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DTA KINETIC ANALYSIS OF METAL–OXIDANT SOLID STATE REACTIONS

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ABSTRACT

The kinetics of the solid-state reaction between zirconium powder and the oxidant MoO_3 was investigated by both isothermal and DTA methods. The reaction is a two-stage process in which the MoO_3 is first reduced to MoO_2 and then to Mo. The isothermal kinetic study, performed between 440 and 475°C, revealed that the first-stage reaction is diffusion controlled at the lower temperature but changes to a kinetically controlled mechanism at the higher temperature. The reaction rate was found to obey the Tammann equation from which rate constants at the various temperatures were obtained which produced an activation energy of 40 kcal mol^{-1}. A similar value was obtained by calculation of the activation energy from binding energy considerations.

A kinetic analysis of the DTA curve, in which thermal activity is first observed above 475°C, revealed that the data follow the Freeman–Carroll equation from which an activation energy of about 65 kcal mol^{-1} was calculated for both the first- and second-stage processes and that, in the temperature range above 500°C, the reaction is kinetically controlled. An argument, based on the thermal theory of ignition of condensed systems, is presented which tends to confirm the value of activation energy. Analysis of the DTA curve in terms of a diffusion controlled mechanism failed to produce a good correlation.

INTRODUCTION

Exothermic reactions of the type $3Zr + 2MoO_3 \rightarrow 3ZrO_2 + Mo$ in which the reaction may occur at a measurable rate in a multistage process and which can ignite and react propagatively in a combustion process, depending on the temperature, are, in many instances, solid-state reactions in the preignition regime[1]. The measurement and interpretation of the solid-state reaction kinetics of metal–oxidant powder mixtures of this type has received little attention in the literature. Spice and Staveley[2] showed that the preignition reaction between iron and barium peroxide is a true

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solid-state process and deduced from a consideration of the kinetics that the process is not diffusion controlled. In contrast, Schwab and Gerlach[3] investigated the reaction between germanium and molybdenum trioxide and showed that the reaction is diffusion controlled.

This laboratory has been involved in a study of the reaction of several metal powders with molybdenum trioxide to identify the successive reactions that occur and to clarify the mechanism. An investigation of the kinetics of the two stages of the reaction of the Zr–MoO_3 system

$$Zr + MoO_3 \rightarrow ZrO_2 + MoO_2$$

$$Zr + MoO_2 \rightarrow ZrO_2 + Mo$$

is described here in which analysis of the rate controlling process, kinetic or diffusion, is made and the use of DTA to obtain kinetic parameters is explored.

EXPERIMENTAL

The rates of reaction of the zirconium(3 μ)–molybdenum oxide (MoO_3) mixture under isothermal conditions were determined in the temperature range of 440 to 475°C by following the reduction of the MoO_3 with time at a given temperature by means of infrared spectrophotometry. Molybdenum trioxide absorbs in the infrared at 870 cm^{-1}. A calibration curve was obtained for MoO_3 and showed that the absorption by the MoO_3 followed Beer's Law up to 5% MoO_3. Thus, in these studies the MoO_3 content of the KBr pellets was always less than 5%.

The Zr–MoO_3 mixture, contained in platinum crucibles, was sealed into an evacuated Vycor tube and heated in a constant temperature furnace for a given length of time and then quenched in an ice bath. Representative portions of the heated samples were then mixed with KBr, pressed into KBr pellets and the percent reaction determined from the intensity in MoO_3 absorption at 870 cm^{-1}.

Measurement of the rate of consumption of MoO_2 was not performed because of the inability to measure its concentration in the presence of MoO_3 and Mo. As a result, the Zr–MoO_2 system was investigated by DTA only.

The thermal analysis of the Zr–molybdenum oxide mixtures was carried out using a Mettler Thermoanalyzer. Approximately 20 mg of the mixture was heated at a rate of 15°C/min in a helium atmosphere at a flow rate of 6 l/h. Simultaneous TG curves revealed no weight loss during the entire heating period.

RESULTS

Isothermal kinetics

The kinetics of the reaction (1) was studied isothermally at temperatures of 440, 450, 463 and 475°C. The results obtained are presented in Fig. 1 and show that the rate of reaction initially is constant after which it begins to decrease with time.

