

ON THE THEORY OF THE CERAMIC DENSIFICATION PROCESS AND OF RECRYSTALLIZATION IN COLLOIDAL SOLUTIONS*

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(Received 5th October 1971)

INTRODUCTION

In the theory of the ceramic densification process the starting point is that the material transport consists mainly of diffusion processes. At least three different contributions are however distinguishable: volume diffusion, grain boundary diffusion and surface diffusion¹. For volume diffusion it has been shown theoretically that in ionic compounds an optimal diffusion rate can be obtained by appropriate control of the crystal lattice defects^{2,3}. In these theories calculations are based upon equilibria and transport of the lattice defects rather than those of the real components. This has the advantage that the methods used are mathematically analogous to those applied to solutions of salts in water.

To demonstrate this we compare a porous crystal of MgO with AgCl crystallites in contact with a saturated solution. In MgO we distinguish two types of lattice vacancies V_{Mg} and V_O with concentrations in accordance with the Schottky equilibrium:

$$[V_{Mg}] \times [V_O] = K_s \quad (1)$$

This is analogous to the solubility product of AgCl in water:

$$[Ag^+] \times [Cl^-] = K_s \quad (2)$$

Generally vacancies in ionic lattices release or attract electrons so that they may have electric charges.

In the same way atomic vacancies in metals may be compared with a saturated solution of a molecular compound. In both cases increased concentrations appear in equilibrium with curved surfaces, governed by the Kelvin relation:

$$n_p = n_0 \exp \frac{2\gamma v}{\rho kT} \quad (3)$$

where n_p denotes the equilibrium concentration around a spherical pore in a metal or around a spherical crystal with radius ρ , n_0 is the equilibrium concentration near a flat surface, γ the specific surface free energy and v the molecular volume. The concentrations are expressed in numbers per unit of volume. An analogous relation holds for

* Dedicated to Professor J. Th. G. Overbeek on the occasion of the 25th anniversary of his appointment as a Professor of Physical Chemistry.

ionic compounds but now for the values of K_s or K_S :

$$K_{s, \rho} = K_{s, 0} \exp \frac{2\gamma(v_+ + v_-)}{kT}$$

KINETIC PART

It is the object of this paper to discuss the theory of the diffusion in the dilute solutions of vacancies or ions mentioned above. The starting point is Fick's diffusion equation:

$$j_{at} = -D_{at} \frac{dn_{at}}{dx} \quad (4)$$

where j is the flux density in numbers of mobile particles per second per unit of surface, D the diffusion coefficient and dn/dx the concentration gradient. For the diffusion of vacancies we use the same equation:

$$j_{vac} = -D_{vac} \frac{dn_{vac}}{dx}$$

As $j_{vac} = -j_{at}$ and $dn_{vac}/dx = -dn_{at}/dx$ the values of D_{vac} and D_{at} are equal.

In our problem the concentration gradient dn/dx originates from the difference in equilibrium concentrations around pores or crystals of different dimensions. In order to derive general rules we consider the simple problem of a small spherical pore in a large crystal with flat surfaces or of a small spherical crystal in a solution with flat crystals at a large distance. For vacancy diffusion in metals Kuczynski⁴ has derived that the total flux ϕ from the surface of a spherical pore can be described by:

$$\phi = 4\pi n_{vac} D_{vac} \frac{2\gamma v_{vac}}{kT} \quad (5)$$

which result is independent of the radius ρ .

In the case of charged vacancies in ionic compounds the diffusion equation has an extra electrical term as a result of the difference in mobilities of the two types of vacancies:

$$j_+ = -D_+ \frac{dn_+}{dx} - n_+ b_+ \frac{dV}{dx} \quad (6a)$$

$$j_- = -D_- \frac{dn_-}{dx} + n_- b_- \frac{dV}{dx} \quad (6b)$$

where the indices $+$ and $-$ denote the positively and negatively charged vacancies and b_+ and b_- the mobilities. For these coupled fluxes a general flux equation can be solved, using the relation of Nernst and Einstein $D/kT = b/q$ where q is the absolute value of the electric charge. According to Ready² and Reynen³ this gives for the total flux from the surface of a pore:

$$\phi_+ = \phi_- = 4\pi \cdot 2 \left(\frac{1}{n_+ D_+} + \frac{1}{n_- D_-} \right)^{-1} \frac{\gamma(v_+ + v_-)}{kT} \quad (7)$$

again independent of the radius ρ .

With $K_s = n_+ n_-$ we then find that the vacancy fluxes are maximal if $n_+ D_+ = n_- D_-$. The concentration ratio n_+/n_- can be realized by appropriate doping.

The same results hold, of course, for the ion fluxes from the surface of a small crystal. It is interesting to recognize in the factor $2(1/n_+ D_+ + 1/n_- D_-)^{-1}$ the relation of Nernst (1888) between the diffusion coefficient of a salt and those of the separate ions.

