536. *Effect of Defect Structure on the Rate of Formation of Spinels.**

By F. Solymosi and Z. G. Szabó.

The effect of electronic and ionic-defect structure on the rate of formation of nickel ferrite spinel was investigated; the reaction was followed by magnetic analysis. Nickel oxide was doped with small amounts of lithium and chromic oxides, and ferric oxide with titanium dioxide. The addition of foreign ions markedly influences the rate of formation of the spinel, especially in the case of nickel oxide doped with chromic oxide. The variation of electrical resistance of these mixed oxides during formation of spinel was also studied.

The rate of reaction between two solid phases is governed by migration of the reactants, which in turn depends on the structure of the reacting crystals or crystallites. Features such as lattice defects and vacant sites promote the migration and thus increase the reaction rate. In this respect the Hedvall effect is an extreme case as the disorder is greatest during lattice transition.

The defect structure in crystals can be changed to a large extent by pretreatment or by doping with foreign ions. Thus it may be expected that the rate of reaction between two solids depends on doping as well as on the morphology of the initial substances. The influence of foreign ions on this rate permits them to be considered as catalysts, since they remain more or less unchanged at the end of the process.

Solid-phase reactions play a major part in the preparation of contact catalysts, consisting of mixtures of oxides, in which the first of several processes occurring is the formation of spinels. We have postulated, on the basis of electrical conductivity measurements, the nature of the catalytic activity and origin of the intermediate states formed during spinel formation.[1] The optimum catalytic activity was to be attributed to a certain state

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[1] Szabó and Solymosi, *Z. Elektrochem.*, 1959, **63**, 1177.

of the solid system, determined by exactly described parameters. The permanence of this optimum state depends both on the conditions of formation and the mechanism of further reaction. The best contact substance is obtained when the optimum catalysing system has been formed under conditions in which the further reaction is negligibly small.

In our experiments the problem of rates of reaction in solid phases has been investigated with mixed oxides of varied composition (*i.e.* with known " Fehlordnung "), with special emphasis on spinel formation. The only analogous investigations are those of Schwab and Rau.[2] The rates of solid-phase reactions are generally difficult to determine. In our experiments the formation of nickel ferrite from nickel oxide and ferric oxide was chosen, since the reaction can be followed by measurement of the magnetic susceptibility, because of the strong ferromagnetic properties of the nickel ferrite formed. The magnetic properties of this spinel and the effect of different gases on the reaction rate have been investigated by Forestier and his co-workers.[3] Electrical conductivity gives a qualitative picture of the possible intermediate states formed during the reaction, so it has also been investigated as a function of the sintering temperature.

EXPERIMENTAL

The nickel oxide was pretreated by heating it in air for 5 hr. at 1000—1050°, and the standardized properties were controlled by electrical-conductivity measurements. Pellets were prepared from nickel and ferric oxides in the proportion 1 : 1, and were sintered for 5 hr. at different temperatures. The sintered product was cooled quickly in order to freeze-in the intermediate states formed. The electrical conductivity of these pellets was then examined at different temperatures. At temperatures below 300° the conductivity soon reached a steady value, while at higher temperatures a longer time was required, but this value was reproducible and remained unchanged by further heating. From these data a value of E, the activation energy of electrical conductivity, was obtained. Figs. 1 and 2 illustrate these results. Both the resistance and activation energies show maxima at a sintering temperature of 700° for lower-temperature, and at a sintering temperature of 800° for higher-temperature measurements.

FIG. 1. *Resistance of mixed oxides at 250°, and the activation energy of conductivity as a function of the reaction temperature.*

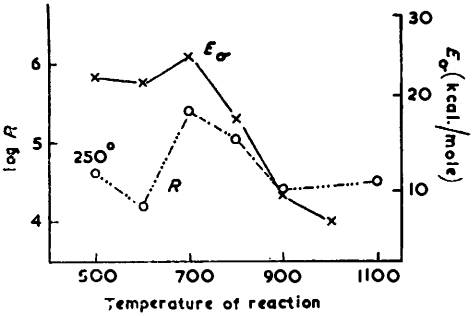
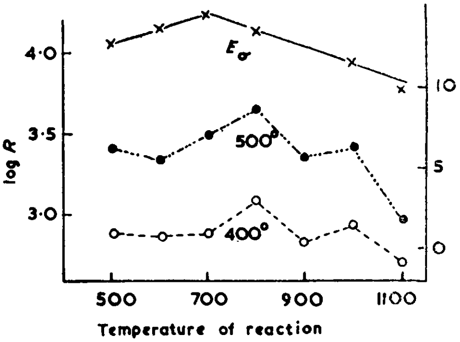