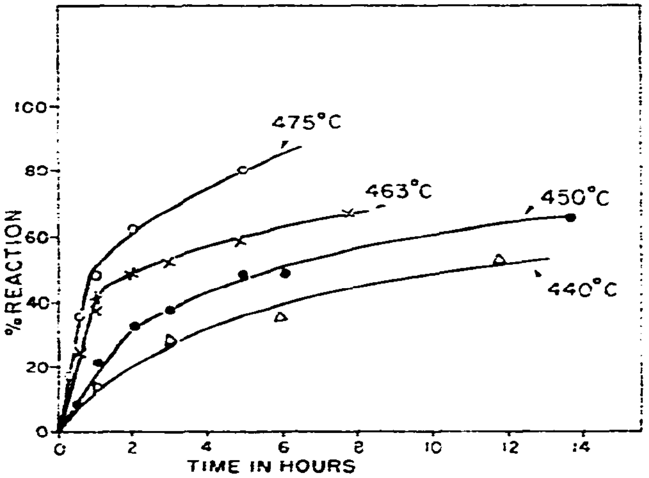

Fig. 1. Reaction rate vs. time and temperature for the reaction $Zn+2MoO_3 \rightarrow ZnO_2+2MoO_2$.

Rate equations based on a diffusion mechanism according to Jander[4] (eqn(1))

$$K_J t = [1-(1-x)^{1/3}]^2 \tag{1}$$

and Ginstling and Brounshtein[5] (eqn(2))

$$K_{GB} t = 1-\tfrac{2}{3}x-(1-x)^{2/3} \tag{2}$$

and an empirical relation according to Tammann[6] (eqn(3))

$$x = K_T \log t + c \tag{3}$$

were used in evaluating the data and calculating the activation energy of the reaction. In the above equations x is the extent of reaction, t is the time, and K is a rate constant which is temperature dependent. The Jander equation has a firm theoretical formulation based on a diffusion mechanism assuming contact between particles to be planar and is applicable to a fine particle mixture. The Ginstling and Brounshtein (GB) equation is for a diffusion controlled reaction based on a spherical model in which the metal powder is embedded in the oxide. The Tammann equation is an empirical relation which has been shown to have some validity in describing the kinetics of solid state reactions in the transition region between a diffusion and kinetic controlled mechanism[7].

The activation energies (E) calculated from the Arrhenius equation

$$K = Ae^{-E/RT} \tag{4}$$

for the Jander, Ginstling–Brounshtein and Tammann formulations are 67, 66.7 and 40 kcal mol^{-1}, respectively. The data obtained at the lower temperatures fit Jander and Ginstling–Brounshtein equations, however there was some scatter and poor fit at the higher temperatures. The reverse was observed with the Tammann equation. The data obtained at 463 and 475 °C adhere to the Tammann equation while at the lower temperature the data did not. This would tend to indicate that there may be a change in mechanism as the temperature is raised. The analysis was therefore extended to include the equation based on a kinetically controlled mechanism.

The equation for a first-order kinetically controlled reaction is

$$-Kt = \ln (1 - x). \tag{5}$$

The results of the analysis by the kinetic and Ginstling–Brounshtein equations are presented in Fig. 2. In these curves the percent reacted is plotted against the reduced time, that is, the time divided by the 50% reaction time, ($t/t_{0.5}$), according to the procedure outlined by Sharp et al.[8]. The solid line (curve B) is the theoretical curve for the Ginstling–Brounshtein equation, which compares favorably with the data obtained at 440 and 450°C but which shows some scatter at 463°C. As will be noted, this scatter may be indicative of the change in the reaction mechanism.

