JOURNAL OF SOLID STATE CHEMISTRY 35, 22–28 (1980)

Electrical Conductivity as a Method to Study Kinetics of Solid-State Reactions

JERZY HABER

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland

AND IRENA OKOŃSKA-KOZŁOWSKA

Institute of Physics, Silesian University, Katowice, Poland

Received August 9, 1979; in revised form November 6, 1979

A model for changes of electrical conductivity in the course of solid-state reaction has been demonstrated; it describes well the changes in the electrical conductivity of the reacting mixture ZnSe + Cr_2Se_3. The measurement method, the experimental data and the results calculated from the formulas derived in a previous publication have been presented. The experimental and theoretical curves of the temperature dependence of the electrical conductivity have similar shape. The theoretical values differ a little from the experimental ones. These differences allowed us to estimate the character of the changes of the concentration of defects in the product in the course of the reaction. Analysis of the assumptions and the application of the formulas previously presented was made.

Introduction

Measurements of electrical conductivity of the powder mixture of different reactants have been suggested many years ago as a method for studies of the mechanism and kinetics of solid-state reactions and applied to investigate the synthesis of complex oxides of the spinel type (*1–6*). In the sixties, however, strong criticism was raised due to complexity of parameters, determining the observed changes of the electrical conductivity and difficulties in the interpretation of the experimental data (*7*). More recently, interest in this method has been revived and it has been used to study the mechanism of the synthesis of complex sulfides and selenides (*8–13*). A correlation was established between the electrical conductivity of the reacting mixture and the degree of conversion. On the basis of the measurements of electrical conductivity at different rates of heating Lutz *et al.* (*10*) found that the characteristic points on different curves correspond to approximately the same degree of conversion. This enabled the kinetics of the reaction in this type of system to be determined (*10–12*).

In an attempt to find a more rigorous basis for the interpretation of these results one of the present authors has derived equations describing changes of the electrical conductivity in the course of solid-state reaction proceeding in a mixture of spherical partides of the reactants (*14*). It seemed of interest to check the validity of the model. The ZnSe + Cr_2Se_3 system was chosen for this purpose, because the elec-

0022-4596/80/130022-07$02.00/0

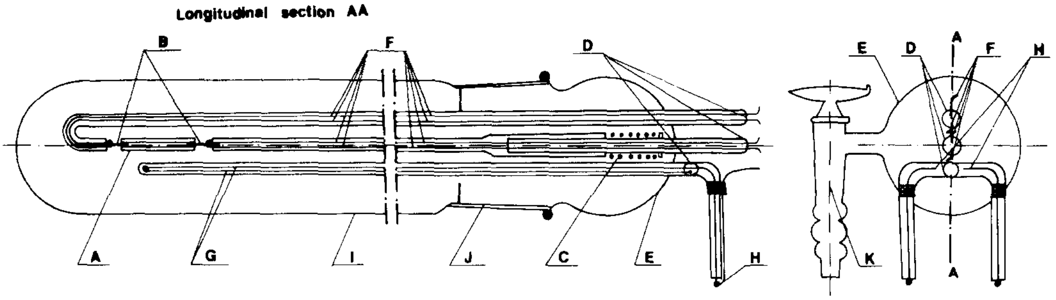

FIG. 1. The measurements ampoule: A—capillary with the sample, B—electrodes, C—spring, D—seals, E—quartz head, F—conductors, G—thermocouple, H—copper conductors, I—quartz ampoule, J—ground joint, K—stop cock.

trical conductivity of the product $ZnCr_2Se_4$ differs considerably from that of the substrate and large variations of the conductivity could be expected in the course of the reaction.

Experimental

Materials. ZnSe, Cr_2Se_3, and $ZnCr_2Se_4$ were synthesized from the elements by heating at 600–800°C in quartz ampoules, which were outgassed and sealed. The preparations were repeatedly heated and ground in an agate mortar. X-Ray powder analysis showed that all products contained only the synthesized phase. Mixtures of ZnSe and Cr_2Se_3 in the molar ratio 1 : 1 were then prepared for studies of the electrical conductivity in the course of the reaction.