THERMODYNAMIC PART

Surprisingly the rather simple results of Ready and of Reynen have not been easily accepted. Their apparent result is that the maximum flux is the result of a maximum of the diffusion coefficient. On the other hand, the vacancy "solubility" has a maximum under stoichiometric conditions, where $n_+ = n_-$ and then the concentration gradients have a maximum too. These gradients are severely decreased if excess concentrations of one of the vacancies are added⁵. This again is completely analogous to the case of the AgCl solubility if Ag^+ or Cl^- ions are added.

A confusion then results if dn/dx is considered to be the "driving force" of the diffusion. From a thermodynamic point of view this is not correct, however. According to the theory of irreversible processes one should use a general flux equation $J = \alpha X$ in such a way that the product of the flux J and the force X represents the dissipation rate \dot{F} of the available free energy F . A simple example is Ohm's law for electric currents:

$$J = \frac{1}{R} \Delta V \text{ with } \dot{F} = J \Delta V$$

Therefore a more useful description of the diffusion is, for example,

$$j_+ = -n_+ \frac{D_+}{kT} \frac{d\mu_+}{dx} - n_+ \frac{b_+}{q} \frac{dq'/dx}{dx} \quad (8)$$

which is essentially identical with eqn. (6a). Here μ denotes the chemical part and qV the electrical part of the free energy f_+ per particle, so that we can also write

$$j_+ = n_+ \frac{D_+}{kT} \cdot \frac{df_+}{dx} \equiv \alpha X \quad (9)$$

In the following we wish to show that the driving force of the diffusion can be derived without any kinetic model of the diffusion. Then also the problem whether the diffusion might be the result of a pressure gradient can be left out of consideration.

Starting with the general flux equation our program is:

- (i) to find the available free energy F
- (ii) to derive an equation for \dot{F}
- (iii) to split this equation in a flux J and a force X
- (iv) to find the relation between J and X .

As a first example we consider a spherical pore with radius ρ in a metal. The total available free energy is:

$$F = 4\pi\rho^2\gamma \quad (10)$$

If by some process the pore shrinks, then:

$$\dot{F} = \gamma \frac{dO}{dt} = \frac{2\gamma}{\rho} \cdot \frac{dV}{dt}$$

if V is the volume and O the surface of the pore. As this expression does not take into account the nature of the shrinkage process, it might as well apply to viscous flow as to diffusion. If we assume a diffusion process then $dV/dt = \phi v_{\text{vac}}$ where ϕ represents the total vacancy flux from the surface of the pore. Then:

$$\dot{F} = \phi v_{\text{vac}} 2\gamma/\rho \quad (11)$$

As we are interested in the vacancy flux ϕ , the driving force will be :

$$X = 2\gamma v_{\text{vac}}/\rho \quad (12)$$

and the flux equation :

$$\phi = \alpha 2\gamma v_{\text{vac}}/\rho \quad (13)$$

The value of α cannot be derived from thermodynamics but needs a special kinetic model. If we therefore compare eqn. (11) with eqns. (5) and (9) we find that α must be :

$$\alpha = 4\pi \frac{nD}{kT} \rho \quad (14)$$

where ρ appears as a geometrical factor.

The case of diffusion in an ionic compound MgO having two types of vacancies V_{Mg} and V_{O} can be solved in an analogous way, leading to :

$$\phi = \alpha' 2\gamma(v_+ + v_-)/\rho \quad (15)$$

Here we really find that the thermodynamic driving force is a constant, independent of the ratio n_+/n_- . The concentrations and diffusion coefficients appear in the coefficient α only. According to eqn. (7), or by applying directly the Nernst equation we find :

$$\alpha' = \frac{4\pi}{kT} \left(\frac{1}{n_+ D_+} + \frac{1}{n_- D_-} \right)^{-1} \rho \quad (16)$$

From eqn. (11) we can also derive the local flux equation by remembering that this equation describes the dissipation rate of the total free energy F . This can also be expressed as the sum of the local dissipations :

$$\dot{F} = \int_{r=\rho}^{r=\infty} 4\pi r^2 j_r \frac{df_r}{dr} dr$$

where j_r is the local flux density at a distance r from the center of the pore (or crystal) and f_r the local value of the free energy per particle. As the total flux $\phi = 4\pi r^2 j_r$ is constant through each spherical surface it follows that :

$$\frac{df_r}{dr} = j_r \frac{2\gamma v_{\text{vac}}}{r^2}$$

Then we find for the local flux equation :

$$j_r = \alpha' \frac{2\gamma v_{\text{vac}}}{r^2} = \frac{nD}{kT} \frac{2\gamma v_{\text{vac}}}{r^2}$$

and with eqns. (15) and (16) a comparable expression for ionic compounds.

