Kinetics of the Solid State Reaction between MoO_3 and $SrCO_3$

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The solid state reaction $MoO_3+SrCO_3 \rightarrow SrMoO_4+CO_2$ has been studied on mixtures of powdered reagents.

Thermogravimetric measurements in the temperature range 412°—498 °C have been made on different mixtures and under different atmospheres. Moreover, optical observations and conductometric measurements have been carried out.

The results show that the reaction is governed by a diffusion mechanism with an apparent activation energy of (60 ± 1) kcal/mole and that the main diffusing species is the Mo^{6+} ion.

Solid state reactions of the type $A+B \rightarrow C+D_{(gas)}$ have been scarcely studied. In particular, very few investigations have been carried out in order to determine the mechanism by which they are governed. On the other hand, these reactions could be very interesting in the production of ferrites, titanates, molybdates and so on, which are very important products in modern electronic devices.

This work, which is a part of a systematic research in progress in our institute, reports the results obtained for the reaction

$$MoO_3+SrCO_3 \rightarrow SrMoO_4+CO_2\,.$$

The kinetics of the process have been investigated isothermally using thermogravimetric analysis between 412° and 498 °C, on MoO_3-SrCO_3 mixtures with 1:1, 1:3, 1:6 molecular ratios. Measurements have been done at a pressure of 1 atmosphere in air and in the case of the 1:6 mixture also in oxygen and in nitrogen ($p_{O_2} < 10^{-2}$ mm Hg).

Moreover, to obtain information on the reaction mechanism, electrical conductivity measurements and observations through a microscope have also been carried out.

The same reaction has been recently analyzed by Zhukovskii et al.[1]: these authors, however, have particularly examined the 1 : 1 mixture.

Experimental

a) Apparatus

The thermogravimetric curves have been recorded by a Du Pont apparatus consisting of a 950 Thermogravimetric Analyzer joined with a 900 Differential Thermal Analyzer. The experimental technique has already been described [2].

Conductometric data were obtained by a Wayne Kerr Autobalance Precision Bridge B 331 ($\nu = 1592$ Hz), while the optical observations were done by a Leitz High Temperature Microscope.

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b) Materials and Procedures

The compounds, MoO_3 (Alfa Inorganics 99.9%) and $SrCO_3$ (C. Erba RP), have been prefired for 12 h at 450° and 700 °C respectively.

It is well known from literature that MoO_3 has a tendency to sublime and $SrCO_3$ to decompose much below their melting points. The temperature values reported for both phenomena, however, are in considerable disagreement [3]. Thus, it has been necessary to determine the thermal stability limit of the two compounds in order to be sure that, in the experimental temperature range of the reaction, MoO_3 would be exclusively in the solid phase and that CO_2 would evolve only by the interaction between MoO_3 and $SrCO_3$.

TG measurements (sensitivity 5 inch/mg; heating rate 3°/min) gave the following information: MoO_3 begins to sublime at 500 °C in air and at 480 °C in nitrogen; $SrCO_3$ begins to decompose at 800 °C in air and at 690 °C in nitrogen.

The electrical conductivity σ ($\Omega^{-1}\,cm^{-1}$) has been measured on MoO_3 pellets pressed at 10^3 kg/cm^2 and then sintered in oxygen atmosphere.

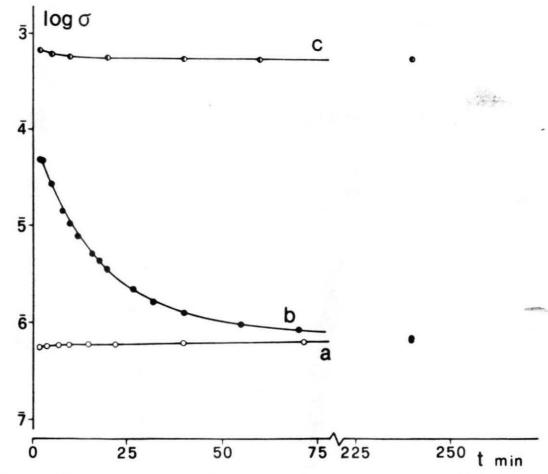

Fig. 1. Values of log σ (electrical conductivity in $\Omega^{-1}\,cm^{-1}$) versus t (minutes) for MoO_3 at 455 °C: a) in oxygen; b) in air; c) in nitrogen ($p_{O_2} < 10^{-2}$ mm Hg).

