

# Kinetics of Formation of $\text{SrWO}_4$ in the Solid State Reaction Between $\text{WO}_3$ and $\text{SrCO}_3$

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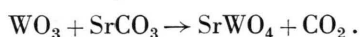
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The solid state reaction  $\text{WO}_3 + \text{SrCO}_3 \rightarrow \text{SrWO}_4 + \text{CO}_2$  was studied with the reactants in form both of separate pellets and of powder mixtures.

As for pellets, by an application of Wagner's method it was possible to state that the governing process is the cation counterdiffusion involving  $\text{W}^{6+}$  and  $\text{Sr}^{2+}$ .

Thermogravimetric measurements in the temperature range  $663^\circ - 755^\circ \text{C}$  on equimolar powder mixtures and with  $\text{SrCO}_3$  in a specially prepared spherulitic form were interpreted using Dünwald-Wagner's equation.

As a part of a research program on solid state reactions<sup>1</sup>, the present paper reports results on the kinetics and transport mechanism of the reaction



As recently observed<sup>2</sup>, little attention has been given so far to reactions of this kind, in which one of the products is in the gaseous state, particularly for what concerns the governing mechanism.

The kinetic process was investigated with the reactants in the form both of separate pellets and of powder mixtures. As for the latter the thermogravimetric isothermal method was applied to equimolar reacting mixtures in the temperature range  $663^\circ - 755^\circ \text{C}$ .

Since the adopted kinetic equation requires a model consisting of uniform radius spheres of one reactant surrounded by smaller particles of the other reactant<sup>3</sup>, particular care was devoted to the preparation of mixtures of known form and size of the particles.

In order to characterize the mechanism, Wagner's method<sup>4</sup> was employed.

## Experimental

### a) Apparatus

TG and isothermal curves on powder mixtures were recorded by a Du Pont "950 Thermogravimetric Analyzer" joined with a "900 Differential Thermal Analyzer" (sample weight  $\sim 20 \text{ mg}$ ; sensitivity  $2.5 \text{ inch/mg}$ ; heating rate (for TG)  $3^\circ/\text{min}$ ).

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For measurements on pellets a tubular horizontal Heraeus furnace (controlled to  $\pm 1^\circ \text{C}$ ) was employed: a good contact between the pellets (inside a quartz tube) was accomplished by two platinum disks spring-pressed against the outer surfaces of the pellets through two nickel rods.

For X-ray diffraction experiments a Philips equipment was used.

### b) Materials and Procedure

**$\text{WO}_3$ :** X-ray analysis on a Koch-Light 99.9% product, prefired at  $800^\circ \text{C}$ , and ball-milled to an average size of the granules of  $\sim 1 \mu\text{m}$ , gave values of interplanar spacing which agreed with those by Gebert and Ackermann<sup>5</sup> for stoichiometric  $\text{WO}_3$ . A weight loss due to  $\text{WO}_3$  sublimation was detected by TG starting from  $800^\circ \text{C}$ . Pellets 8 mm wide and  $\sim 1.5 \text{ mm}$  thick were obtained by pressing  $\sim 400 \text{ mg}$  of the powder at  $10^3 \text{ kg/cm}^2$ , and then sintered by heating 5 h at  $800^\circ \text{C}$ .

$\text{SrCO}_3$  and  $\text{SrWO}_4$  pellets of the same size were also prepared at  $10^3 \text{ kg/cm}^2$ .

**$\text{SrCO}_3$ :** Spherulitic  $\text{SrCO}_3$  for TG and isothermal measurements was prepared by precipitation from solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{SrCl}_2$  (both C. Erba RP) in the presence of gelatine as suggested by Morse and Donnay<sup>6</sup>, prefired at  $750^\circ \text{C}$  for 5 h, and finally classified by sieving and by repeated sedimentation from an acetone suspension, thus isolating a fraction in which 80% of spherules was  $10 \pm 2 \mu\text{m}$  in diameter. A thermal decomposition of this sample was detectable by TG only from  $800^\circ \text{C}$  upwards: any weight loss revealed during the kinetic study (temperature range:  $663 - 755^\circ \text{C}$ ) may be therefore attributed to  $\text{CO}_2$  development in the reaction course.



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A Koch-Light 99.999% product (average granule size:  $\sim 1 \mu\text{m}$ ) was used for the preparation of  $\sim 200 \text{ mg}$  pellets, subsequently sintered (5 h at  $700^\circ\text{C}$ ).

**$\text{SrWO}_4$ :** A ROC/RIC 99.9% product was employed for  $\sim 300 \text{ mg}$  pellets, also sintered before use (5 h at  $750^\circ\text{C}$ ).

**Mixtures  $\text{WO}_3$ – $\text{SrCO}_3$  (1 : 1):**  $\text{WO}_3$  ( $1 \mu\text{m}$ ) and  $\text{SrCO}_3$  ( $10 \mu\text{m}$ ) were mixed by suspending both powders in acetone and then evaporating with stirring to dryness; thus avoiding the breaking of the rather brittle spherulites.

