The Solid State Displacement Reaction $CsCl + NaI \rightarrow CsI + NaCl$

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The solid state reaction $CsCl + NaI \rightarrow CsI + NaCl$ was investigated, employing diffusion couples with two different contents of divalent cation impurities, in the temperature range 350–419 °C.

From kinetic determinations, inert marker experiments and X-ray diffraction analysis it was possible to deduce that the rate — determining step is the diffusion of I^- in CsI via $V_I^{\cdot}$.

Possible characteristics of solid state reactions of the type $AX + BY \rightarrow AY + BX$ are manifold, depending on the ionic mobilities and the mutual solubilities of the components[1], but our present knowledge comes only from Wagner's work[2] on the reaction $AgCl + NaI \rightarrow AgI + NaCl$, in which the cations are faster than the anions and solid solutions of AgCl and NaCl are formed over the whole concentration range. In the present work the process $CsCl + NaI \rightarrow CsI + NaCl$ has been studied, which is the mathematical reaction in the reciprocal ternary system Cs, Na/Cl, I[3], characterized by two eutectics at 433 and 420 °C.

The thermodynamic, transport and structural properties of the four components are well-known: this allows to deduce the reaction mechanism and to independently evaluate the rate constants.

The kinetic process was investigated by the diffusion couple method[4] in the temperature range 350 – 419 °C, using pellets of reagents containing about 30 ppm of total divalent cation impurities in the first set of measurements (the starting materials were Merck "suprapur" CsCl and NaI) and about 600 ppm in the second set. The latter concentration was obtained by doping the starting CsCl with $CaCl_2$.

The results are plotted in Fig. 1 as x^2 (x = average thickness of the product layer as measured microscopically) vs. t (time): apparently the process rate is not influenced by the content of divalent cation impurities.

The product layer growth satisfactorily fits the parabolic law $x^2 = 2\,k\,t$ (k = reaction rate constant); the $\log k$ values show a linear dependence on $1/T$ according to the equation

$$\log k = -0.55 - 26{,}825/4.576\,T$$

were k is in $cm^2\,sec^{-1}$ and T in K.

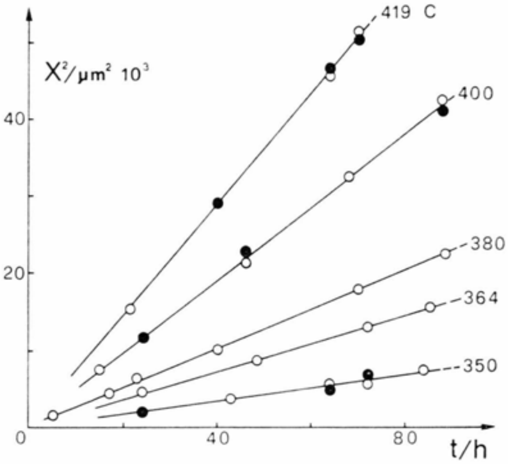

Fig. 1. Isotherms for the reaction $CsCl + NaI \rightarrow CsI + NaCl$. Open circles: reagents with ~30 ppm of divalent cation impurities; filled circles ~600 ppm.

Information on the reaction mechanism was obtained by the inert marker method (Pt wires) and by X-ray diffraction measurements.

A typical result of a marker experiment carried out at 400 °C for 46 *h* (product layer thickness about 140 microns) is shown in Fig. 2 a; the fact that the Pt wires lie at the interface NaI | Products means that the transport mechanism involves the diffusion of Na^+ and I^- through the product layer.

The diffraction measurements were performed on a diffusion couple submitted to the same thermal

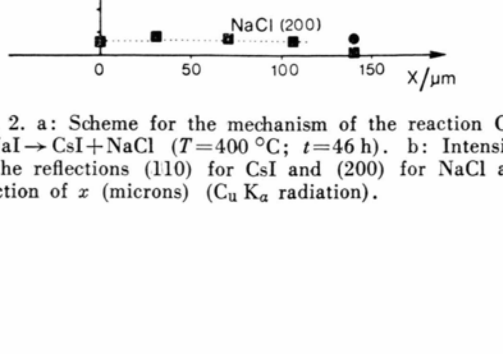

Fig. 2. a: Scheme for the mechanism of the reaction $CsCl + NaI \rightarrow CsI + NaCl$ (T=400 °C; t=46 h). b: Intensities of the reflections (110) for CsI and (200) for NaCl as a function of x (microns) ($C_u\ K_\alpha$ radiation).

