Thermochimica Acta, 79 (1984) 217–230
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE THERMAL DECOMPOSITION OF OXALATES. PART 19. THE THERMAL DECOMPOSITION OF BARIUM OXALATE HEMIHYDRATES

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(Received 30 March 1984)

ABSTRACT

The thermal decomposition of barium oxalate hemihydrate is described and the scheme for its decomposition given as

$$Ba\cdot C_2O_4\cdot 0.5\ H_2O \xrightarrow{\text{endothermic}} 0.5\ BaC_2O_4 + H_2O \text{ (weight loss} = 3.84\%)$$

the barium oxalate then decomposes

$$BaC_2O_4 \xrightarrow{\text{endothermic}} BaCO_3 + CO \text{ (weight loss} = 11.5\%)$$

there is also a phase change

$$\gamma\text{-}BaCO_3 \xrightarrow{\text{exothermic}} \beta\text{-}BaCO_3$$

and for each reaction the associated activation energy is given.

INTRODUCTION

The thermal decomposition of barium oxalate is a two-stage decomposition; viz. a dehydration stage, and a carbonate conversion stage. Several workers have studied the thermal decomposition of barium oxalate. The results quoted are not altogether consistent and seem to depend upon the technique employed and the apparatus used.

Zagorchev [1] studied the decomposition of barium oxalate into barium carbonate with increasing temperature by the emanation method. He found a difference in the decomposition curves depending on the method of preparation of the barium oxalate. Gunther and Rehaag [2] studied the thermal decomposition of barium oxalate by plotting the amount of carbon monoxide gas evolved against time. The curves obtained were not identical.

0040-6031/84/$03.00

They suggested that the reaction was autocatalytic and that the primary products on ignition of barium oxalate were peroxydioxalates rather than carbonates. Similarly, Tuccarlasi and Haldun [3] suggested that displacements on thermolysis curves of barium oxalate showed the formation of intermediate oxalate–carbonate compounds stable between 340 and 420 °C. Terem and Tuccarlasi [4] also reported that hydrated barium oxalate could not be completely dehydrated by heating in air at 90 °C. According to these authors, the decomposition of the partially hydrated products between 340 and 420 °C gave a composite intermediate of oxalate–carbonate which was hydrated and passed to the carbonate state at 540 °C. Conversely, Duval [5] constructed pyrolysis curves using a Chevenard thermobalance and found that hydrated barium oxalate was stable up to 76 °C, the anhydrous form was stable between 110 and 346 °C, and above 476 °C the carbonate was formed. Ugai [6] also quoted temperatures of dehydration and decomposition of barium oxalate. Erdey and Paulik [7] reported the thermogravimetric (TG) analysis and the differential thermal analysis (DTA) of barium oxalate. They stated that the carbon monoxiode evolved could retard the decomposition and increase the decomposition temperature. Tsymorechkhi and Peshev [8] reported the DTA of barium oxalate in the range 20–1100 °C at a heating rate of 10 °C min^{-1}. The DTA exhibited an endothermic peak at 230 °C, indicating conversion into barium carbonate. Peaks at 485, 590, 855 and 1010 °C were assigned to the rearrangement and transition into different crystal structures.

Glasson [9] carried out an ignition series of BaOx for 5 h at temperatures of 300, 400, 500 and 600 °C in air. The specific surface area was measured after each ignition. A maximum specific surface area of 6 $\text{m}^2\ \text{g}^{-1}$ was found at 450 °C. Different forms of barium oxalates exist, and these have been studied by Walter-Levy and Lanieppce [10], also by Mutin and Watelle-Marion [11], these oxalates are the acid salts of barium oxalate, and contain oxalic acid within the oxalate molecule. In this article, however, barium oxalate hemihydrate is dealt with.

EXPERIMENTAL

Barium oxalate

The salt was white and finely divided. It was supplied by Hopkins and Williams as technical reagent and on analysis was found to be $BaC_2O_4 \cdot 0.5\ H_2O$.

Differential thermal analysis

This was carried out in oxygen and nitrogen, three peaks were recorded in each case.