Figure 1 reports the isotherms (at 455 °C) log σ against time, as obtained in oxygen, air and nitrogen. It can be observed that

a) in oxygen, the conductivity is practically constant;
b) in air, the conductivity is initially higher than in oxygen and decreases progressively with time, reaching the oxygen value;
c) in nitrogen, the conductivity is even higher than in air and remains constant at that value.

Analogous phenomena have been interpreted by Deb and Chopoorian [4] in terms of colour centre formation due to the presence of Mo^{5+} ions and free electrons trapped in oxygen ion vacancies. These colour centres would be constantly present in the inert atmosphere, while in air they would disappear after prolonged heating.

Optical observations have been carried out by following at 450 °C, the reaction between a large size ($\cong 100\ \mu$) particle of MoO_3, obtained by sublimation, and an environment of finely powdered ($\cong 2\ \mu$) $SrCO_3$.

The reaction mixtures, used for thermogravimetric measurements, have been prepared with MoO_3 and $SrCO_3$ particles having an average size of 9 μ (specific surface 0.89 m^2/g) and 2 μ (specific surface 1.32 m^2/g) respectively. These mixtures yielded, as the only solid product of the reaction, the normal molybdate in stoichiometric quantity.

Results and Discussion

Figure 2 (a, b, c) reports, for the 1:1, 1:3, 1:6 MoO_3-SrCO_3 mixtures, the quantity α (ratio of the $SrCO_3$ reacted at time t to that reacted at $t=\infty$), against reduced time, $t/t_{0.5}$ ($t_{0.5}$ being the time at which $\alpha=0.5$) for the different isotherms studied in air.

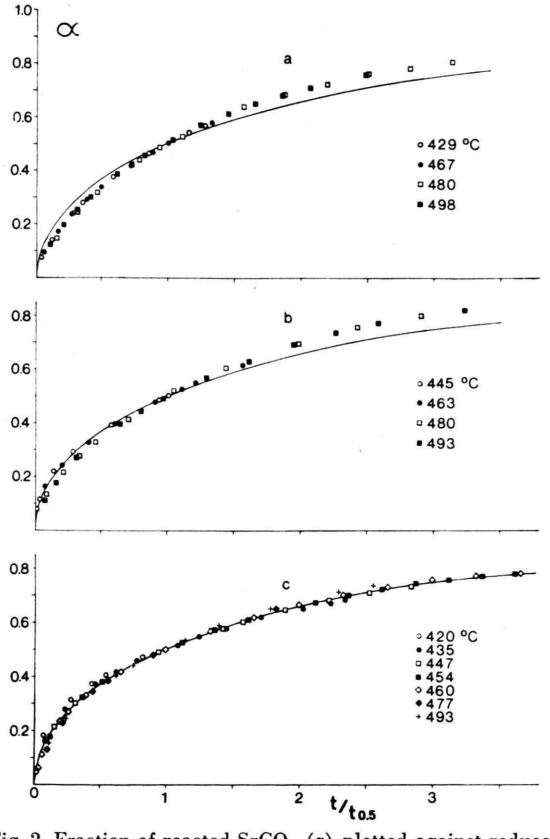

Fig. 2. Fraction of reacted $SrCO_3$ (α) plotted against reduced time ($t/t_{0.5}$) for 1 : 1 (a), 1 : 3 (b), 1 : 6 (c) MoO_3-SrCO_3 mixtures at various reaction temperatures. The continuous curve, common to the three sections, has been calculated by Equation (1).

