

7. Electrochemical transport

Electrochemical potential

In the chapter on diffusion we learned that random diffusion is driven by thermal energy and that it in crystalline solids requires defects. Moreover, we learned that a net flux of a species can result from a gradient in its chemical potential. In the chapter on electrical conductivity we furthermore saw that a net flux of charged particles would result in a gradient of electrical potential.

In ionic media (materials, liquids, and solutions) the chemical and electrical potentials act simultaneously, and it is often convenient to combine them into an electrochemical potential. For the species i we have

$$\eta_i = \mu_i + z_i e \phi \quad (7.1)$$

This is true whether the species is real or a defect, but in general we shall onwards deal mainly with real species and real charges z_i .

The electrochemical potential gradient is accordingly, in the one-dimensional case,

$$\frac{d\eta_i}{dx} = \frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx} \quad (7.2)$$

The combination of chemical and electrical potentials and potential gradients forms the basis for the treatment of all mass transport processes involving charged species (ions) in ionic solids, and is the theme of this chapter. The theory is termed Wagner-type after Carl Wagner, who was the first to derive it, originally to describe oxidation of metals.

Flux equations – Wagner theory

General derivation of Wagner-type flux expressions

We have seen in a preceding paragraph that a force, expressed as gradient in a potential P_i acting on a species i , gives rise to a flux density of that species which is proportional to its self-diffusion coefficient D_i . By assuming that the potential acting is the electrochemical potential, we obtain

$$j_i = \frac{-D_i c_i}{kT} \frac{dP_i}{dx} = \frac{-D_i c_i}{kT} \frac{d\eta_i}{dx} = \frac{-D_i c_i}{kT} \left[\frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx} \right] \quad (7.3)$$

Via the Nernst-Einstein equation we may substitute conductivity for the random diffusivity and obtain the following alternative expression for the flux density:

$$j_i = \frac{-\sigma_i}{(z_i e)^2} \left[\frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx} \right] \quad (7.4)$$

If the species is charged, the flux density for i gives rise to a partial current density i_i :

$$i_i = z_i e j_i = -\frac{\sigma_i}{z_i e} \left[\frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx} \right] \quad (7.5)$$

The net current density in the sample is obtained by summing the partial current densities over all the species k :

$$i_{tot} = \sum_k z_k e j_k = -\sum_k \frac{\sigma_k}{z_k e} \left[\frac{d\mu_k}{dx} + z_k e \frac{d\phi}{dx} \right] \quad (7.6)$$

The sample is next assumed to be connected to an external electric circuit. This may be real, with electrodes and wires and an electrical supply or load, or it may be absent, in which case we say that we have an open circuit. Since the sample makes a series connection with the external circuit, the current in the sample must be the same as in the external circuit.

For a bare sample, a gas permeation membrane, or for an open-circuit fuel cell or other electrochemical device, the total current is zero. For fuel cells or electrolyzers in operation, on the other hand, the current is non-zero.

By using the definition of total conductivity, $\sigma_{tot} = \sum_k \sigma_k$, and the definition of transport number, $t_k = \frac{\sigma_k}{\sigma_{tot}} = \frac{\sigma_k}{\sum_k \sigma_k}$, we obtain the following very important expression:

$$\frac{d\phi}{dx} = -\frac{i_{tot}}{\sigma_{tot}} - \sum_k \frac{t_k}{z_k e} \frac{d\mu_k}{dx} \quad (7.7)$$

This relates the electrical potential gradient to the total (net, external) current density, the total conductivity, and the transport number and chemical potential gradient of all charge carriers.

From charged to neutral species: the electrochemical reaction

The chemical potentials of charged species are not well-defined, and we need to represent them instead by chemical potentials of neutral species. For this purpose we may assume equilibria between neutral and charged species and electrons, i.e. in the electrochemical red-ox-reaction



where S is a neutral chemical entity and z may be positive or negative. The equilibrium condition for this is expressed in terms of the chemical potentials of products and reactants:

$$d\mu_{S^z} + z d\mu_{e^-} - d\mu_S = 0 \quad (7.9)$$

and can be rearranged with respect to the ionic species:

$$d\mu_{S^z} = d\mu_S - z d\mu_{e^-} \quad (7.10)$$

We insert this for all ionic species n in the expression for the electrical potential gradient. The entry (among k) for electrons is left unsubstituted. By using $\sum_k t_k = 1$ we obtain

$$\frac{d\phi}{dx} = -\frac{i_{tot}}{\sigma_{tot}} - \sum_n \frac{t_n}{z_n e} \frac{d\mu_n}{dx} + \frac{1}{e} \frac{d\mu_e}{dx} \quad (7.11)$$

for which the chemical potentials now refer to the neutral forms of each carrier.