In oxygen the first peak started at 122 °C, reached a maximum at 154 °C, was endothermic, of small area, and attributed to the dehydration of the oxalate. The second peak started at 390 °C, reached a maximum at 433 °C, was exothermic, of large area, and attributed to the decomposition of oxalate to carbonate. The third peak started at 764 °C, reached a maximum at 778 °C, was exothermic, of small area, and was attributed to the transition from γ-carbonate (witherite) to β-carbonate.

Three peaks were also obtained in nitrogen but with important differences. The first peak started at 140 °C, reached a maximum at 161 °C, was endothermic, of small area, and attributed to the dehydration of oxalate. The second peak started at 456 °C, reached a maximum at 478 °C, was endothermic, of small area, and was attributed to the decomposition of oxalate into carbonate. The third peak started at 778 °C, reached a maximum at 786 °C, was exothermic, of small area, and attributed to the transition from γ-carbonate to β-carbonate.

Thermogravimetric analysis

This was done on a Stanton thermobalance in air, nitrogen and oxygen. The rate of temperature increase was 4 °C min^{-1} and the temperature range was 20–1000 °C.

In air, the total percentage weight loss was 17.1% which was achieved at 540 °C. A plateau on the decomposition curve existed at 4.7% weight loss and extended from 160 to 395 °C. The dehydration temperature of the oxalate was 122 °C and the decomposition temperature 495 °C.

In nitrogen the total percentage weight loss was again 17.1% and, as in air, a plateau existed on the decomposition curve at 4.7% loss. The dehydration temperature was 142 °C and the decomposition temperature 517 °C.

In oxygen the total percentage weight loss was 17.1% and a plateau in the decomposition curve existed at 4.7% weight loss. The dehydration temperature was found to be 147 °C and the decomposition temperature 519 °C.

Isothermal decomposition

The barium oxalate used for isothermal decompositions had been previously dehydrated by heating at 300 °C for 0.5 h, and subsequently stored in a desiccator.

The isothermal decompositions are considered in two separate series or groups. The first series of isothermals are separated by about 10 °C and were obtained by using a Stanton thermobalance at the required constant temperature. The second series of isothermals are separated by about 4 °C and were obtained by replacing the Stanton voltage supply by a constant voltage supply from a Variac instrument, and by measuring the temperature of the sample independently on a potentiometer.

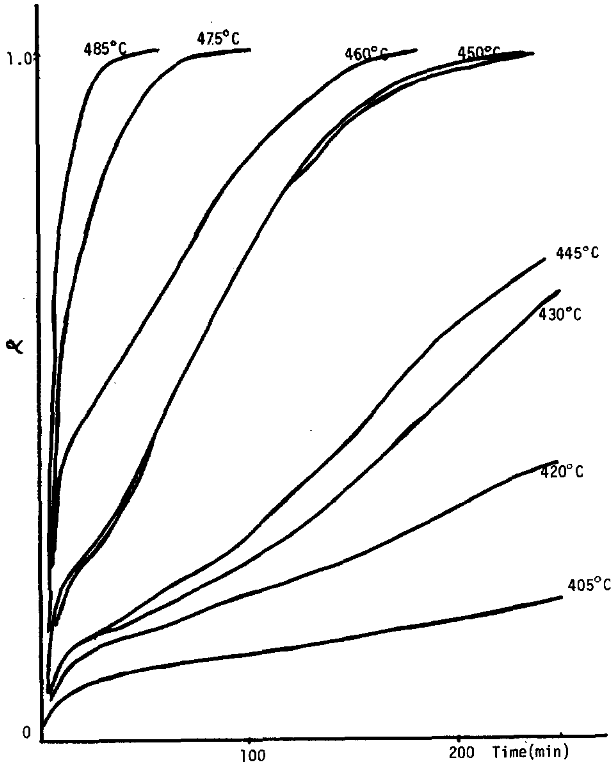

Fig. 1. Isothermal decomposition of barium oxalate, first series.