Apparatus. The preparations were pressed into quartz capillaries (d = 0.65 mm, l = 25 mm), which were placed in the apparatus shown in Fig. 1. Two Pt–Ir 20% electrodes (B) of 0.5 mm diameter were pressed to the preparation (A) by a spring (C). Four Pt leads, as well as a Pt–PtRh10 thermocouple, were sealed through the quartz head. The head was linked to the quartz ampoule (I) by a ground joint (J). The stop cock (K) enabled outgassing of the ampoule, which was placed in a tubular furnace, driven by a temperature programmer to obtain linear increase of temperature at a given rate. Measurements of the electrical conductivity of substrates ZnSe and Cr_2S_3, product $ZnCr_2Se_4$, and the reacting mixture were carried out by the current–voltage method (Fig. 2). The XY_1Y_2 recorder Riken–Denshi D72B plotted current measured as a potential drop Y_1 on a standard resistance and potential drop Y_2 on the sample as functions of temperature, given by the EMF of the thermocouple.

Results

Figure 3 shows the changes of the electrical conductivity of the substrates ZnSe (curve 1) and Cr_2Se_3 (curve 2), the product $ZnCr_2Se_4$ (curve 3) as well as the reacting mixture on heating with a linear program at two different rates: 60°C/hr (curve 4) and

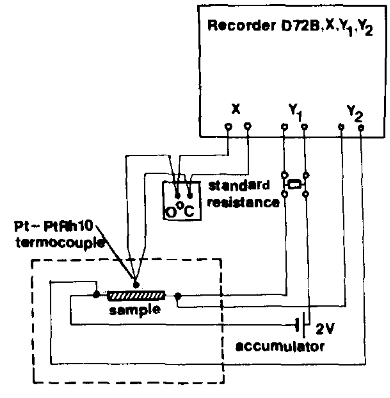

FIG. 2. The measurement system.

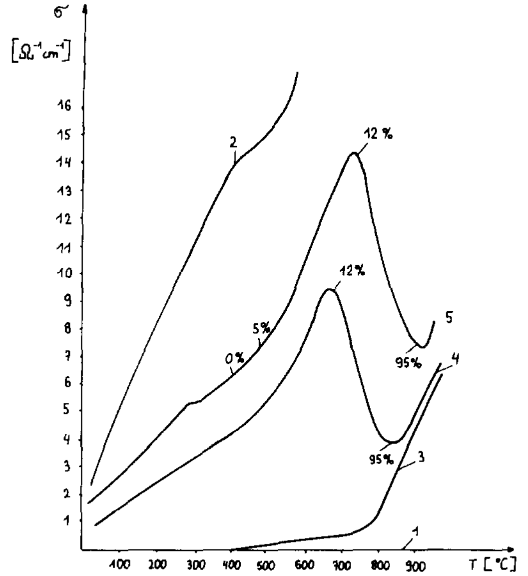

FIG. 3. The temperature dependence of the electrical conductivity with the linear increase of temperature at a given rate: (1) ZnSe—240°C/hr (2) Cr_2Se_3—240°C/hr (3) $ZnCr_2Se_4$—240°C/hr (4) ZnSe + Cr_2Se_3—60°C/hr (5) ZnSe + Cr_2Se_3—420°C/hr.

420°C/hr (curve 5). In some runs the measurements were stopped at certain temperatures and the composition of the samples was determined by X-ray analysis. The degree of conversion of the reacting mixture, corresponding to the characteristic points of the conductivity vs temperature curves, is given on Fig. 3. It may be seen that with the heating rate at 420°C/hr the degree of conversion at 400°C is still negligible, but at 470°C it amounts already to about 5%. The reaction starts at about 460°C. With increasing degree of conversion the intensity of the diffraction lines of the substrates decreases without noticeable changes of the relative intensities of ZnSe and Cr_2Se_3, whereas the intensity of the diffraction lines of the product increases. No other phases could be detected. Independent of the rate of heating of the reacting mixture, the degree of conversion corresponding to the maximum on the conductivity vs temperature curve amounts to 12%, whereas at the point of the minimum of this curve the reaction is practically complete, the degree of conversion amounting to 95%. Using the formulas derived by Lutz *et al.* (*10*), the activation energy was calculated from the shift of the maxima as being 62 kcal $mole^{-1}$ and, from the shift of the minima, 56 kcal $mole^{-1}$. The rate constant is $K = 1.1 \times 10^9 \text{ sec}^{-1}$.

The differential thermal analysis of the reacting mixture, carried out with the help of Linseis L-62 Thermoanalyser showed an exothermic peak (Fig. 4) corresponding to the maximum of the electrical conductivity. The enthalpy of formation of $ZnCr_2Se_4$ is very small and was estimated to be less than 3 kcal $mole^{-1}$.