FIG. 2. *Resistance of mixed oxides at 400° and 500°, and the activation energy of conductivity as a function of the reaction temperature.*



Magnetic susceptibility and X-ray diffraction investigations were performed to interpret this behaviour. The magnetic susceptibility measurements were made by Gouy's method and the values at two different field strengths are shown in Fig. 3. These values indicate that spinel formation begins at 650—700°, whereas the less sensitive method by X-ray powder photograph first detected nickel ferrite lines at 750°. From these measurements we can state that at the beginning of spinel formation an intermediate state with special properties appears.

The nature of this intermediate state was clarified by experiments carried out at different

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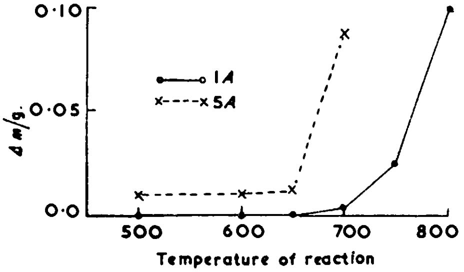
[2] Schwab and Rau, *Z. phys. Chem. (Frankfurt)*, 1956, **9**, 127; 1958, **17**, 257.

[3] Forestier and Kiehl, *J. Chim. phys.*, 1950, **47**, 165; *Compt. rend.*, 1949, **229**, 47; Forestier and Haasser, *Compt. rend.*, 1947, **225**, 188.

partial pressures of oxygen. Before spinel formation, the conductivity of the mixed oxides increases with the partial pressure of oxygen, while after spinel formation the conductivity changes inversely with the partial pressure of oxygen. However, at 700° the conductivity changes from the defect conductivity of mixed oxides to the electron conductivity of spinels, with the resulting maxima of resistance and activation energy already noted.

FIG. 3. *Changes in magnetic susceptibility expressed as the increase of weight related to* 1 *g. of substance as a function of reaction temperature. Time of reaction*: 5 *hr.*



The rate of reaction of the solid phase can be estimated from the changes in magnetic susceptibility. One hour's sintering produced a change of only —0·05—1·0%; thus only a surface reaction has occurred.

In addition to these pure oxide mixtures, doped oxides have been investigated. The conductivity was increased by addition of lithium oxide to nickel oxide, but decreased by addition of chromium(III) oxide, in accordance with the *p*-conducting character of nickel oxide. The doped oxides were sintered separately for 5 hr. at 850—900°, mixed in equal proportions in a ball mill for several hours and then heated for 1 hr. After the reaction the mixture was powdered in an agate mortar and the susceptibility determined in a glass tube (3 mm. diam.).

The data obtained are shown in Fig. 4 and are averages of four readings, obtained by use of two sensitivities together with a reversal of current.

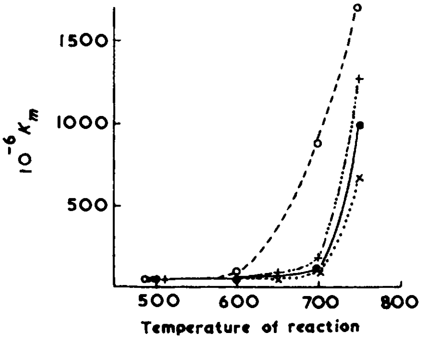


FIG. 4. *Changes in magnetic susceptibility at* 5A *as a function of temperature. Time of reaction*: 1 *hr.*

———— $NiO–Fe_2O_3$.
········ $NiO–Fe_2O_3 + 1\%\ TiO_2$.
------ $NiO + 1\%\ Cr_2O_3–Fe_2O_3$.
··—·· $NiO + 1\%\ Li_2O–Fe_2O_3$.