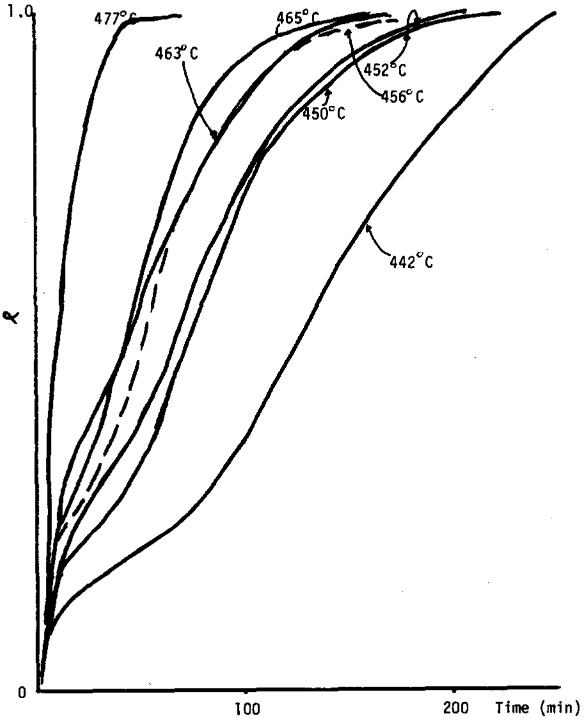

Fig. 2. Isothermal decomposition of barium oxalate, second series.

(a) First series

The isothermal decomposition of anhydrous barium oxalate in air was reached at 405, 420, 430, 445, 450, 460, 475 and 485 °C (Fig. 1).

(b) Second series

The isothermal decomposition of anhydrous barium oxalate in air was recorded at 448, 450, 452, 456, 460, 463, 465 and 477 °C (Fig. 2).

RESULTS AND DISCUSSION

The thermogravimetric analysis of barium oxalate in air, nitrogen and oxygen, shows an overall weight loss of 17.1% in each case. A plateau is produced on the decomposition curve at 4.7% weight loss in each case. This plateau does not correspond to dehydration by the loss of one molecule of water (7.4%), and the percentage weight loss is somewhat higher than that due to the loss of half a molecule of water (3.84%), suggested by Duval [5]. However, the barium oxalate sample is known to be hygroscopic and the 4.7% weight loss was attributed to dehydration by the loss of half a molecule of water from the oxalate crystals plus the loss of water present due to the hygroscopic nature of the oxalate. The percentage weight loss after dehydration (12.4%) corresponds favourably to the formation of barium carbonate from anhydrous barium oxalate by the evolution of carbon monoxide (12.44%). Thus, the decomposition of barium oxalate hydrate is a two-stage process and probably occurs as follows

$$BaC_2O_4 \cdot 0.5\ H_2O \xrightarrow{\text{dehydration}} BaC_2O_4 + 0.5\ H_2O$$

$$BaC_2O_4 \xrightarrow{\text{decomposition}} BaCO_3 + CO\uparrow$$

There is good agreement between the temperature of dehydration in oxygen and the temperature of dehydration in nitrogen (147 and 142 °C, respectively), but in air the temperature of dehydration is somewhat lower (122 °C).

Similarly, the temperature of decomposition is almost identical in oxygen and nitrogen (519 and 517 °C, respectively) whereas in air it is lower (495 °C). A probable explanation for these temperature differences is that in the nitrogen and oxygen analyses the gas flows over the sample, producing a cooling effect so that the sample is actually at a lower temperature than that recorded, whereas in the air analysis, decomposition is simply carried out in the atmosphere with no gas flow and, thus, no cooling effect. The DTA of barium oxalate produces three peaks when performed in nitrogen and oxygen. However, the peaks obtained in nitrogen appear at higher temperatures than the similar peaks in oxygen. This may be explained by the fact that the recording of these temperatures depends upon the conductivity of the powdered sample which is closely related to the conductivity of the gas which fills its voids. Thus, different gases, having different conductivities, may produce different temperatures of decomposition, dehydration, etc.