Many equations have been suggested to interpret the kinetics of solid state reactions, some valid for processes governed by nucleation and by progression of the reaction interface [5], others valid for processes governed by diffusion [6]. Among the latter, the most frequently used and versatile equation is that proposed by GINSTLING and BROUNSHTEIN [7]:

$$1-\tfrac{2}{3}\alpha-(1-\alpha)^{2/3}=K\,t \qquad (1)$$

where K is a constant dependent on temperature (for its meaning see the original work).

The solid lines in Fig. 2 are calculated [8] according to (1). As it can be noted, on going from 1:1 to 1:3 to 1:6 mixtures, the coincidence of the calculated curves with the experimental data improves. Moreover, it has been found that the reaction rate for the 1:6 mixture is ten times that of the 1:1 mixture.

Figure 3 (a) plots log K values, as deduced by Eq. (1) ($0.05<\alpha<0.80$), against $1/T$ for the mixture 1:6; by the least square method an apparent activation energy $E=60.6$ kcal/mole is obtained. ZHUKOVSKII et al. [1], for the mixture 1:1, report a value $E=(58.5\pm5)$ kcal/mole. This value is very close to ours, but the comparison must be done with some reservations since, as shown in Fig. 2, the kinetics relative to the 1 : 1 and 1:3 mixtures are not satisfactorily governed by Equation (1).

Figure 3 (b) shows the Arrhenius plot for the 1:6 mixture obtained by the measurements under oxygen atmosphere; the deduced apparent activation energy ($E_{O_2}=59.7$ kcal/mole) is very close to that obtained for the same mixture in air. It can be noted that the reaction rate is higher in air than in oxygen. Possibly, the reason for this fact is the different behaviour (owing to the defects) of MoO_3 in the two atmospheres (see Figure 1).

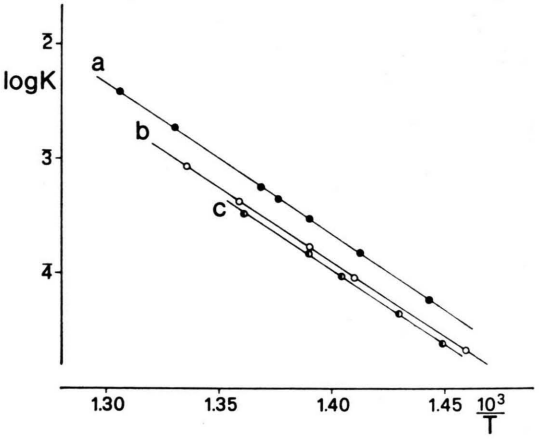

Fig. 3. Arrhenius plots for 1 : 6 MoO_3-SrCO_3 mixtures: a) in air; b) in oxygen; c) in nitrogen ($p_{O_2}<10^{-2}$ mm Hg).

The results reported so far confirm a diffusion controlled mechanism but do not indicate the nature of the diffusing species. Different authors [1, 9] who studied the reaction between MoO_3 and alkaline-earth carbonates state that MoO_3 is the component responsible for the diffusion. Our optical observations, following the already described procedures, are in agreement with these conclusions. Since in the experimental tempera-

ture range MoO_3 does not sublime, molybdenum may diffuse as Mo^{6+} ion through the product layer.

Because of the relatively large size of the O^{2-} ion and the particular structure of MoO_3 [10], it is likely that oxygen is transported through the vapour phase. This hypothesis seems to be confirmed by the measurements under a nitrogen atmosphere ($p_{O_2} < 10^{-2}$ mm Hg) whose Arrhenius plot ($E_{N_2} = 60.1$ kcal/mole) is shown in Figure 3 (c). It can be noted, in fact, that, even though the MoO_3 defects persist under a nitrogen atmosphere (see Fig. 1), the reaction rate is smaller then that observed in air and in oxygen.