Mixtures containing nickel oxide doped with lithium and chromic oxides show a considerable increase in susceptibility over pure mixed oxide mixtures, even after 1 hr. On the other hand, addition of titanium dioxide to ferric oxide reduces the susceptibility. Thus doping by chromic oxide represents a catalysed reaction, and by titanium dioxide an inhibited reaction.

Fig. 5 shows the rate data in detail, but the ordinate plotted here is the weight increase related to 1 g. of the mixture.

The increase in the weight of the mixture can be considered as the reaction rate. Satisfactory linear functions can be obtained by plotting the logarithms of these values against $1/T$ between 700° and 800°.

From these relations the following apparent activation energies have been calculated:

$NiO–Fe_2O_3$, 95·9; $NiO + 1\%Li_2O–Fe_2O_3$, 80·0;
$NiO + 1\%Cr_2O_3–Fe_2O_3$, 59·4; and $NiO–Fe_2O_3 + 1\%TiO_2$, 132·3 kcal./mole.

These values are in good agreement with those of Schwab and Rau [2] (58—82 kcal./mole) and of Hopkins [4] (57, 102 kcal./mole) for the reaction of zinc oxide and ferric oxide.

FIG. 5. *Changes in magnetic susceptibility at* 1A *expressed as the increase of weight related to* 1 *g. of substance as a function of reaction temperature. Time of reaction*: 1 *hr.*

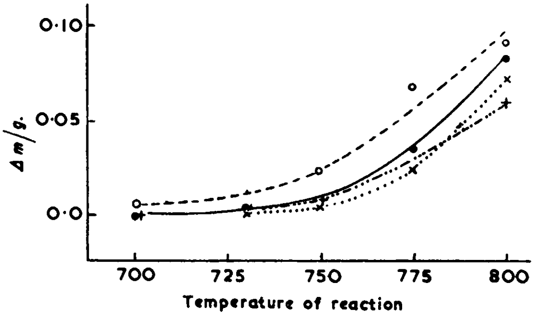
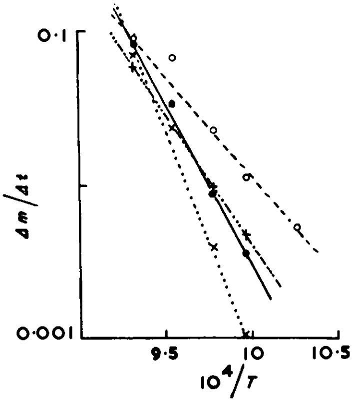


FIG. 6. *Logarithm of weight increase related to* 1 *g. of substance as a function of* 1/T.



——— $NiO-Fe_2O_3$. ········· $NiO-Fe_2O_3 + 1\% TiO_2$. – – – – – – $NiO + 1\% Cr_2O_3-Fe_2O_3$.
··—·· $NiO + 1\% Li_2O-Fe_2O_3$.

DISCUSSION

The results obtained can be interpreted in the light of the " Fehlordnung " theory. The decrease in the rate of reaction on doping ferric oxide with titanium dioxide is probably due to the formation of ferrous ions. Verwey and his associates [5] have concluded, from conductivity measurements, that iron(II) ions are formed and that the larger diameter of these ions reduces their mobility and consequently their rate of diffusion.

According to Wagner and Hauffe's theory the product of the concentrations of the vacant nickel sites and the defect electrons is constant under a constant pressure of oxygen. This explains the effect of chromium(III) oxide on nickel oxide, when the conductivity decreases, *i.e.*, the concentration of defect electrons decreases and so the number of vacant sites increases. Thus, both the diffusion and consequent rate of reaction are increased.

Doping with lithium oxide results in the formation of Ni^{3+} ions in the nickel oxide lattice, and the greater mobility of these increases the reaction rate.[2]

Summarizing, we can say that in the nickel oxide–ferric oxide system, the rate of spinel formation depends on the defect structure of the initial substances. When the defect structure of these is altered by doping a catalytic or inhibiting effect on the reaction rate is observed.

UNIVERSITY OF SZEGED, INSTITUTE FOR INORGANIC AND ANALYTICAL CHEMISTRY,
SZEGED, HUNGARY.
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[4] Hopkins, *J. Electrochem. Soc.*, 1949, **96**, 195.
[5] Verwey, Haayman, and Romeyn, *Chem. Weekblad*, 1948, **44**, 705.