The DTA data were analysed in the light of the TG analysis data. The first peak in nitrogen and oxygen was attributed to energy changes involved in dehydration. These peaks reached a maximum at 154 (oxygen) and 161°C (nitrogen) which compares favourably with the temperature of dehydration in oxygen and nitrogen (147 and 142°C, respectively) obtained from TG data.

The second peak which is exothermic and of large area in oxygen undergoes a marked change in nitrogen, becoming endothermic and of small area. The temperatures at which these peaks occur suggest that they are due to the decompositon of the oxalate to the carbonate. The great difference between the peak in oxygen and the peak in nitrogen may be explained by the fact that the peak in oxygen represents more than one reaction. It is suggested that the exothermic peak in oxygen is, in fact, due to the oxidation of carbon monoxide (decomposition product) to carbon dioxide at the surface of suitable catalysts by the oxygen flow. The catalyst could be the barium carbonate surface, but is more probably the surface of the sample holder, or even the thermocouples. This reaction would be so exothermic that it would mask the endothermic peak for the decomposition of oxalate into carbonate. In nitrogen, the oxidation of carbon monoxide cannot occur, and the resultant exothermic peak represents solely the decomposition of oxalate into carbonate.

The third peak occurs at a high temperature (778°C in oxygen, 786°C in nitrogen), and, according to the TG data, there is no decomposition at these temperatures. Consequently, this peak must be due to some physical change in the sample, and is, in fact, attributed to the transition from γ- to β-barium carbonate at 811°C.

Kinetic interpretation

Two series of experiments were performed in which the isothermal decomposition of anhydrous barium oxalate to barium carbonate was followed. In the first of these, the experiments were performed over a total temperature range of 405–485°C. In the second series the temperature range was narrowed to 448–477°C and the temperature interval between successive isothermal decompositions reduced to a few degrees.

First series of isothermals

The general shape of these isothermal decompositions showed three regions. The general shape of the α–t plots can be compared with the type "d" plot quoted by Garner and Jacobs in which there is an initial evolution of gas. The first region covers the initial evolution of gas and effectively disappears as the temperature is raised. The second region is an accelerating region. In the third region the reaction is becoming progressively slower.

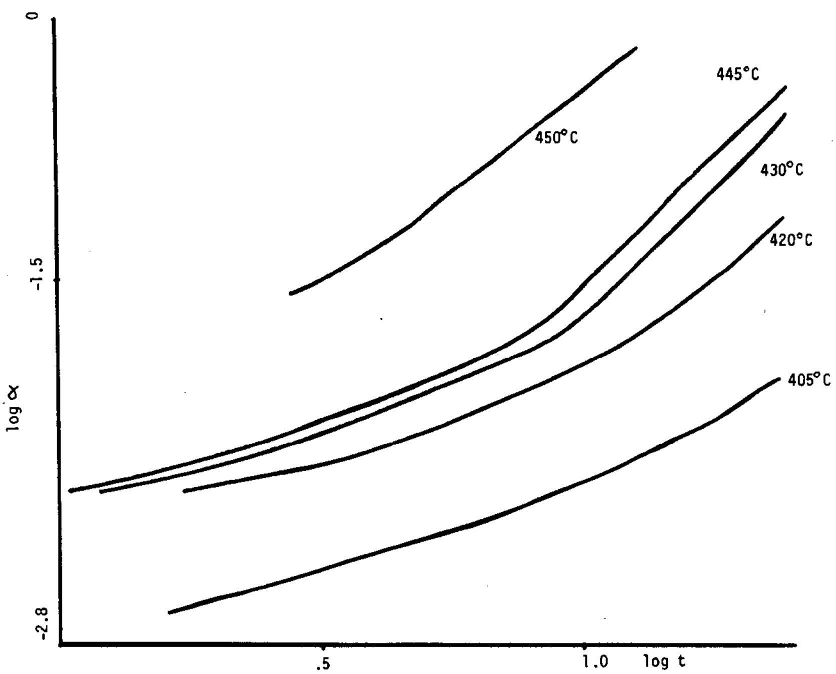

Fig. 3. Application of the power law to the first series of isothermals.