Discussion of the Results

The temperature dependence of the conductivity of the reacting mixture of selenides may be divided into three ranges. In the first range, at temperatures below about 450°C, no reactions take place in the system and the conductivity of the reacting mixture is proportional to the conductivity of Cr_2Se_3. This follows from the general formula derived in (*14*), Eq. (34) taken for a nonreacting mixture, where $\alpha = 0, x = y =$

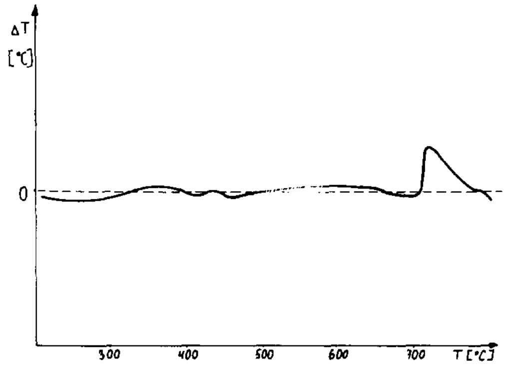

FIG. 4. The DTA diagram of the mixture: ZnSe + Cr_2Se_3.

$u = w = 1$:

$$\sigma = (1 + b)^{-2} [\sigma_B + 4b(\sigma_A^{-1} + \sigma_B^{-1})^{-1} + \sigma_A b^2]. \quad (1)$$

Taking into account that the conductivity of Cr_2Se_3 is about five orders of magnitude greater than the conductivity of ZnSe, $\sigma_A \ll \sigma_B$, formula (1) simplifies to

$$\sigma = (1 + b)^{-2}\sigma_B,$$

where b is the ratio of the molar volumes of ZnSe and Cr_2Se_3 and amounts to 0.436.

The second temperature range corresponds to the progressing reaction. With increasing degree of conversion the conductivity decreases due to formation of the layer of spinel, which has much lower conductivity. Taking the conductivity of spinel as given by curve 3 in Fig. 3, the value of the rate constant $K = 1.1 \times 10^9$ sec^{-1} and activation energy $E_A = 62$ kcal mole^{-1}, the theoretical dependence of the electrical conductivity of the reacting mixture on temperature was calculated on the basis of the formula [(*14*), Eq. (34)]

$$\sigma(\alpha, q, T) = \frac{\ln(2 - c/c)}{(1 + b)^2} \left(\frac{1}{B(\alpha, q, T)} + \frac{2b}{C(\alpha, q, T)} + \frac{b^2}{A(\alpha, q, T)}\right), \quad (2)$$

where q is the rate of heating, A, B, C describe the conductivities of the substrates and the product as defined in (*14*), and results of the calculations are compared with the experimental data in Figs. 5–7. It may be seen that the maxima of the conductivity appear on the theoretical curve at much smaller degrees of conversion than found experimentally. This may be due to the fact that the product formed at the interface in the course of the reaction contains a much greater concentration of defects and thus shows much higher conductivity than the well-crystallized product obtained from fully reacted mixture. In order to account for this difference a "defect function" $f(\sigma_S, T, q)$ was introduced

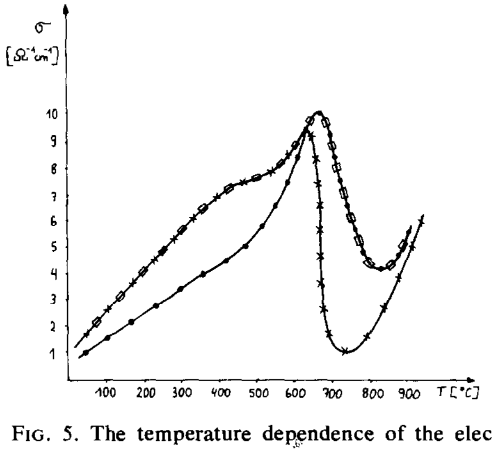

FIG. 5. The temperature dependence of the electrical conductivity (rate: 60°C/hr) of ZnSe + Cr_2Se_3, ●, the experimental data; ×, the theoretical curve without taking into account the "defect function"; □, the theoretical curve taking into account the "defect function."