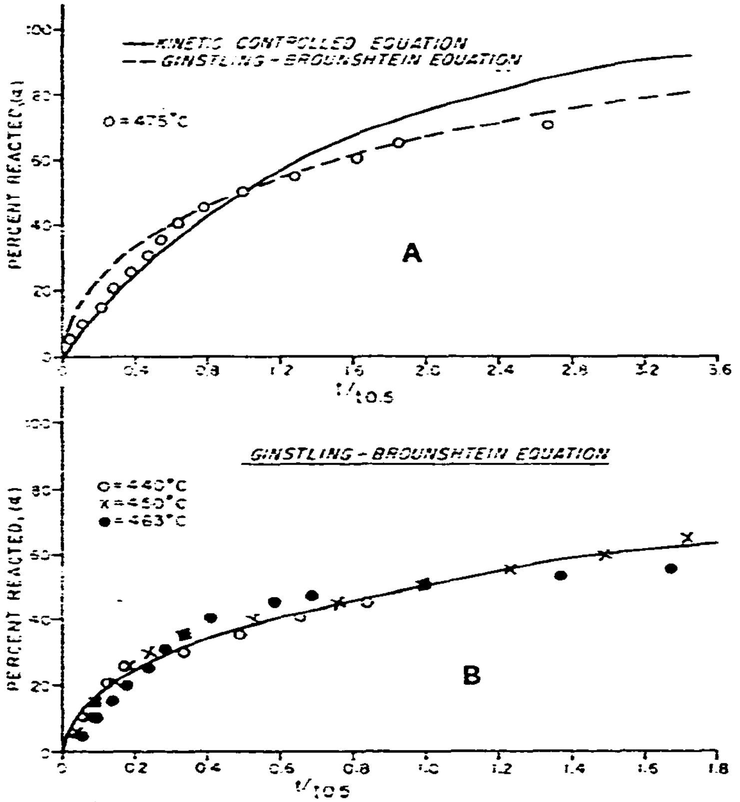

Fig. 2. Percent reacted (α) vs. reduced time ($t/t_{0.5}$) for Zn/MoO_3 mixture at various temperatures.

The upper half of Fig. 2 (curve A) shows the analysis of the data obtained at 475°C. The solid line is the theoretical curve for the first-order kinetic equation while the dashed line is for the Ginstling–Brounshtein diffusion controlled equation. The data at first fit the first-order equation. However, at about 40% reaction, the data deviates from the kinetic equation and follows the Ginstling–Brounshtein equation. Thus, it appears that the reaction

$$Zr+2MoO_3 \rightarrow ZrO_2+2MoO_2$$

is diffusion controlled at lower temperatures. At higher temperatures it is first-order kinetically controlled until an oxide coat is formed and then it reverts back to diffusion control, i.e., it is in a transition region.

Budnikov and Ginstling[7] have shown that, under certain conditions, the equation describing mixed kinetics reduces to the Tammann eqn (3). This presumes that reaction occurs over an extended period of time in which log *t* is much larger than the temperature dependent rate constants and that the diffusion layers are planar, as per Jander's assumption. Nevertheless, it was observed that the isothermal kinetic data at 463 and 475 °C follow the Tammann expression very well. It therefore appears that scatter of the 463 °C data shown in Fig. 2 (curve B) is also indicative of the onset of the transition from one mechanistic regime to another.

DTA kinetics

The DTA of a stoichiometric mixture of Zr–MoO_3 consists of two overlapping exotherms as shown in Fig. 3A. The first exotherm is due to the reduction of MoO_3 to MoO_2 and the second to the reduction of the MoO_2 to elemental Mo[1]. Only the second exotherm is obtained when a Zr and MoO_2 mixture is thermally analyzed (Fig. 3B). By subtracting the exotherm obtained for the Zr–MoO_2 reaction (Fig. 3B) from the overlapping exotherms in Fig. 3A, the exotherm for the reaction of MoO_3 to MoO_2 is obtained. If an excess of Zr is reacted with MoO_3 the curve shown in Fig. 4 is obtained in which one exotherm, peaking at 613 °C with a shoulder at 649 °C, is observed. The shoulder is undoubtedly due to the reduction of MoO_2 to Mo and

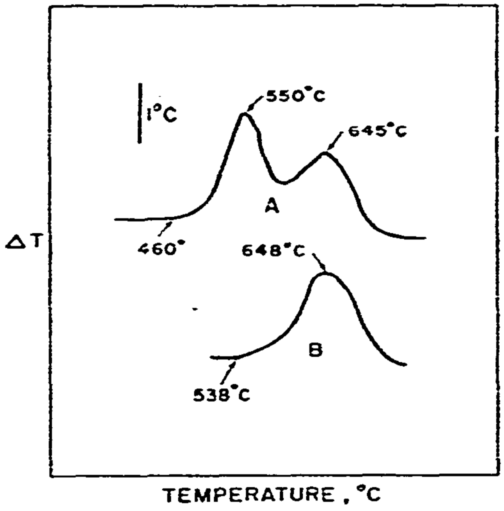

Fig. 3. (A) DTA of Zn + MoO_3 (stoichiometric). (B) DTA of Zn + MoO_2.