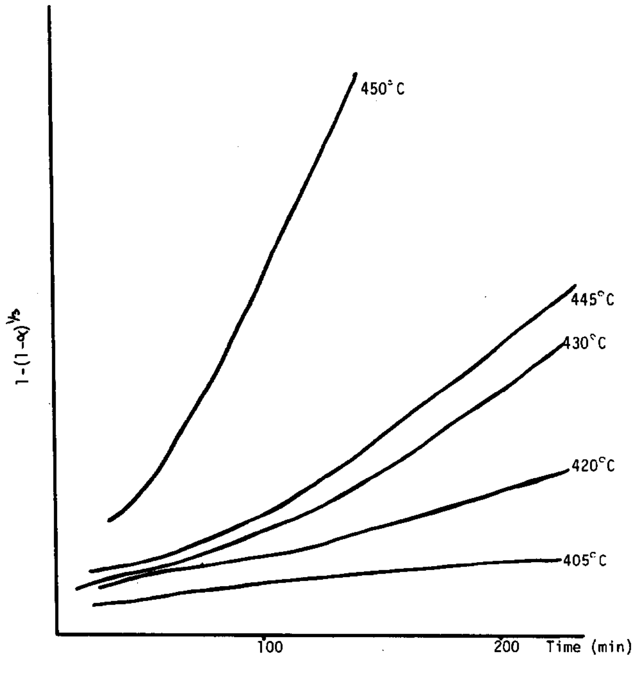

Fig. 4. Application of the Mampel law to the first series of isothermals.

The first region, covering the initial evolution of gas, has not been analysed.

The region where the reaction rate was accelerating has been analysed and Fig. 3 indicates the application of the power law to this data. (Isothermal data, 405, 420, 430, 445 and 450 °C.) The results indicate that only for the 430, 445 and 450 °C decompositions was a law of this type predominant, between α values 0.3–0.7 with a tendency for these values to shift upwards with temperature increase, and an n value between 1 and 2 (Fig. 1 at 460 °C represents the best fit).

The final decay region of this series of isothermal decompositions was analysed to see how it fitted the Mampel intermediate law and the first-order decay expression. The application of the Mampel expression is illustrated in Figs. 4 and 5. These show that the Mampel law holds over the following range of α values.

Temp. (°C)	α range	
0		
405	0.14–	Reaction not completed
420	0.23–	
430	0.34–	
445	0.38–	
450	0.60–0.95	
460	0.65–0.95	
475	0.70–0.95	
485	0.70–0.95	

Attempts to fit a first-order decay law to the kinetic curves are shown in Figs. 6 and 7. It would seem that these experiments tend to obey such a law towards the end of each experiment when the reaction rate was very slow and the distinction between the various decay mechanisms is made difficult.

Second series of isothermals

The second series of isothermal decompositions were performed in the region 488–477 °C where the initial region was greatly diminished. They provided more accurate data than the first series. The fits to the Mampel expression (Fig. 8) are similar to those obtained in the first series. The same is true of the first-order decay law (Fig. 9). The range of the Mampel expression is as follows.

Temp. (°C)	α range
448	0.38–0.88
452	0.50–0.95
456	0.50–0.95
463	0.58–0.98
465	0.60–0.98
477	0.65–0.98

