Notizen

Kinetics and Mechanism of MAg_4I_5 Formation in the Solid-State Reactions Between β-AgI and MI (M = K, Rb, NH_4)

Giorgio Flor, Vincenzo Massarotti, and Riccardo Riccardi

Centro di Studio per la Termodinamica ed Elettrochimica dei Sistemi Salini Fusi e Solidi del C.N.R., c/o Istituto di Chimica Fisica dell'Università, Pavia, Italy

(Z. Naturforsch. **30 a**, 909–910 [1975]; received May 27, 1975)

The kinetics of MAg_4I_5 (M=K, Rb, NH_4) formation from β-AgI and MI are investigated on pellets by the contact method.

For all the three reactions involved, the governing mechanism is found to be the cation counter-diffusion while the rate-determining step is the diffusion of M^+.

On the basis of Wagner's theory the self-diffusion coefficients of K^+, Rb^+ and NH_4^+ are evaluated in the three compounds.

The high-conductivity solid electrolytes MAg_4I_5 (M = K, Rb, NH_4) may be prepared by the solid-state reaction

$$4\,AgI + MI \rightarrow MAg_4I_5\,.$$

The present kinetic study reports on the formation of these compounds from β-AgI and MI, in the temperature range 46 – 141 °C. Couples of reagent pellets were used and the thickness of the product layer was measured by optical microscopy.

From the rate constants of the three reactions considered it was possible, on the basis of Wagner's [1] and Schmalzried's [2] classical treatment of solid-state reactions, to evaluate the self-diffusion coefficients of K^+, Rb^+, NH_4^+ in the corresponding compounds.

As regards the kinetics of KAg_4I_5 and $RbAg_4I_5$ formation, previous results by Bradley and Greene [3] are known: these authors, however, restricted the study for the temperature range 110 – 133 °C to an initial stage where a constant growth rate of the product could be observed.

Fluka "puriss." materials were used. AgI (originally γ) was transformed in the stable β form by melting and slow cooling to room temperature [4]. Apparatus and techniques were described in previous works [5].

Reprint requests to Prof. R. Riccardi, Istituto di Chimica Fisica dell'Università, Viale Taramelli, 16. *I-27100 Pavia* (Italy).

Results and Discussion

From marker experiments on the diffusion couples AgI | MI at $100 < t < 140$ °C, it was observed that the marker position always divided the product layer about in a 4:1 ratio. X-ray analysis on the finely powdered products and on the product surfaces in contact with MI and AgI did show only reflections from the compounds MAg_4I_5 [6], in agreement with what observed by Bradley and Greene for (K, Rb)Ag_4I_5 [3].

Therefore, the formation of the three compounds is governed by the cation counter-diffusion mechanism according to the reaction scheme

$$Ag^+ + 5/4\,MI \rightarrow 1/4\,MAg_4I_5 + M^+\,,$$
$$M^+ + 5\,AgI \rightarrow MAg_4I_5 + Ag^+\,.$$

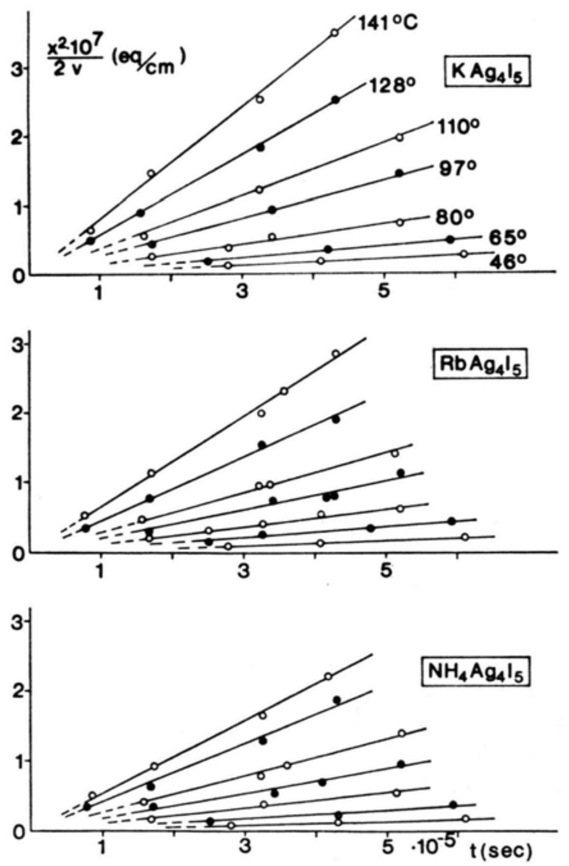

Fig. 1. Isotherms for the reaction $4\,AgI + MI \rightarrow MAg_4I_5$. The v values for KAg_4I_5, $RbAg_4I_5$ and $NH_4Ag_4I_5$ formation are 259.7, 267.7, 264.2 $cm^3\,eq^{-1}$ respectively.

Previous works[7] on these compounds showed that the current is carried almost entirely by Ag^+, the transport numbers of M^+ being of the order of 10^{-7} and that of I^- even smaller[6].

The above information allows to deduce that the rate-determining step is the diffusion of K^+, Rb^+ and NH_4^+ in the respective product layer.