The voltage over a sample

We now integrate the electrical potential gradient over the thickness of the sample, from side 1 to side 2, in order to obtain the voltage over the sample:

$$\int_I^II d\phi = -\int_I^II \frac{i_{tot}}{\sigma_{tot}} dx - \sum_n \int_I^II \frac{t_n}{z_n e} d\mu_n + \int_I^II \frac{1}{e} d\mu_e \quad (7.12)$$

$$\phi_{II} - \phi_I = -\int_I^II \frac{i_{tot}}{\sigma_{tot}} dx - \sum_n \int_I^II \frac{t_n}{z_n e} d\mu_n + \frac{1}{e} (\mu_{e,II} - \mu_{e,I}) \quad (7.13)$$

We further assume that the voltage is measured on each side using the same inert metal, e.g. Pt. This eliminates the difference between chemical potentials of electrons on the two sides, and the voltage measured between the two sides is

$$U_{II-I} = \phi_{II} - \phi_I = -\int_I^II \frac{i_{tot}}{\sigma_{tot}} dx - \sum_n \int_I^II \frac{t_n}{z_n e} d\mu_n \quad (7.14)$$

Under open circuit conditions, $i_{tot}=0$, and we obtain

$$U_{II-I} = -\sum_n \int_I^{II} \frac{t_n}{z_n e} d\mu_n \quad (7.15)$$

We shall later see how this is used to calculate transport numbers based on open circuit voltage measurements of cells exposed to a well-defined gradient in chemical activities. Alternatively, if t_n is known to be unity for ionic charge carriers this expression will yield the open circuit voltage of a fuel cell or a galvanic sensor.

If current is drawn from the sample, as in a fuel cell or battery under load, we need to know how i_{tot} varies with x . If we assume that it is constant, we get

$$U_{II-I} = -\frac{i_{tot} X}{\sigma_{tot}} - \sum_n \int_I^{II} \frac{t_n}{z_n e} d\mu_n = -i_{tot} r_{tot} - \sum_n \int_I^{II} \frac{t_n}{z_n e} d\mu_n \quad (7.16)$$

where X is the thickness of the sample and r_{tot} is the area-specific resistance of the sample. Alternatively, $i_{tot} r_{tot}$ (current density and area specific resistance) may be replaced by RI , (sample resistance and current):

$$U_{II-I} = -IR - \sum_n \int_I^{II} \frac{t_n}{z_n e} d\mu_n \quad (7.17)$$

The voltage of a fuel cell or battery is thus composed of a thermodynamic part that arises from the chemical gradient, and the well-known “IR”-term which arises from the limiting kinetics (transport) in the sample. The letters “IR” may be taken to reflect current times resistance, or to mean “internal resistance”. We will later see that the direction of the current ends up such that the IR-term reduces the voltage over the fuel cell or battery.

Flux of a particular species

One of the general expression for the electrical potential gradient can now be inserted in an expression for the flux density of an individual species (Eq. 7.4) or the corresponding partial current density (Eq. 7.5). Since these two sum over chemical potential gradients of charged species, we may conveniently use Eq. 7.7 for our purpose. Inserting this into Eq. 7.4 and rearranging yields

$$j_i = \frac{t_i i_{tot}}{z_i e} - \frac{\sigma_i}{(z_i e)^2} \left[\frac{d\mu_i}{dx} - z_i \sum_k \frac{t_k}{z_k} \frac{d\mu_k}{dx} \right] \quad (7.18)$$

The first term in the right hand side simply says what we expect: If there is a net current, a flux density of species i will be set up proportional to the total current density and the transport number t_i , divided by the species' charge.

The equation above is a rather general expression that we can use to calculate flux densities of one charged species in the company of many other species. However, it reflects the flux density and gradients and properties at a particular point through the membrane. The gradients will adjust according to the varying materials properties so as to maintain a constant flux density everywhere – what we call steady state. In order to implement this, we integrate the flux density expression over the thickness of the membrane and require that the flux density remains constant:

$$\int_l^II j_i dx = j_i X = \int_l^II \frac{t_i i_{tot}}{z_i e} dx - \int_l^II \frac{\sigma_i}{(z_i e)^2} \left[d\mu_i - z_i \sum_k \frac{t_k}{z_k} d\mu_k \right] \quad (7.19)$$

If the transport number t_i and the total current density i_{tot} can be taken as constant through the membrane we further obtain:

$$j_i X = \frac{t_i i_{tot}}{z_i e} X - \int_l^II \frac{\sigma_i}{(z_i e)^2} \left[d\mu_i - z_i \sum_k \frac{t_k}{z_k} d\mu_k \right] \quad (7.20)$$

Wagner-type transport theory case studies

Oxides with transport of oxide ions and electrons

General equations

We will now apply the general theory to a number of cases. The cases we will consider first is an oxide that conducts oxygen ions and electrons. Flux equations for the two are