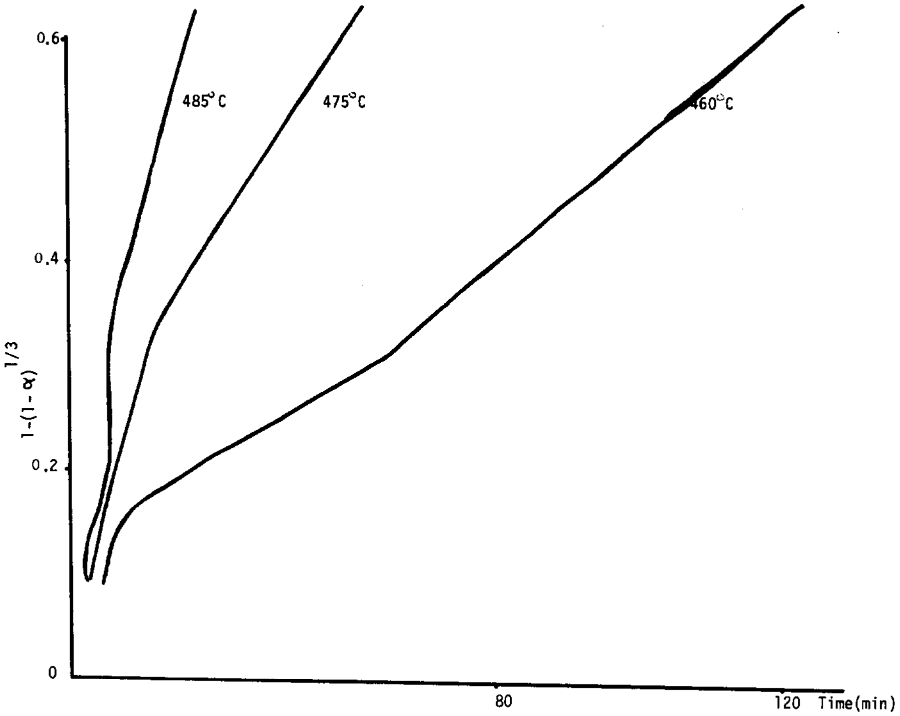

Fig. 5. Application of the Mampel law to the first series of isothermals.

A very general expression has been deduced by Erofeev, viz.

$$\alpha = 1 - \exp\left(-\int_0^t p\,\mathrm{d}t\right)$$

when

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = p\exp\left(-\int_0^t p\,\mathrm{d}t\right) = p(1-\alpha)$$

where p represents the probability of an individual molecule to react in the interval t, $t + \mathrm{d}t$.

Applying this to certain isothermal decompositions reactions Erofeev found that

$$\alpha = 1 = \exp(-Kt^n)$$

It is possible to show that the decomposition laws followed by various systems can form special cases of the general Erofeev expression. The linear law $\alpha = Kt$, follows from the Erofeev equation when $n = 1$, then

$$\alpha = 1 - \mathrm{e}^{-Kt}$$
$$= \sum_{n'=1}^{n'=} \frac{(-Kt)^{n'}}{n'}$$

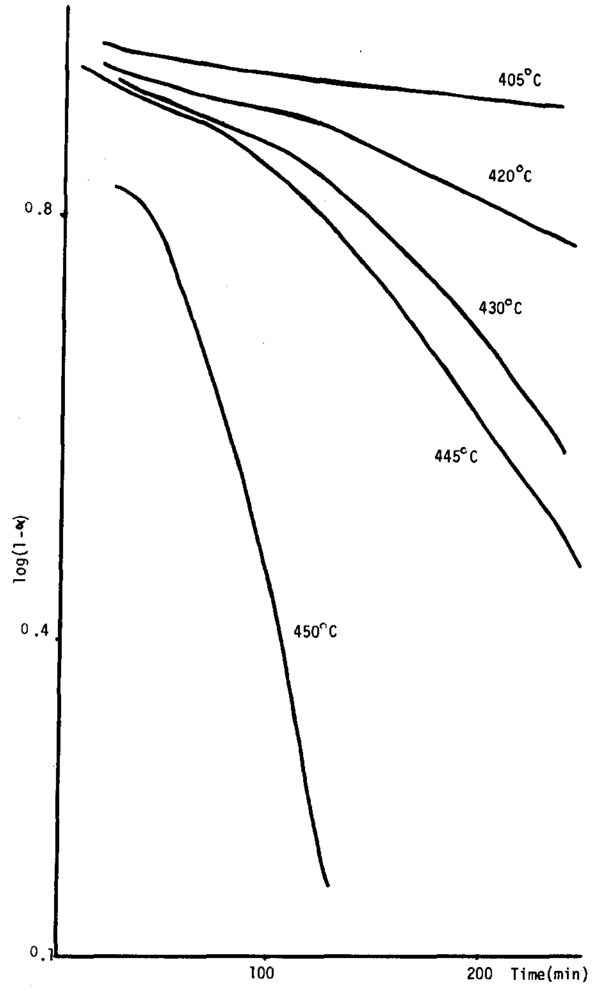

Fig. 6. Application of the decay law to the first series of isothermals.