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treatment, on surfaces (obtained by progressively grinding off product layers of 35 μm average thickness) parallel to the interface NaI | Products.

The trend of the most intense reflections of CsI and NaCl, (110) and (200) respectively, as a function of the distance from the interface is reported in Figure 2 b.

The observed intensity ratio, about 7, is far from the value 1.15 which would result from the ratio of the squares of the structure factors. This is not easy to explain: so far it is only possible to say that it cannot be due to an oriented growth of both products, since for each of them the relative intensities of significant reflections were found to be in agreement with those reported in the corresponding ASTM "identification cards".

From the kinetic constants, by the application of Wagner[5] and Schmalzried[1, 6] theory, the average values of the diffusion coefficient, $\bar{D}$, of the rate-determining ion in the product layer were calculated and plotted in Figure 3. They follow the equation

$$\log \bar{D} = -1.05 - 1.17/k\,T\,.$$

The results obtained with marker experiments (see Fig. 2) suggest that the reaction progress is due to the diffusion of I^- and Na^+ through the product layer.

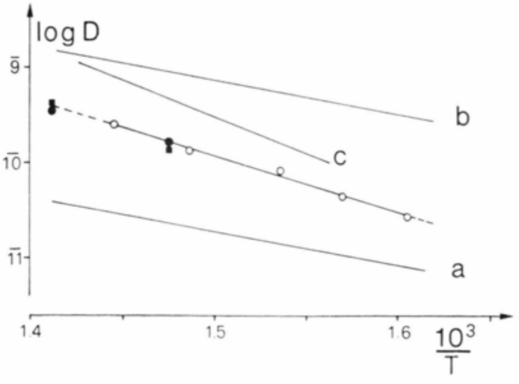

Fig. 3. Arrhenius plots. Open circles: $\bar{D}$ values as obtained by kinetic measurements; filled circles: D_{I^-} in CsI single crystals[9]; filled squares: D_{I^-} in CsI polycrystalline samples[9]; a: D_{Na^+} in NaCl with a molar fraction of divalent cations $c \sim 0.15 \cdot 10^{-4}$; b: D_{Na^+} in NaCl with $c \sim 6.0 \cdot 10^{-4}$; c: D_{Na^+} in CsI[10].

In order to individuate the rate-determining ion, several diffusion coefficients have been plotted in Fig. 3. Curves a and b show calculated trends of the diffusion coefficient of Na^+ in NaCl for two divalent cation impurity concentrations. Since in the considered temperature range NaCl is far from the intrinsic region, the D_{Na^+} values were evaluated by the equation[7]

$$D_{Na^+} = 4\,\nu_{Na^+}\,a^2\,f\,x_{Na^+}\,\exp\{-\Delta g_{Na^+}/k\,T\}\ {}^*$$

where ν_{Na^+} vibrational frequency,
a cation-anion separation distance,
f correlation factor (0.7815),
Δg_{Na^+} free energy of V'_{Na} migration,
x_{Na^+} molar fraction of V'_{Na^+} on the cation sublattice.

Curve c shows the trend of D_{Na^+} as measured in the CsI compound[10].

Figure 3 also shows our $\bar{D}$ values and some values of D_{I^-} obtained by Klotsman et al.[9] for single crystals and polycrystalline samples of CsI; for this compound the doping influence may be considered as negligible both because the solubility of the divalent ions in CsI is very low[8] and, above all, because the latter iodide, in the temperature range 350 – 419 °C, is well inside its intrinsic region.

From Fig. 3 the diffusion coefficients of I^- in CsI appear to be in good agreement with $\bar{D}$. Since the experimental rate constants are practically independent of the divalent impurity concentration (see Fig. 1), Na^+ diffusion in NaCl cannot represent the rate-determining step of the reaction. On the basis of D_{Na^+} in CsI (see Fig. 3 c) it seems evident, on the other hand that Na^+ is transported in this compound, at least for low impurity concentrations.

One thus arrives at the conclusion that the rate-determining step is the diffusion of I^- in CsI via $V_I^{\cdot}$: this conclusion is supported also by comparing the activation energies for the reaction (1.17 eV) and for the migration, in the intrinsic field, of $V_I^{\cdot}$ in CsI (1.20 eV)[8].

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[*] The numerical values of ν_{Na^+}, a and Δg_{Na^+} were taken from Nadler and Rossel[8]; x_{Na^+} was considered equal to the divalent cation impurities concentration c: the latter in turn is put equal to the concentration of the divalent impurities present in the reagents and soluble in NaCl (cf. Figure 3 a, b).

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