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Note

KINETICS OF SOLID STATE REACTION BETWEEN $CaCO_3$ AND MoO_3

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ABSTRACT

Attempts have been made to study the kinetics of the solid state reaction between $CaCO_3$ and MoO_3 by thermogravimetry. The data show a good fit with the Ginstling–Brounshtein equation for three-dimensional diffusion. An apparent activation energy of 362.2 ± 2.8 kJ mol^{-1} has been obtained for this reaction.

INTRODUCTION

Solid state reactions can be followed by different techniques depending on whether there is a change in weight associated with the liberation of a gaseous product or the reaction of a solid with a gaseous reactant, or whether the reactants and products have a different X-ray pattern, colour, or any other physical property. The formation of $CaMoO_4$ in the solid state reaction between $CaCO_3$ and MoO_3 is associated with a change in weight due to evolution of carbon dioxide gas.

$$CaCO_3 + MoO_3 \rightarrow CaMoO_4 + CO_2 \uparrow$$

Hence this reaction can be followed by measuring the volume or pressure of carbon dioxide at various time intervals [1] or by monitoring the weight loss in the mixture as a function of time.

EXPERIMENTAL

Molybdenum oxide (Mallikrodt A.R. grade) and calcium carbonate (E. Merck grade) were dried at 473 K for about 12 hours. Then they were powdered and sieved separately. The fraction with particle size −100 and +150 mesh were used throughout this study.

Thermogravimetric curves were recorded separately for the decomposition of $CaCO_3$, vaporization of MoO_3 and the thermal reaction of a homogeneous 1 : 1 mixture of $CaCO_3$ and MoO_3 in air at 4 K min^{-1} heating rate.

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All isothermal experiments were carried out in a resistance furnace whose temperature was controlled with an accuracy of ±1°C. A sample size of about 20 mg was used in all experiments.

In following the progress of the reaction by isothermal weight loss, samples of 1 : 1 mixtures of $CaCO_3$ and MoO_3 were heated in platinum crucibles. After heating the samples were cooled in a desiccator and weight losses and fraction conversions were determined. The fraction conversion data were obtained for different reaction times at five different temperatures between 799 and 839 K. The fit of the experimental data to the Ginstling–Brounshtein equation was tested. The activation energy for this reaction was obtained from the slope of the Arrhenius plot.

RESULTS AND DISCUSSIONS

Figure 1 shows the thermogravimetric curves for the decomposition of $CaCO_3$ in air, the vaporization of MoO_3 and the thermal reaction of a 1 : 1 mixture of $CaCO_3$ and MoO_3 in air. It can be seen that in the presence of MoO_3, the decomposition temperature is lowered by about 137 K, accompanied by the simultaneous formation of $CaMoO_4$. Because the vaporization of MoO_3 starts at about 961 K, the weight loss in the mixture of $CaCO_3$ and

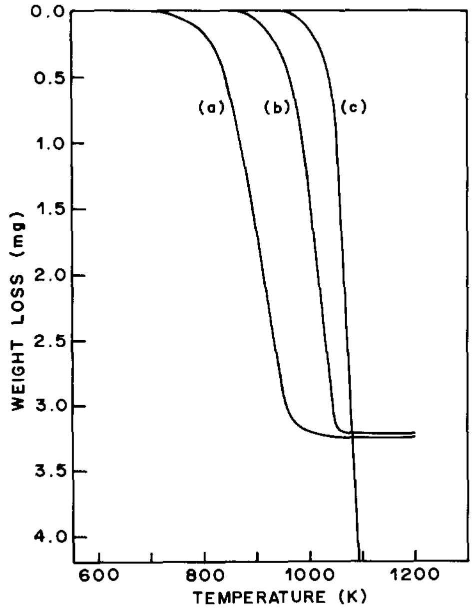

Fig. 1. Thermogravimetric curves in air for: (a) 1 : 1 mixtures of $CaCO_3$ and MoO_3 (sample weight = 18.15 mg) (b) decomposition of $CaCO_3$ (sample weight = 7.40 mg) (c) vaporization of MoO_3 (sample weight = 9.9 mg).

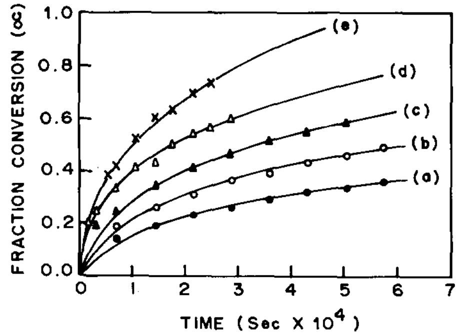

Fig. 2. The fraction conversion (α) plotted against time (t) at various reaction temperatures for 1 : 1 mixtures of $CaCO_3$ and MoO_3: (a) 799 K, (b) 810 K, (c) 818 K, (d) 828 K and (e) 839 K.