For small values of t this becomes

$\alpha = t \times \text{const}$

A plot of $\log[-\log(1-\alpha)]$ against $\log t$ for the second series allows the value of n in the Erofeev expression to be calculated. The appropriate graphs are shown in Fig. 10. The values of n deduced from these graphs are as follows.

Temp. (°C)	Value of n in Erofeev expression
448	2.0
452	1.5
456	1.2
463	0.86
465	0.77

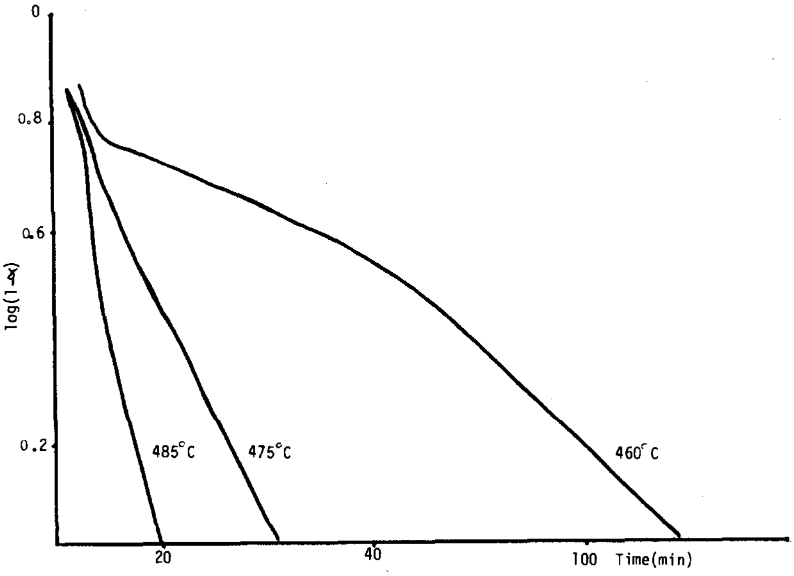

Fig. 7. Application of the decay law to the first series of isothermals.

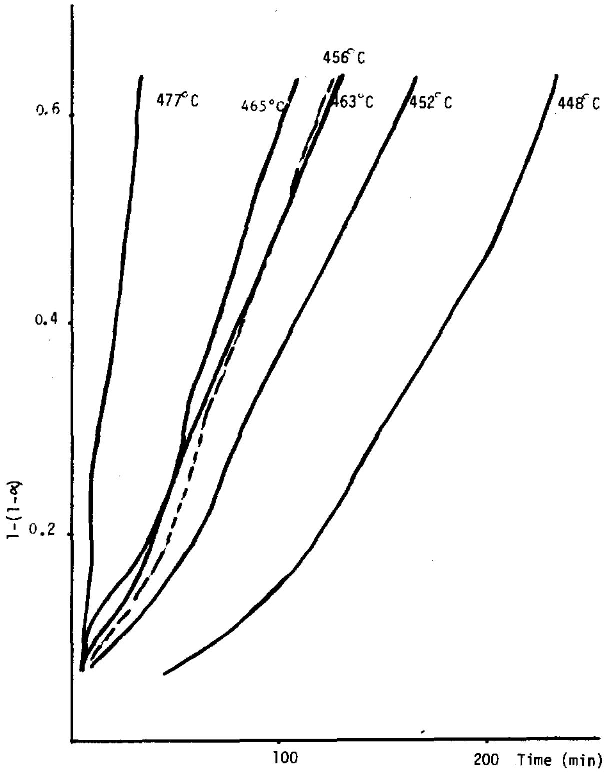

Fig. 8. Application of the Mampel law to the second series of isothermals.

