The approximation to the true values would obviously become closer, the closer the experimental conditions are to the equilibrium conditions.

Hence it is to be expected that in any thermogravimetry curve, the starting temperature of decomposition would be more or less independent of the heating rate, whereas the final temperature would be strongly dependent. Also this effect should be much more pronounced with comparatively fast heating rates. The results prove these expectations.

*That such considerations can, at least in some cases, materially affect the temperatures of decomposition has been clearly demonstrated by Nott and Jaffe in the case of anhydrous uranyl sulphate [*J. Amer. Chem. Soc.*, 1960, 43, 53].

In Fig. 1 the first step decomposition (dehydration) of the 100-125-mesh material is shown for heating rates of 8°, 6° and 4° per minute. The initial temperatures of decomposition are in these cases 183°, 182° and 183° respectively, which can be regarded as constant, keeping in mind the accuracy of temperature measurement attainable. The final temperatures, on the other hand, show a marked fluctuation, the temperatures for the three heating rates being 367°, 312°, and 297°. The drag of the curve naturally increases with the faster rate of heating since in this dynamic experiment, the temperature is increasing at a very rapid rate, but the weight stabilisation is not so rapid. Thus even with constant particle size, constant initial weight, and identical packing, the final temperatures in fifteen measurements with three different heating rates ranged from 294° to 379°, yielding a large spread of 85°. Also variations of the heating rate were found to affect not only the final temperatures of decomposition but also their reproducibilities. On the other hand, the heating rates had hardly any effect on the temperature of inception of decomposition. In all cases the variation was not more than $\pm 2^\circ$, the normal variation to be expected. Thus for the first step in fifteen measurements and with three different heating rates, the initial temperature did not have a spread of more than 5° and was always between 180° and 185°. In contrast, the final temperatures of $367^\circ \pm 12^\circ$, $312^\circ \pm 5^\circ$, and $297^\circ \pm 3^\circ$ showed a marked dependance on the heating rate. Thus there was a spread of 24° in the final temperatures recorded in the set of five experiments for a heating rate of 8°/min. which reduced to a spread of only 6° as the heating rate was reduced to 4°/min. Similar results were obtained for the other two steps as well as with different mesh sizes.

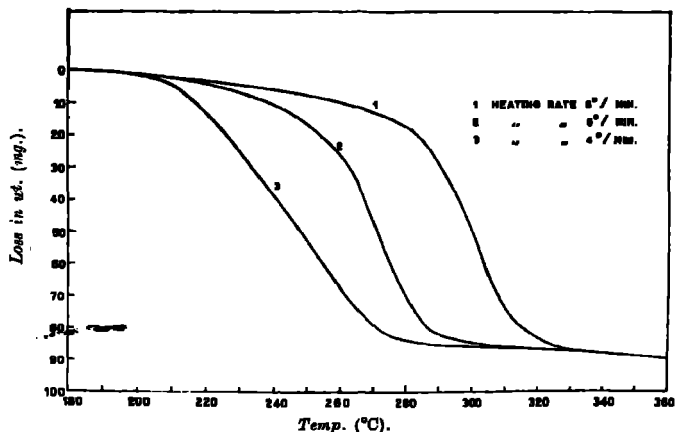


FIG. 1. Effect of heating rate on thermogravimetric curves (100-125 mesh).

Particle Size

The effects shown by variation in particle size on the thermogravimetric curves were not uniform. With the faster heating rates, in case of both the very coarse and the very fine particles, there was a considerable drag in the final temperatures. Thus with parti-

cles of very fine size (300-325 mesh), there were no sharp demarcations between the steps, as seen from Table I.

TABLE I

	100-125-Mesh (150 to 125 μ).			200-240-Mesh (75 to 67 μ).		300-325-Mesh (52 to 45 μ).	
Heating rate:	8°/min.	6°/min.	4°/min.	8°/min.	4°/min.	8°/min.	4°/min.
1st Step:							
Beginning temp.	183° \pm 2°	182° \pm 2°	183° \pm 3°	180° \pm 2°	182° \pm 3°	180° \pm 4°	180° \pm 2°
Final temp.	367° \pm 12°	312° \pm 5°	207° \pm 3°	340° \pm 7°	305° \pm 5°	ca. 370°	290° \pm 10°
Weight loss (mg.)	88 \pm 2	87 \pm 2	86 \pm 1	90 \pm 2	86 \pm 1	86	86 \pm 1
[Theoretical: 86 mg.]							
2nd Step:							
Beginning temp.	391° \pm 4°	390° \pm 3°	392° \pm 2°	390° \pm 2°	390° \pm 2°	ca. 390-390°	390° \pm 5°
Final temp.	570° \pm 12°	514° \pm 6°	497° \pm 3°	525° \pm 5°	490° \pm 3°	ca. 600°	510° \pm 20°
Weight loss (mg.)	130 \pm 3	131 \pm 2	131 \pm 2	131 \pm 2	131 \pm 2	134	134
[Theoretical: 134 mg.]							
3rd Step:							
Beginning temp.	682° \pm 3°	684° \pm 3°	684° \pm 3°	670° \pm 3°	670° \pm 2°	ca. 630°-650°	ca. 650°
Final temp.	854° \pm 14°	813° \pm 5°	878° \pm 5°	840° \pm 5°	888° \pm 2°	950° \pm 10°	900° \pm 10°
Weight loss (mg.)	206 \pm 2	200 \pm 2	200 \pm 3	207 \pm 2	200 \pm 2	210	210
[Theoretical: 210 mg.]							