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Elastische und thermoelastische Konstanten des $LiBaF_3$

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Elastic and Thermoelastic Constants of $LiBaF_3$

The elastic and thermoelastic constants of cubic $LiBaF_3$ are measured by ultrasonic methods. As a consequence of the larger packing density which results from the higher coordination number of the Ba ions in $LiBaF_3$ the values for the mean elastic stiffness and for the refractive index exceed those of LiF and BaF_2. A quantitative explanation of these properties is given. The values of many other properties range between those of LiF and BaF_2.

In der vorliegenden Arbeit soll die Frage diskutiert werden, ob die elastischen Eigenschaften eines binären Fluorids ($LiBaF_3$) aus dem elastischen Verhalten der konstituierenden einfachen Fluoride (LiF und BaF_2) mit einfachen Modellvorstellungen erklärt werden können.

Das in einem Antiperowskitgitter kristallisierende $LiBaF_3$ wurde erstmals von Neuhaus et al. [1] aus einer $LiF-BaF_2$-Mischschmelze nach dem Czochralski-Verfahren in Form von Einkristallen gezüchtet. Mit Hilfe eines verbesserten Verfahrens, über das an anderer Stelle ausführlich berichtet werden soll, konnten wir homogene Kristalle hoher optischer Qualität mit Längen bis zu 50 mm und Durchmessern bis zu 30 mm herstellen.

Die Kristalle wurden nach der Züchtung zum Abbau der mechanischen Spannungen mehrere Tage bei einer Temperatur von etwa 750 °C getempert. Sie waren wasserklar und völlig frei von Rissen. Beim Sägen und Schleifen entstanden jedoch einzelne größere Sprünge, die wohl auf noch vorhandene Restspannungen zurückzuführen sind. Die Qualität der Kristalle reichte aber dennoch für die im folgenden beschriebenen Messungen aus.

Homogenität und Orientierung der für die Messungen der elastischen Konstanten benutzten Kristalle wurden mit Hilfe von Laue-Rückstrahl-Aufnahmen überprüft. An zwei großen Individuen ergab sich mit dem Auftriebverfahren übereinstimmend eine Dichte von 5,2376 $g \cdot cm^{-3}$ für 20 °C. Dieser Wert kommt dem Idealwert sehr nahe und zeigt, daß die Kristalle weitgehend frei von chemischen Baufehlern sind. Die elastischen Konstanten c_{ij} wurden aus den Ausbreitungsgeschwindigkeiten longitudinaler und transversaler elastischer Wellen in Richtung [110] mit Hilfe des Schaefer-Bergmann-Verfahrens (Beugung von monochromatischem Licht an stehenden Ultraschallwellen bei etwa 30 MHz) bestimmt. Zur Kontrolle wurden auch Messungen in anderen Richtungen durchgeführt. Die thermoelastischen Konstanten $T_{ij} = \mathrm{d} \log c_{ij}/\mathrm{d}T$ wurden bestimmt aus der Abhängigkeit der Eigenfrequenzen dikker Platten von der Temperatur T in einem Intervall von ca. 25 °C bis −25 °C. Die thermische Ausdehnung α wurde mit einem Fizeau-Interferometer im selben Temperaturintervall gemessen. In Tab. 1 sind die Meßwerte zusammen mit den für die Diskussion benötigten Daten für LiF und BaF_2 zusammengestellt [2, 3]. Die relativen wahrscheinlichen Fehler liegen unter folgenden Schranken:

$c_{11}, c' = (c_{11} + c_{12} + 2\,c_{44})/2$,
$c_{44}, c'' = (c_{11} - c_{12})/2$: 0,4%;
c_{12}: 1%. T_{11}, T',
T_{44}, T'': 3%; T_{12}: 8%; α: 3%.

Diskussion

$LiBaF_3$ weist als Folge der höheren Koordinationszahl 12 des Bariumions gegenüber der Koordinations-

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