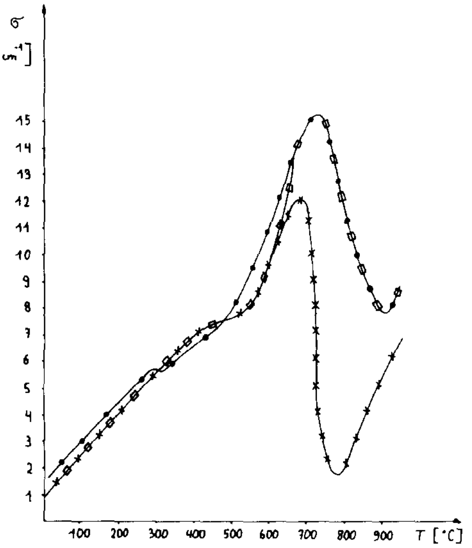

FIG. 6. The temperature dependence of the electrical conductivity (rate: 420°C/hr) of ZnSe + Cr_2Se_3 ●, the experimental data; ×, the theoretical curve without taking into account the "defect function"; □, the theoretical curve taking into account the "defect function."

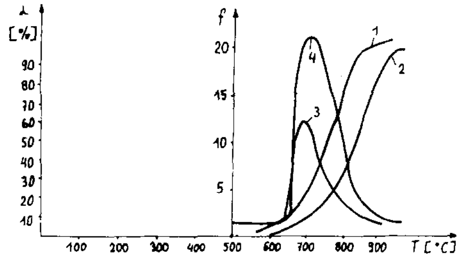

FIG. 7. The temperature dependence of the "calculated" degree of conversion: (1) $ZnSe + Cr_2Se_3$—60°C/hr, (2) $ZnSe + Cr_2Se_3$—420°C/hr. The temperature dependence of the "defect function": (3) $ZnSe + Cr_2Se_3$—60°C/hr, (4) $ZnSe + Cr_2Se_3$—420°C/hr.

into formula (2) and calculated by numerical adjustment. Results of these calculations are shown in Fig. 7.

Formula (2) describing the changes of conductivity in the course of a solid-state reaction was derived under the following assumptions:

1. Reaction in the powder mixture proceeds by counter diffusion of ions through the product layer formed at intergranular contacts. Only one product is formed.
2. The grains are spheres flattened at contacts.
3. The volume and shape of grains remain unchanged in the course of the reaction.
4. The distribution of the grains of the two reactants is statistical.
5. The electrical field within the grains is homogeneous. Surface conductivity, contact resistances, and the influence of various capacitances in the system are neglected.
6. The temperature increase is linear.

Formula (34) in (*14*) depends only on four parameters: average number of contacts per grain (J), the ratio of the height of the flattening part of the grain to its radius (c), rate constant of the reaction K_0, and its activation energy E_A, by formulas (17), (18), (19), in Ref. (*14*).

Assumption (1) is related to the type of reaction. Many results indicate that counterdiffusion is operating in the reactions of oxides (*15*), sulfides (*9*, *10*), and selenides (*16*). The remaining assumptions are due to approximations necessary in order to solve the problem analytically. In real systems, the grains have different shapes depending on the method of preparation. However, as the product of the reaction in the powder mixture is always isotropic, the best approximation seems to be spherical shape of reacting grains with intergranular contacts approximated by small flat surfaces. When the volume of the product formed on one type of grains is equal to that on the other type, the shape and volume of grains remain unchanged in the course of the reaction. When this condition is not fulfilled, the grains of one substrate increase and those of the other decrease. In the case of reactions of the type: $aA_nX_m + tB_pX_r \rightarrow A_{na}B_{pt}X_{ms+rt}$ the electroneutrality condition leads by counterdiffusion to equality of the ratio of the volumes of products formed on grains B_pX_r and A_nX_m to $(b\ r\ t/m\ s)$, where b is the ratio of the specific volumes of the substrates A_nX_m and B_pX_r. For $ZnSe + Cr_2Se_3 \rightarrow ZnCr_2Se_4$ the ratio of the volume of product formed on the Cr_2Se_3 grain to that on the ZnSe grain is equal to 1.308. Thus, if before the reaction the grains of both substrates had the same size, the ratio of their radii after the reaction would have been 1.09.