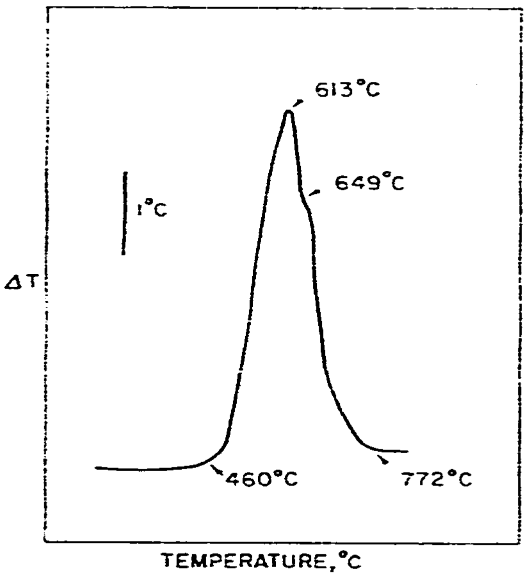

Fig. 4. DTA of excess $Zn+MoO_3$.

therefore the total curve represents the heat release associated with the overall reaction

$$3Zr+2MoO_3 \rightarrow 3ZrO_2+2Mo$$

From the DTA curves, the kinetics of the reduction of MoO_3 to MoO_2 and MoO_2 to Mo were deduced using various DTA kinetic expressions. In addition, the percent reaction was calculated from the DTA curve and the data were used to determine if a diffusion mechanism applies in controlling the reaction rate.

Kinetically controlled equations

The DTA kinetic equations used in the analysis are presented in Table 1. Where K is the rate constant, ΔT is the observed temperature difference between the sample and reference substance at temperature T, A is the area under the whole thermal curve, a is the area under the curve up to temperature T, λ is the heating rate, T_p is the peak temperature, T_s is the temperature at which the exotherm starts and r_s is the slope of the DTA curve. The slopes of the lines obtained from each equation multiplied by R, the gas constant, will yield a value for E, the activation energy. The intercept of the line obtained with the Freeman–Carroll equation is the order of reaction, which in these solid-state reactions were first order.

The activation energy, obtained for the excess $Zr+MoO_3$ overall reaction (Fig. 4), the $MoO_3 \rightarrow MoO_2$ reaction and the $Zr+MoO_2$ reaction by the various equations are tabulated in Table 2. The data show that the most consistent results are obtained with the Freeman–Carroll equation. For the first stage of the reaction, i.e., the reduction of MoO_3 to MoO_2, the Freeman and Carroll and Piloyan values were approximately the same (61.2 and 64 kcal mol^{-1}), while that of Borchardt and Daniels is considerably higher (81 kcal mol^{-1}). The values derived from the Freeman–

TABLE 1

NON-DIFFUSION EQUATIONS

Investigator	*Equation*	*Plot*	*Ref.*
Borchardt and Daniels	$K = \Delta T/(A-a)$	$\ln K$ vs. $(1/T)$	9
Freeman and Carroll	$\Delta \ln (\Delta T) = n\Delta \ln (A-a)-(E/R)\Delta(1/T)$	$\frac{\Delta \ln (\Delta T)}{\Delta \ln (A-a)}$ vs. $\frac{\Delta(1/T)}{\Delta \ln (A-a)}$	10
Kissinger	$\ln (\lambda/T^2p) = -E/RT_p+\ln AR/E$	$\ln (\lambda/T_p^2)$ vs. $(1/T_p)$	11
Piloyan et al.	$\text{in} (\Delta T) = C-E/RT$	$\ln (\Delta T)$ vs. $(1/T)$	12
Stammler	$\ln r_s = C-E/RT$	$\ln r_s$ vs. $(1/T_s)$	13

TABLE 2

ACTIVATION ENERGIES OF Zr-MoO_2 AND Zr-MoO_3 REACTIONS

Reaction	*Activation energy (kcal mol^{-1})*				
	Borchardt and Daniels	*Freeman and Carroll*	*Piloyan et al.*	*Kissinger*	*Stammler*
$Zr+MoO_2 \rightarrow ZrO_2+Mo$[a]	73.6	68.9	52.0	36.6	126
[b]	49.4	54.6	38.2		
$Zr+MoO_3 \rightarrow ZrO_2+Mo$[c]	56.4	58.4	50.6		
$Zr+MoO_3 \rightarrow ZrO_2+MoO_2$[d]	81	61.2	64		

[a] Reaction of mixture of Zr and MoO_2. [b] Second half of two overlapping exotherms (Fig. 3B); second stage of two stage reaction. [c] Excess Zr used→1 curve (Fig. 4). [d] First half of two overlapping exotherms (Fig. 3A).