In general, the initial and final temperatures of the various steps for materials of 200-240 and 300-325 mesh (Fig. 2) tended to be lower than those for 100-125 mesh size.

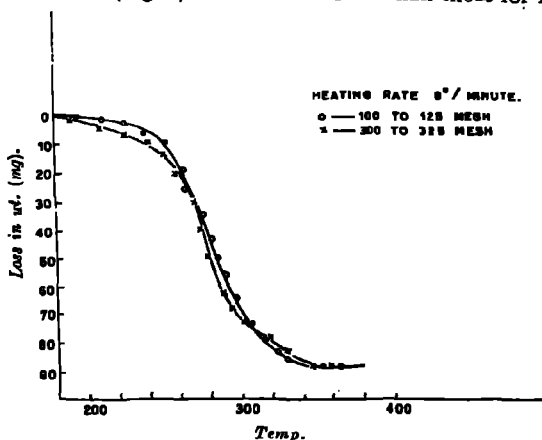


FIG. 2. Effect of particle size on T. G. curves.

With the 300-325-mesh material, somewhat higher values were, however, obtained for the end of the second and subsequent steps. The effect with the 300-mesh material could be due to the *in situ* sintering of and grain growth in the material. This is inferred from the fairly dense cake obtained at the end of the runs.

The lowering of the temperatures with decrease in particle size is to be expected since the transport of the released gases through the smaller grain is achieved much more readily.

Also the surface area to volume ratio is relatively very high for the small particles. Hence the larger surface permits more widespread inception of the reaction as well as easier escape of the products.

Calculation of Rate Parameters

The 'activation energy' and 'order of the reaction' were obtained from the Freeman-Carroll equation¹:

$$\frac{-E^*}{2.3R} \Delta \left(\frac{1}{T} \right) = -x + \frac{\Delta \log dw/dt}{\Delta \log W_r}$$

where E^* = activation energy; R = gas constant; T = absolute temperature; W_r = the difference between total weight loss and weight loss up to time t ; dw/dt = rate of change of weight loss with time; x = order of reaction. The values of E^* and x were calculated for the first step only because of the suspected grain growth during subsequent steps. These results are recorded in Table II.

TABLE II
Order of reaction and energy of activation for various steps.

Step No.	Mesh size.	Order of reaction for heating rate of		Energy of activation (E^*) for heating rate of		E^* (Freeman & Carroll).
		4°/min.	8°/min.	4°/min.	8°/min.	
1	100-120	0.47	1.10	33.4	41.1	22
	300-325	1.00	1.20	20.9	21.1	
2	100-120	0.60	1.31	108.0	101.0	96
	300-325	0.90	1.20	89.0	90.0	

For any given reaction, the activation energy and order of reaction are constant. Due to the inherent nature of the thermogravimetric method, only apparent values of these quantities are obtained. It is observed that experimental variables that affect the thermogravimetry curve even to a small extent produce a large variation in the values calculated from it. The effect of the heating rate is most clearly seen for the 100-125-mesh material. The apparent value of the order of the reaction is more than doubled when the heating rate is doubled. This effect is, however, minimised as the particle size is reduced. The effect of the particle size is equally marked. Even Freeman and Carroll¹ had explained that the disparity between their values for E^* and those obtained in the literature could be due to differences in particle size. The value for the 300-325-mesh material is almost identical with that reported by them.

These results demonstrate that the variables studied have pronounced effects on the heating curves and hence on the parameters calculated. It is essential therefore to decrease the heating rate as much as possible and decide on one particle size. The range of 240-300 mesh with a reasonably slow heating rate of about 4°/min. seems to be optimum in presenting a reasonable compromise for obtaining values of these rate parameters as a fair approximation of the true values.

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