## Results and Discussion

### Measurements on pellets

Since preliminary X-ray analysis showed that in  $\text{WO}_3|\text{SrCO}_3$  couples held  $\sim 50 \text{ h}$  at  $700^\circ\text{C}$ – $800^\circ\text{C}$  the  $\text{Sr}_3\text{WO}_6$  compound<sup>7</sup> formation was detectable only when  $T > 760^\circ\text{C}$ , kinetic measurements were performed in the range  $700^\circ\text{C}$ – $750^\circ\text{C}$ . The reacted couples were easily separable into two distinct pieces: X-ray analysis of the surfaces showed that the produced  $\text{SrWO}_4$  adhered on the  $\text{SrCO}_3$  pellet only. Further, the latter, when cut parallel to the diffusion direction and subjected to microscopic observation, did not reveal a distinct separation line between the layers of the formed  $\text{SrWO}_4$  and  $\text{SrCO}_3$ . This prevented to study the reaction kinetics by measuring the thickness of the product layer.

To characterize the transport mechanism of the diffusing species, according to Wagner<sup>4</sup> two pellets of the product were sandwiched between those of the reactants and the weight changes due to reaction were evaluated.

In the present case, the sequence



was heated for 240 h at  $740^\circ\text{C}$ . The pellets weight changes (mg) of three runs, in all of which it was possible to separate the pellets without losses, are reported in Table 1, where the values in brackets are calculated from the amount of  $\text{SrWO}_4$  formed.

Table 1. Weight changes (mg) of the pellets (240 h,  $740^\circ\text{C}$ ).

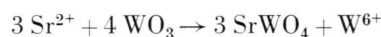
$\text{WO}_3$	$\text{SrWO}_4(\text{I})$	$\text{SrWO}_4(\text{II})$	$\text{SrCO}_3$
−4.2 (−1.9)	+1.8	+1.0	−2.5 (−1.2)
−4.1 (−1.5)	+1.5	+0.6	−2.0 (−0.9)
−3.8 (−1.8)	+1.7	+0.9	−2.3 (−1.1)

After separation, the contact surfaces of both pellets (I) and (II) with the reactants, as well as those of the reactants themselves, revealed by X-ray analysis their typical reflections only.

In all three runs the weight losses of  $\text{WO}_3$  and  $\text{SrCO}_3$  were larger than the calculated ones, the differences agreeing with the losses occurring when  $\text{WO}_3$  and  $\text{SrCO}_3$  pellets were heated separately for the same time and at the same temperature.

From the weight increase, occurring in both  $\text{SrWO}_4$  pellets, it is apparent that the process-governing mechanism is the cation counterdiffusion through the product layer.

Thence it can be deduced that the following reactions:



respectively occur at the interfaces  $\text{WO}_3|\text{SrWO}_4(\text{I})$  and  $\text{SrWO}_4(\text{II})|\text{SrCO}_3$ .

This reaction scheme requires that the ratio of the weight increases for pellets (I) and (II) should be 3. From the data in Table 1, a value of the ratio  $2.1 \pm 0.3$  is evaluated, which can be considered satisfactory if allowance is made of the fact that both  $\text{WO}_3$  sublimation<sup>8</sup> and  $\text{SrCO}_3$  decomposition are already effective at  $740^\circ\text{C}$ .

### Measurements on powders

Preliminary TG measurements on the 1 : 1 molar mixture (reasonably conforming to the model already described, since the surface of a sphere of  $10 \mu\text{m}$  diameter can be completely coated by 440 spheres of  $1 \mu\text{m}$ , whereas in the present case the ratio of the number of particles of  $\text{WO}_3$  to that of

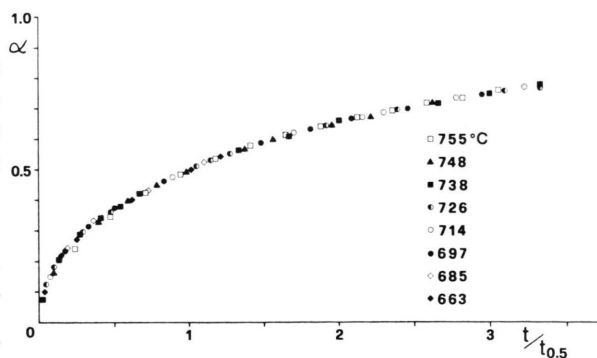


Fig. 1. Fraction reacted,  $\alpha$ , plotted vs. reduced time ( $t/t_{0.5}$ ) for 1 : 1  $\text{WO}_3$ – $\text{SrCO}_3$  mixture at various reaction temperatures.

$\text{SrCO}_3$  amounts to about 830) showed that the only solid reaction product is the normal tungstate in stoichiometric amount.

The experimental  $\alpha$  (ratios of the weight loss at time  $t$  to that at  $t = \infty$ ) are plotted in Fig. 1 for the different isothermal runs versus the reduced time  $t/t_{0.5}$  ( $t_{0.5}$  being the  $t$  value when  $\alpha = 0.5$ ). All the data can be fitted with a single curve, over the explored range of  $\alpha$ .