Carroll and Piloyan et al.'s equations agree fairly well with the values obtained in the isothermal study (66–67 kcal mol^{-1}).

When a mixture of Zr and MoO_2 was heated at a rate of 15°C/min, the activation energy values obtained by the Borchardt–Daniels and Freeman–Carroll equations agreed within 5% (73.6 vs 68.9 kcal mol^{-1}). Using heating rates of 5 and 10°C/min did not alter these values by more than 10%. The value obtained from Piloyan et al.'s equation was lower (52.0 kcal mol^{-1}). The Kissinger and Stammler equations do not appear to hold for the solid state reaction since the Kissinger value was about 50–60% of the Borchardt–Daniels and Freeman–Carroll values while the Stammler value was almost twice that obtained with the Freeman–Carroll equation.

The two overlapping exotherms, obtained when a stoichiometric mixture of Zr and MoO_3 are reacted, were separated into two separate curves as mentioned previously. The activation energies were then calculated from the reconstructed DTA curve for the reduction of MoO_2 to Mo using the Borchardt–Daniels, Freeman–

Carroll and Piloyan et al. expressions. These values were all lower than those obtained from the reaction of a mixture of Zr and MoO_2 (see Table 2). The lower value can be explained as follows: The reaction between Zr and MoO_2 is first-order kinetically controlled as showed by the intercept of the line obtained with the Freeman–Carroll equation. However, when it is the second stage of the Zr–MoO_3 reaction, the Zr reacting with the MoO_2 formed is coated with ZrO_2 formed in the first stage and is, therefore, partially diffusion controlled thus having a lower activation energy.

The activation energy, obtained from Fig. 4 for the overall reaction of $MoO_3 \rightarrow Mo$, showed that the Borchardt–Daniels and Freeman–Carroll equations gave approximately the same values (56.4 and 58.4 kcal mol^{-1}), while the Piloyan et al. equation produced a slightly lower value of 50.6 kcal mol^{-1}.

Diffusion equation

The method devised by Borchardt and Daniels[9] to determine the fraction reacted from experimental DTA curves is expressed by the equation

$$-\frac{dn}{dt} = \frac{n_0}{KA}\left[C_p \frac{d\Delta T}{dt} + a\right] \tag{6}$$

where n = number of moles of starting material at time t, n_0 = number of moles of starting material at start ($t = t_0$), C_p = heat capacity of sample, ΔT = temperature difference between sample and standard, K = constant, A = total area under the DTA curve, and a = part of area under the DTA curve up to time t.

Borchardt[14] had found experimentally that $C_p(d\Delta T/dt)$ is an order of magnitude smaller than "a" and therefore can be neglected. Then for the fraction reacted

$$\alpha = \frac{N_0 - n}{n_0} = \frac{a}{A}. \tag{7}$$

The values for α were then inserted into the equations of Jander and Ginstling–Brounshtein, which assume three-dimensional diffusion and spherical symmetry, in order to obtain the rate constants (k) which in turn were used in the Arrhenius expression to obtain the activation energy. The activation energies calculated in this manner for the Zr–MoO_3 and Zr–MoO_2 reactions gave values ranging from 115 to 130 kcal mol^{-1}. These values are considerably higher than might be expected for a diffusion controlled reaction and, in fact, are twice that obtained by the isothermal method in which it was shown that diffusion is rate controlling at the lower temperatures only. It is therefore likely that at the temperature encompassing the DTA curve the reaction is kinetic controlled and confirms the trend indicated in the isothermal kinetic study.

DISCUSSION

This study has shown that the reaction between Zr and MoO_3 is diffusion controlled at 440 to 450 °C and changes to a kinetically controlled mechanism as the temperature is increased. It was also shown that the interpretation of the DTA curves in terms of reaction kinetics, in which the exothermic process becomes observable at about 500 °C, leads to the conclusion that the reaction is kinetically controlled.

Intimate mixtures of Zr powder and MoO_3 will ignite at a temperature in the vicinity of 490 ± 10 °C and will burn propagatively. Thus, the results obtained here provide some insight into the ignitability of such a mixture. That is, if the mixture is heated slowly in the preignition regime, ignition may not occur if the diffusion-controlled mechanism is operative and an oxide layer builds up on the reactant, which maintains this mechanism. If, on the other hand, the mixture is heated at a high rate, build-up of the oxide layer is minimized, the reaction becomes kinetic controlled and ignition occurs, provided, of course, that the temperature is in the ignition regime.