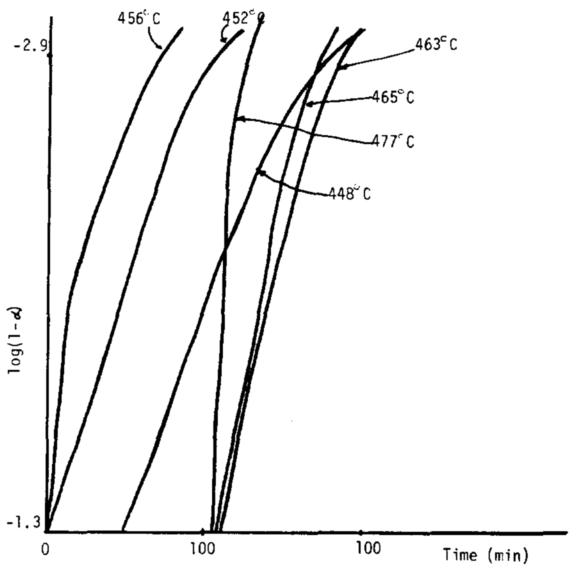

Fig. 9. Application of the decay law to the second series of isothermals.

At 448 °C, $n = 2$, and this value corresponds to a two-dimensional growth of nuclei. At higher temperatures, $n < 2$ and the system departs from the Erofeev model.

The Mampel one-third law can be correlated with the Erofeev equation by putting the former into the differential form

$$\frac{d\alpha}{dt} = (1 - \alpha)f(t)$$

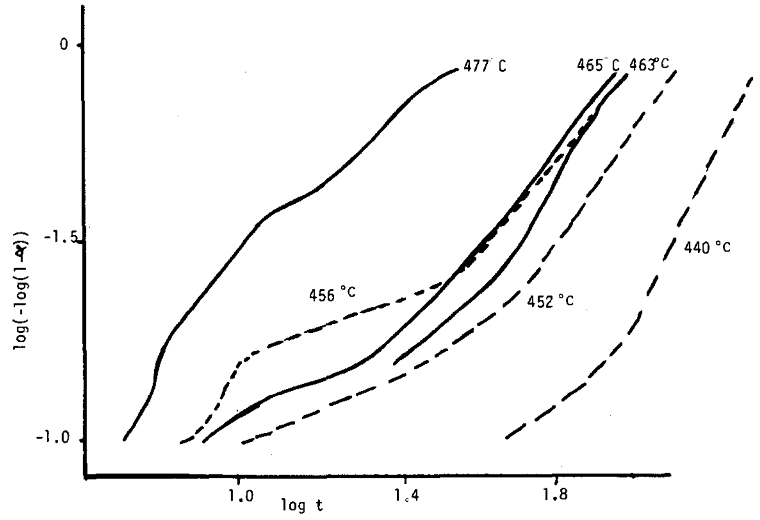

Fig. 10. Application of the Erofeev law to the second series of isothermals.

and identifying f(t) with p. Under these conditions

$$p=\frac{-3K}{1-Kt}=\frac{-3K}{(1-\alpha)1/3}\simeq\frac{3}{t}$$

where

$$K=\frac{V}{2}=\frac{\text{velocity of advance of interface}}{\text{radius of particle}}$$

A similar treatment of the power law is as follows

$$\alpha=Kt^n$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=K^1t^{n-1}$$

$$=K^1(1-\alpha)\frac{t^{n-1}}{(1-\alpha)}$$

$$(1-\alpha)=1-Kt^n$$

Therefore

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=K^1(1-\alpha)\frac{t^{n-1}}{1-Kt^n}$$

$$\simeq-\frac{K^1}{K}(1-\alpha)\frac{1}{t}$$

whence

$$p=\frac{K^1t^{n-1}}{1-Kt^n}$$

$$\simeq-\frac{K^n}{t}$$

The first-order decay law can also be treated in a similar fashion. In this case $p=K=\text{const.}$, when

$$\alpha=1-\exp(-Kt)$$

which is the usual first-order expression. These values for barium compare with data for calcium oxalate decomposition of around 213 kJ mol^{-1}, and would seem reasonable.

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