Since in the present case the mechanism based on cation counterdiffusion was shown to be effective by the experiments carried out according to Wagner's procedure, a suitable means for treating the experimental data was thought to be Dünwald-Wagner's equation<sup>3</sup>:

$$\alpha = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\{-n^2 K t\}$$

where  $K = \pi^2 D/R^2$ ;  $D$  = diffusion coefficient;  $R$  = radius of the coated spheres.

The above equation was originally proposed for the study of reactions between a solid phase formed with spherical particles of uniform radius and a gaseous phase, whenever the slowest step in the process is diffusion into or out of the solid particles. However, it was also commonly applied to solid-solid reactions and proved particularly useful in certain cases governed by cation counterdiffusion such as spinel formation reactions<sup>9</sup>.

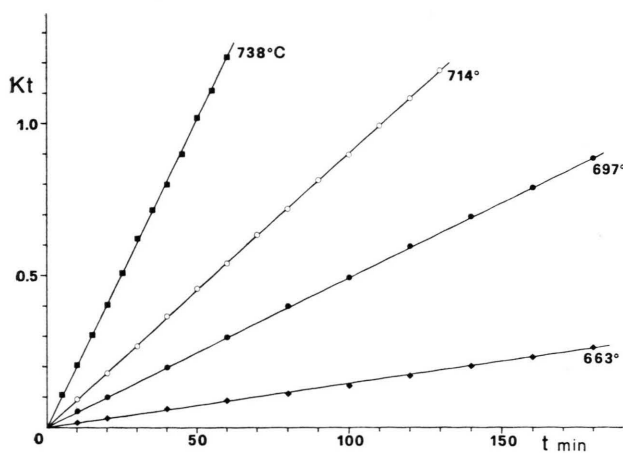


Fig. 2. Plots of  $Kt$  vs.  $t$  for some of the studied isotherms.

\* The values of  $Kt$  as a function of  $\alpha$  have been interpolated from those tabulated by Giess<sup>10</sup>.

Typical plots of  $Kt^*$  versus  $t$  for some of the isotherms studied are reported in Fig. 2: the experimental data satisfy Dünwald-Wagner's equation over the entire range studied. The same good fitting was observed with all the other isotherms.

Finally, Fig. 3 shows a straightline dependence of  $\log K$  on  $1/T$ , according to the equation

$$\log K = 13.45 - 69.994/4.576 T$$

where  $K$  is expressed in  $\text{min}^{-1}$ .

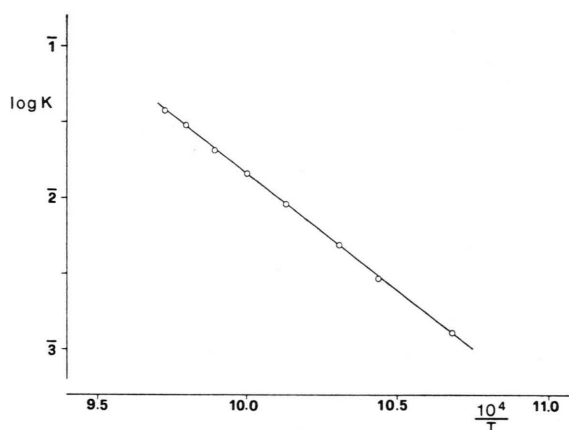


Fig. 3. Arrhenius plot for 1:1  $\text{WO}_3$ - $\text{SrCO}_3$  mixture.

Previous results<sup>1</sup> concerning the reaction of  $\text{MoO}_3$  with  $\text{SrCO}_3$  showed that the formation of  $\text{SrMoO}_4$  proceeds at a markedly lower temperature ( $412^\circ - 498^\circ \text{C}$ ) than is found in the present work for  $\text{SrWO}_4$ ; further, the formation of  $\text{SrMoO}_4$  is governed by the diffusion of a single species ( $\text{Mo}^{6+}$ )<sup>11</sup>, not by cation counterdiffusion.

Considering that  $\text{Mo}^{6+}$  and  $\text{W}^{6+}$  have the same value of the ionic radius ( $0.62 \text{ \AA}$ ), and that both  $\text{SrMoO}_4$  and  $\text{SrWO}_4$  have the same scheelite type structure with almost identical values of the cell volume ( $349.6$  and  $350.0 \text{ \AA}^3$ )<sup>12</sup>, it appears reasonable to emphasise the difference in the Tammann-temperatures of  $\text{MoO}_3$  ( $280^\circ \text{C}$ ) and  $\text{WO}_3$  ( $635^\circ \text{C}$ ). This might account for the much lower temperature range for  $\text{SrMoO}_4$  formation. On the other hand, at such lower temperature the  $\text{Sr}^{2+}$  ion would not possess a sufficient mobility (since the Tammann-temperature for  $\text{SrCO}_3$  is  $647^\circ \text{C}$ ) and therefore would not be allowed to take part as diffusing species in the reaction between  $\text{MoO}_3$  and  $\text{SrCO}_3$ .

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