CONCENTRATION DISTRIBUTION IN CONTACT MELTING IN NITRATE—NITRITE SYSTEMS

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The concentration distributions have been determined in contact melting in nitrate—nitrite systems from theory and experiment.

Contact crystal melting has been widely used [1] to produce mixtures with given concentrations and also to examine heat and mass transfer. The melting may occur under kinetic conditions, when the thickness of the liquid phase is minimal and the rate is determined by the dissolution kinetics [2], or under diffusion-limited conditions, where the kinetics may be determined by the component diffusion in the liquid [3]. Two forms of diffusion-limited condition are distinguished: nonstationary diffusion, where the thickness of the liquid phase increases with time in accordance with the laws of diffusion, and stationary diffusion, where the thickness of the liquid phase is kept constant. Various papers [2-5] deal with the concentration distributions in the contact melting of metallic systems under diffusion-limited conditions, whereas much less has been published on ionic crystals [6]. Fick's diffusion equations are used to calculate the concentration distribution in the contact zone for the metal system, whereas the Nernst—Planck equations have to be used for ionic crystals:

$$\frac{\partial c_i}{\partial t} = \operatorname{div}\left[D_i \operatorname{grad} c_i + \frac{Z_i F c_i}{RT} \operatorname{grad} \varphi\right]. \quad (1)$$

One uses the condition for electrical neutrality $\rho = \Sigma Z_i c_i = 0$ or $\Sigma Z_i \operatorname{grad} c_i = 0$ and the condition for the absence of electric current to transfer to the equation

$$\frac{\partial c_i}{\partial t} = \operatorname{div}(D_i \operatorname{grad} c_i). \quad (2)$$

We assume that $dN_{is} \ll c_{is} S d l_i$ [5] in order to calculate the concentration distribution from (2). This enables one to specify the boundary conditions for this state: $D \frac{\partial c_i}{\partial x} = c_{il} \frac{dl_i}{dt}$. The initial distribution is written as $c(x, 0) = ac(x)$. Then the contact melting is described by a differential equation of parabolic type with boundary conditions of the third kind and a linear initial distribution. The problem may be solved by a difference method [7]. As the mutual-diffusion coefficient is dependent on the concentration, one has to use an inexplicit difference scheme

$$c_i^{n+1} - c_i^n = \frac{\Delta t}{h}\left[a_{i+1}(c_i)\frac{c_{i+1}^{n+1} - c_i^{n+1}}{h} - a_i(c_i)\frac{c_i^{n+1} - c_{i-1}^{n+1}}{h}\right].$$

When one calculates diffusion processes, it is more accurate to use an equation for $a_i(c_i)$ written in the form $a_i(c_i) = 0.5[D(c_{i-1}) + D(c_i)]$ [8], which incorporates the dependence of the diffusion coefficient on the concentration. Usually, the dependence can be put as

$$1)\ D(c_i) = D_i(1 + \lambda c_i); \quad 2)\ D(c_i) = D_i/(1 + \lambda c_i);$$
$$3)\ D_i = [D_{i1} D_{i2}(Z_{i1}^2 c_{i1} + Z_{i2}^2 c_{i2})]/[D_{i1} Z_{i1}^2 c_{i1} + D_{i2} Z_{i2}^2 c_{i2}].$$

The system of difference equations was solved by the pivot method, with the program written in FORTRAN and the calculations performed with an ES 1020 computer for the systems $NaNO_3$—KNO_3 and $NaNO_3$—$NaNO_2$, with the boundary concentrations chosen from the phase diagrams for temperatures of 513, 523, and 533°K. The same systems were used with the given temperatures in contact melting, and the concentration distributions were determined by measuring the

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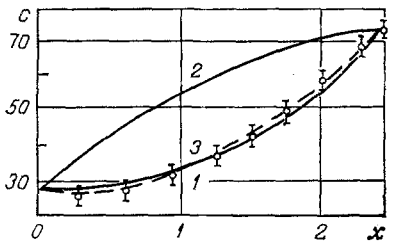

Fig. 1. Concentration distributions in the KNO_3—$NaNO_3$ system for various forms of D(c): 1) experiment; 2) calculation with $D(c_i) = D(1 + \lambda c_i)$; 3) calculation with $D(c_i) = \frac{D_{i1} \cdot D_{i2}(Z_{i1}^2 c_{i1} + Z_{i2}^2 c_{i2})}{D_{i1} Z_{i1}^2 c_{i1} + D_{i2} Z_{i2}^2 c_{i2}}$; x in 10^{-3} m and c in at. %.

coloring strength in the solutions with an SF-14 spectrophotometer. The solutions were prepared and analyzed by the usual methods of analytical chemistry [9].

Figure 1 shows the experimental and calculated concentration profiles for the KNO_3—$NaNO_3$ system, which show that in this type of system there is good agreement between theory and experiment only with $D(c_i)$ incorporating the concentrations and charges of the diffusing ions. Also, it was found that the boundary concentrations and the thickness of the diffusion zone at a given time varied with temperature, whereas c(x) remained of the same form. Only the thickness of the diffusion zone altered as the run time increased, while the form of c(x) was retained.

One assumes that these regularities apply for other systems of this type.

NOTATION

x, spatial coordinate; D_i, diffusion coefficient; Z_i, ionic charge; c_i, concentration of component i; F, Faraday number; φ, potential; $d\ell_i$, absolute boundary displacement; λ, constant; S, cross-sectional area; dN_{is}, increase in the amount of solid phase in time t; $a_i(c_i)$, coefficient incorporating D(c); Δt, time step; h, coordinate step; R, universal gas constant.

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