MoO_3 below this temperature is due to the decomposition of $CaCO_3$ with simultaneous $CaMoO_4$ formation. This is supported by the observed weight loss during the heating process. Secondly, no phase other than $CaCO_3$, MoO_3 and $CaMoO_4$ was identified by X-ray powder diffraction in the mixture after any time of reaction. These observations enabled the study of this reaction by the isothermal weight loss method.

Figure 2 gives the fraction conversion as a function of time of reaction (t) for 1 : 1 mixtures of $CaCO_3$ and MoO_3 at different temperatures.

Various kinetic equations have been proposed depending on the mechanism of the reaction and the rate determining steps. A solid state reaction may be controlled by the reaction taking place at the phase boundary [2], by nucleation of the product phase at the active sites in the crystal, or by diffusion through the product layer [3]. The isothermal data obtained at each temperature show a good fit with the Ginstling–Brounshtein [4] model for three-dimensional diffusion. The expression used can be represented as

$$1-\tfrac{2}{3}\alpha-(1-\alpha)^{2/3}=Kt. \tag{1}$$

where K is the rate constant and α is the fraction conversion at time (t).

Figure 3 shows the plots of $[1-(2/3)\alpha-(1-\alpha)^{2/3}]$ against time (t) at different temperatures. A linear least-squares method has been used to construct the straight lines through the data points at each temperature. The linearity observed is very good which confirms that the reaction rate is controlled by diffusion through the layers of reaction products on uniform spherical reactant particles. The rate constants have been computed from the slopes of these least-squares-fitted straight lines.

The temperature dependence of the reaction rate is expressed by the Arrhenius equation as

$$K=A\,e^{-E/RT} \tag{2}$$

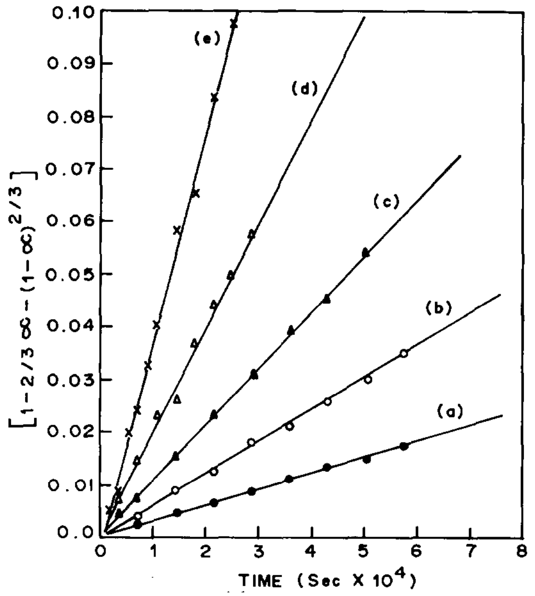

Fig. 3. Plot of $[1-2/3\alpha-(1-\alpha)^{2/3}]$ against time for 1 : 1 mixtures of $CaCO_3$ and MoO_3 at different temperatures: (a) 799 K, (b) 810 K, (c) 818 K, (d) 828 K and (e) 839 K.

where K is the rate constant, E is the activation energy, T is the temperature (K) and A is the pre-exponential factor which is the reaction rate at infinite temperature.

Figure 4 shows the plot of log K against $1/T$ for 1 : 1 mixtures of $CaCO_3$ and MoO_3. Application of the least-squares method yields an activation energy (E) of 362.2 ± 2.8 kJ mol^{-1} and pre-exponential factor (A) of

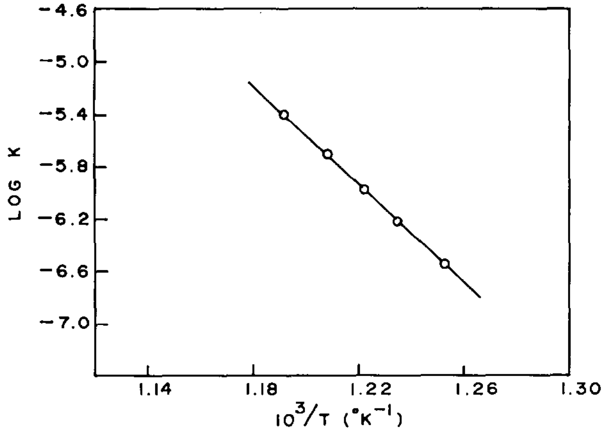

Fig. 4. Arrhenius plot for 1 : 1 mixture of $CaCO_3$ and MoO_3.

1.40×10^{17} s^{-1}. Hence the rate constant for this reaction is given by

$K = 1.40 \times 10^{17} \times e^{-43568/T}$

Jander [1] has reported a value of $E/R = 43170$ in eqn. (2). This gives an activation energy of 358.9 kJ mol^{-1}. The small difference between this value and that obtained in the present work is due to the use of different models to obtain the kinetic parameters.

CONCLUSION

This study shows that a simple method in which the mixtures are heated in a resistance furnace and, after cooling, the weight losses are recorded, can produce as accurate and as precise a value for the activation energy as can any other automatic method. Furthermore, it has been established that the reaction is controlled by a diffusion process according to the Ginstling–Brounshtein model.

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