The activation energy of the reaction

$$Zr + 2MoO_2 \rightarrow ZrO_2 + 2MoO_2$$

has been calculated to be about 65 kcal mol^{-1} over the temperature range of 440 to 460 °C. This value is derived from the isothermal kinetic study for a diffusion-controlled mechanism. This value appears somewhat high because the rate of diffusion-controlled reactions generally have relatively low temperature coefficients. If mixed kinetics are assumed, and the Tammann equation is used to calculate the activation energy, a value of about 40 kcal mol^{-1} is obtained and this value appears more reasonable. A supporting argument is as follows: a mean bonding energy B for a Me–O bond is given by the expression

$$B = \frac{1}{2n}\left[Q_B + \frac{n}{2}Q_D\right] \tag{8}$$

where Q_D is the heat of dissociation of a mole of oxygen (117 kcal mol^{-1}), Q_B is the heat of formation of the oxide and n is the number of oxygen atoms in the oxide. Using Q_B values of 258 kcal mol^{-1} for ZrO_2 and 180 kcal mol^{-1} for MoO_3, $B = 94$ kcal mol^{-1} for ZrO_2, 60 kcal mol^{-1} for MoO_3 and 62 kcal mol^{-1} for MoO_2. According to Schwab and Gerlach[3], about two thirds of B is the activation energy for diffusion via vacancies. The oxygen must diffuse through both the MoO_2 and the ZrO_2 layer and the MoO_3 is the source of the oxygen. Therefore it is safe to assume that activation energy calculated from the Me–O bond in MoO_3 represents the activation energy of the first-stage reaction, which agrees closely with the value calculated from the Tammann expression.

The activation energy (E) of the kinetic controlled first and second stage reaction appear to be about the same, in the vicinity of 65 kcal mol^{-1}. A supporting argument for this value can be given using the thermal theory of ignition[15]. If it is assumed that the mixture is cylindrical shaped and that the kinetic frequency factor, A, is 10^{14}, the following expression can be used to determine the ignition temperature (T_M) which is an experimental value.

$$T_M = \frac{E/R}{\ln\left(\tau QAE/CRT_M^2\delta\right)} \tag{9}$$

where R is the gas constant, τ is a time constant which is a ratio of the radius of the charge squared to the thermal diffusivity, Q is the heat of reaction, C is the heat capacity and δ is a shape factor equal to 2 for cylinders. For a charge 7.5 mm is radius, the ignition temperature was calculated to be 500°C, which agrees closely with the DTA and isothermal experimental value (490 ± 10°C) and thus confirming that the activation energy is about 65 kcal mol^{-1}.

REFERENCES

1 A. D. Kirshenbaum and A. J. Beardell, *Thermochim. Acta*, 4 (1972) 239.
2 J. E. Spice and L. A. K. Staveley, *J. Soc. Chem. Ind.*, 68 (1949) 313.
3 G. M. Schwab and J. Gerlach, *Z. Phys. Chem.*, 56 (1967) 121.
4 W. Jander, *Angew. Chem.*, 41 (1929) 79.
5 A. M. Ginstling and B. I. Brounshtein, *Zh. Prikl. Khim. (Leningrad)*, 23 (1950) 1249.
6 G. Tammann, *Z. Anorg. Allg. Chem.*, 111 (1920) 78.
7 P. P. Budnikov and A. M. Ginstling, translated by K. Shaw, *Principles of Solid State Chemistry*, Gordon and Breach, New York, 1968, p. 205.
8 J. H. Sharp, G. W. Brindley and B. N. Narahari Acher, *J. Amer. Ceram. Soc.*, 49 (1966) 379.
9 H. J. Borchardt and F. Daniels, *J. Amer. Chem. Soc.*, 79 (1957) 41.
10 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
11 H. E. Kissinger, *J. Res. Nat. Bur. Stand.*, 57 (1956) 217.
12 G. O. Piloyan, I. D. Ryabchikov and O. S. Novikova, *Nature*, 212 (1966) 217.
13 M. Stammler, in R. F. Schwenker and P. D. Garn (editors), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1135.
14 H. J. Borchardt, *J. Inorg. Nucl. Chem.*, 12 (1960) 252.
15 J. Zinn and R. N. Rogers, *J. Phys. Chem.*, 66 (1962) 2646.