The changes of the shape and size of grains may be also caused by recrystallization of both the substrates (*5*, *9*, *10*) and the product. However, the resulting changes of conductivity would not contribute to a more serious deviation from the value given by formula (2) because

—the formula does not contain any function of the grain radii;

—the values of conductivities of substrates and product used for calculations are taken from experiment, i.e., include the recrystallization effects;

—although the recrystallization effects

are accounted for in excess by taking for calculation the value of the well-crystallized product instead of highly defected layer formed in the course of the reaction, this is compensated by the "defect function";

—on heating the reaction mixture with a linear program the recrystallization processes can usually be neglected in comparison with the reaction itself.

Although in the model the additional contact resistances and surface conductivity of grains are not directly considered, they are indirectly included through the experimental values of the conductivities of substrates and product. The capacitances do not play any role in case of dc measurements (*9–13*), and in the frequency range of 50–10^5 Hz their influence is negligible (*2*) and only a slight increase of conductivity is observed without any change of its temperature dependence.

The number of intergranular contacts (J) appears only in the kinetic equation (*14*). It is difficult to estimate and may vary from 6 in loosely packed powder to 12 in a closed-packed arrangement. It follows from the derived equations that the number of grains N in a unit volume and their radius r have no influence on the electrical conductivity of the mixture when the latter has the same degree of compression as the substrates and the product, conductivities of which have been used for calculation. For grains with shape of cut spheres the degree of compression may change for $J = 6$ from 0.52 to 0.965 when c varies from 0 to 0.293, and for $J = 12$ from 0.74 to 0.964 on variation of c in the range 0–0.134. In the case of larger c the equations are no longer applicable.

As seen from Fig. 7, the concentration of defects in the product layer at first rapidly increases, passes through a maximum and then decreases. Thus, the assumption made in many studies (*17*) that the concentrations of defects at both interfaces of the product layer are fixed and their gradient in the layer is decreasing, is not always valid in the description of the electric conductivity, although it may lead to adequate kinetic results (*17*). The appearance of new interfaces in the first stage of the formation of the product phase may result in great changes of the conductivity. This highly defected region may constitute the main path for the current and determine the conductivity of the mixture. The compact layer of product is formed only after a certain degree of conversion had been attained. Ordering of the lattice is taking place as is reflected in the decrease of the "defect function" resulting in decrease of the conductivity.

References

1. D. J. Bevan and J. F. Anderson, *Discuss. Faraday Soc.*, **8**, 238 (1950).
2. A. Bielański, J., Dereń, J. Haber, and E. Polaczkowa, *Z. Anorg. Allg. Chem.* **294**, 269 (1958).
3. A. Bielański, J. Dereń, and Z. Barutowicz, *Z. Anorg. Allg. Chem.* **305**, 169 (1960).
4. A. Bielański, J. Dereń, and E. Duczymińska, *Z. Anorg. Allg. Chem.* **316**, 75 (1962).
5. Z. G. Szabo and F. Solymosi, *Z. Anorg. Allg. Chem.* **301**, 225 (1959).
6. A. N. Coop, M. Nakahira, and G. W. Brindley, *J. Electrochem. Soc.* **113**, 237 (1966).
7. J. Dereń and J. Haber, *J. Electrochem. Soc.* **113**, 1349 (1966).
8. H. D. Lutz, *Z. Anorg. Allg. Chem.* **348**, 30 (1966).
9. H. D. Lutz, H. J. Scholz, and H. Randolph, *Z. Anorg. Allg. Chem.* **378**, 291 (1970).
10. H. D. Lutz, H. Randolph, G. P. Görler, and H. J. Scholz, *Z. Anorg. Allg. Chem.* **390**, 41 (1972).
11. I. Okońska-Kozłowska, J. Heimann, and A. Chełkowski, *Z. Anorg. Allg. Chem.* **407**, 109 (1974).
12. I. Okońska-Kozłowska and J. Heimann, *Z. Anorg. Allg. Chem.* **447**, 230 (1978).
13. I. Okońska-Kozłowska and J. Krok, *Z. Anorg. Allg. Chem.* **447**, 235 (1978).

14. I. Okońska-Kozłowska, *J. Solid State Chem.* **31,** 1 (1979).

15. J. S. Armijo, *Oxid. Met.* **1,** 171 (1969).

16. I. Okońska-Kozłowska, *in* "The Study of the Mechanism of Solid State Formation of Spinels with the VI Group Elements," Silesian University Press, Katowice, Poland (1978). [in Polish]

17. J. Dereń, J. Haber, and R. Pampuch, "Solid State Chemistry," PWN Press, Warszawa, Poland (1975). [in Polish]