APPLICATIONS

(i) Ionic conductivity

It is interesting to compare the condition for the optimal diffusion rate with

that for the extreme value of ionic conduction σ :

$$\sigma = n_+ qb_+ + n_- qb_-$$

where q denotes the electric charge and b_+ and b_- the mobilities of the mobile particles, respectively. As according to Nernst-Einstein $D/kT = b/q$, we can also write $\sigma = q^2/kT (n_+ D_+ + n_- D_-)$. In this case the condition $n_+ D_+ = n_- D_-$ corresponds to a minimum of the conductivity.

(ii) The ceramic sintering process

In many oxides the diffusion is mainly a vacancy process. In such cases there is an enormous difference in diffusion constants of the metal ion vacancies D_M and the oxygen ion vacancies D_O . D_O has the lower value, probably as a result of the large size of the oxygen ions. Therefore the sintering rate can be improved by increasing the oxygen vacancy concentration by slight reduction or by appropriate additions. Many experimental results are given in ref. 3. An example is given in Fig. 1 for the sintering experiments on Al_2O_3 .

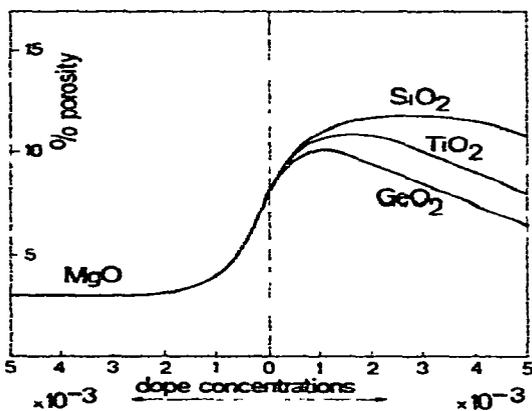


Fig. 1. Porosities of ceramic samples of Al_2O_3 after 6 h firing at $1850^\circ C$ in air in dependence on different dope concns. (after Reynen³)

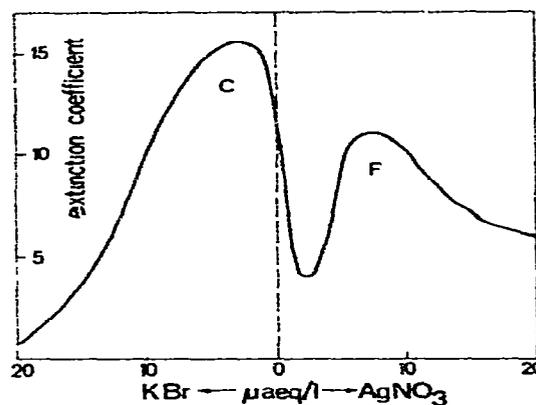


Fig. 2. Extinction coefficients (proportional to mean particle diameter) of freshly prepared AgBr sols containing $20 \mu\text{mol AgBr l}^{-1}$, after 2 h aging (after Jonker and Kruyt⁸). C = recrystallization maximum, F = zero point flocculation maximum.

(iii) Recrystallization in fresh colloidal solutions of "insoluble" salts

For equally charged ions (with exception of H^+ and OH^- ions) in water the difference in ionic radius is mainly compensated by the thickness of the hydration layer so that the differences in diffusion constants are small in comparison with those of ions in crystals. Therefore the maximum of the diffusion constant of a salt will generally be quite near the stoichiometric composition of the solution, and as a result the maximum rate of recrystallization will be found in colloidal solutions where no excess of one of the components is added. In many cases the zero-point of charge is found at a different composition of the solution, having a clear excess of one of the components. This is especially well known for the silver halides in water⁶. As a result, under favourable circumstances, two separate types of particle growth may be dis-

tinguished, one by recrystallization and one by flocculation, as is shown in Fig. 2. As, moreover, at higher excess concentrations flocculation of colloids will also occur, rather complicated patterns of particle growth will appear in a series of colloidal solutions prepared with a variation in the excess concentration of the components. This has led to confusion in the literature as regards the properties of freshly prepared colloidal solutions of silver halides^{7,8}. In work described in ref. 8 the recrystallization phenomenon could be distinguished from flocculation by using protecting hydrophilic colloids. Moreover electron microscope pictures have later shown that true single crystals are formed in this area of compositions. In contradistinction to the explanations used in refs. 7 and 8 our present impression is that the theory of diffusion rates offers the simplest explanation.

SUMMARY

In a short survey the analogy between the theories on diffusion in solids and in solutions is shown. As a result, analogous theories are developed for the ceramic sintering process and the recrystallization in colloidal solutions. By a thermodynamic method a description is given of the available free energy, the diffusion flux and the driving force.

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