For KAg_4I_5, $RbAg_4I_5$ and $NH_4Ag_4I_5$ the formation kinetics measurements in the temperature range $46-141$ °C (see Fig. 1) proved that the product layer growth follows the well known parabolic law[2]

$$x^2/2\,v = k\,t$$

where x = thickness of the product layer at time t, v = volume increase of the reaction layer caused by transfer of one equivalent, k = reaction rate constant.

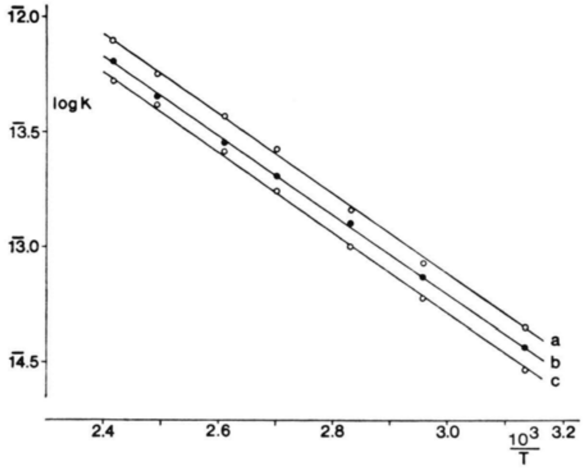

Fig. 2. Arrhenius plots for KAg_4I_5 (a), $RbAg_4I_5$ (b), $NH_4Ag_4I_5$ (c) formation.

Figure 2 shows a straightline dependence of $\log k$ on $1/T$ for the three reactions according to the equations

for KAg_4I_5: $$\log k = -7.87 - 1750/T\,, \qquad (1)$$

for $RbAg_4I_5$: $$\log k = -8.08 - 1706/T\,, \qquad (2)$$

for $NH_4Ag_4I_5$: $$\log k = -7.96 - 1779/T \qquad (3)$$

where k is expressed in eq $cm^{-1}\,sec^{-1}$.

Average values of the self-diffusion coefficients for the rate-determining ions ($\bar{D}_{M^+}$) can be obtained by the equation[2]

$$\bar{D}_{M^+} = 4/5\,k\,R\,T/(c_{M^+}\,|\Delta G^0|)$$

where c_{M^+} is the equivalent concentration of M^+ in the reaction product and ΔG^0 is the standard free energy of the considered reaction *.

For Rb^+, the following relation

$$\log \bar{D}_{Rb^+} = -6.65 - 1549/T$$

is found, whereas for K^+ and NH_4^+, only the $\bar{D}_{M^+}$ values at 25 °C can be deduced using k values calculated by Eq. (1) and (3) respectively, if one assumes their validity at this temperature.

The $\bar{D}_{M^+}$ and t_{M^+} (transport number) values at 25 °C for K^+, Rb^+ and NH_4^+, reported in Table 1, show the expected trend. The t_{M^+} values were obtained through the Nernst-Einstein equation employing for all the three compounds the electrical conductivity value of 0.26 $ohm^{-1}\,cm^{-1}$ (see[10]).

Table 1.

Cations	$\bar{D}_{M^+}\cdot 10^{12}$ ($cm^2\,sec^{-1}$)	$t_{M^+}\cdot 10^7$
K^+	18.4	12.5
NH_4^+	3.0	2.0
Rb^+	1.5	1.0

As concerns $RbAg_4I_5$, the D_{Rb^+} mean value (Table 1) is much lower than that of Ag^+ in the same compound ($2.6\cdot 10^{-6}\,cm^2\,sec^{-1}$ at 25 °C[11]): this remark is once more consistent with the assumption that Rb^+ is the rate-determining ion.

* For $RbAg_4I_5$[8], ΔG^0 (kcal/mole) $= -0.87 - 0.0092\ (T273)$; for $NH_4Ag_4I_5$[8], $\Delta G^0_{298} = -0.4$ kcal/mole; for KAg_4I_5 the value estimated at 25 °C ($\Delta G^0 = -0.1$ kcal/mole) is deduced from the standard free energies of formation from the elements for KAg_4I_5[8], β-AgI and KI[9].

1 C. Wagner, Z. phys. Chem. **B 34**, 309 [1936].
2 H. Schmalzried, Z. physik. Chem. N.F. **33**, 111 [1962].
3 J. N. Bradley and P. D. Greene, Trans. Faraday Soc. **63**, 1023 [1967].
4 T. Takahashi, K. Kuwabara, and O. Yamamoto, J. Electrochem. Soc. **116**, 357 [1969].
5 G. Flor, V. Massarotti, and R. Riccardi, Z. Naturforsch. **29 a**, 503 [1974]. — G. Flor, V. Massarotti, and R. Riccardi, Z. Naturforsch. **30 a**, 304 [1975].
6 J. N. Bradley and P. D. Greene, Trans. Faraday Soc. **63**, 2516 [1967].
7 B. B. Owens, "Solid Electrolyte Batteries" in Advances in Electrochemistry and Electrochemical Engineering. Vol. 8. Ed. C. W. Tobias, J. Wiley and Sons Inc., New York 1971, p. 36.
8 L. E. Topol and B. B. Owens, J. Phys. Chem. **72**, 2106 [1968].
9 "Selected Values of Chemical Thermodynamic Properties" NBS Circular 500 (1952).
10 See Ref. 7, pp. 32, 33.
11 G. G. Bentle, J. Appl. Phys. **39**, 4036 [1968].