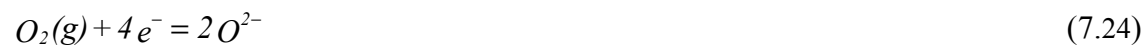
$$j_{O^{2-}} = \frac{-\sigma_{O^{2-}}}{4e^2} \left[\frac{d\mu_{O^{2-}}}{dx} - 2e \frac{d\phi}{dx} \right] \quad (7.21)$$

$$j_{e^-} = \frac{-\sigma_{e^-}}{e^2} \left[\frac{d\mu_{e^-}}{dx} - e \frac{d\phi}{dx} \right] \quad (7.22)$$

By summing up the currents from the two we obtain (as in Eq. 7.7) the expression for the potential gradient:

$$\frac{d\phi}{dx} = -\frac{i_{tot}}{\sigma_{tot}} + \frac{t_{O^{2-}}}{2e} \frac{d\mu_{O^{2-}}}{dx} + \frac{t_{e^-}}{e} \frac{d\mu_{e^-}}{dx} \quad (7.23)$$

In order to relate the potential gradient to the chemical potential of neutral species we introduce electrochemical equilibria between neutral and charged species of oxygen:



for which equilibrium can be expressed by

$$d\mu_{O_2(g)} + 4d\mu_{e^-} = 2d\mu_{O^{2-}} \quad (7.25)$$

Introducing this we get

$$\frac{d\phi}{dx} = -\frac{i_{tot}}{\sigma_{tot}} + \frac{t_{O^{2-}}}{4e} \frac{d\mu_{O_2(g)}}{dx} + \frac{t_{O^{2-}}}{e} \frac{d\mu_{e^-}}{dx} + \frac{t_{e^-}}{e} \frac{d\mu_{e^-}}{dx} \quad (7.26)$$

and knowing that the sum of transport numbers for oxygen ions and electrons in the oxide we have defined is unity, we further get

$$\frac{d\phi}{dx} = -\frac{i_{tot}}{\sigma_{tot}} + \frac{t_{O^{2-}}}{4e} \frac{d\mu_{O_2(g)}}{dx} + \frac{1}{e} \frac{d\mu_{e^-}}{dx} \quad (7.27)$$

whereby we have exemplified Eq. 7.11. We now integrate over the thickness of the sample to obtain the voltage over it, eliminating the chemical potential of electrons (as in Eq. 7.14 and onwards):

$$U_{II-I} = -IR + \frac{1}{4e} \int_I^{II} t_{O^{2-}} d\mu_{O_2(g)} \quad (7.28)$$

Using

$$\mu_{O_2(g)} = \mu_{O_2(g)}^0 + kT \ln p_{O_2} \quad (7.29)$$

$$d\mu_{O_2(g)} = kT d \ln p_{O_2} \quad (7.30)$$

we get

$$U_{II-I} = -IR + \frac{kT}{4e} \int_I^{II} t_{O^{2-}} d \ln p_{O_2} \quad (7.31)$$

If $t_{O^{2-}}$ is independent of the oxygen partial pressure, or if we can assume as an approximation that an average $\overline{t_{O^{2-}}}$ is constant over the pressure range applied, then

$$U_{II-I} = -IR + \overline{t_{O^{2-}}} \frac{kT}{4e} \ln \frac{p_{O_2}^{II}}{p_{O_2}^I} = -IR + \overline{t_{O^{2-}}} E_N \quad (7.32)$$

where E_N is the Nernst-voltage of the oxygen concentration cell.

Open circuit voltage of concentration cell for transport number measurements

The equation above can be used to measure the average oxygen ion transport number, by measuring the open circuit voltage (OCV) over a sample exposed to a small, well-defined gradient in partial pressure of oxygen:

$$\overline{t_{O^{2-}}} = \frac{U_{II-I}}{E_N} \quad (7.33)$$

Galvanic oxygen sensor

By using a material with $t_{O^{2-}} = 1$, i.e. a solid electrolyte, and a well-defined reference partial pressure of oxygen, the OCV can be used for measuring an unknown partial pressure:

$$U_{II-Ref} = \frac{kT}{4e} \ln \frac{p_{O_2}^{II}}{p_{O_2}^{Ref}} \quad (7.34)$$

Fuel cell

If we apply a solid electrolyte with $t_{O^{2-}} = 1$ and expose it to a gradient in oxygen partial pressure, we get

$$U_{II-I} = -IR + \frac{kT}{4e} \ln \frac{p_{O_2}^{II}}{p_{O_2}^I} = -IR + E_N \quad (7.35)$$

This would be the voltage of a fuel cell. With $I = 0$, we obtain the OCV of the cell to be the Nernst voltage, of course. We furthermore see that the cell voltage diminishes due to the IR loss at increasing current, I . A plot of U vs I gives $-R$ as the slope.

The power delivered by the cell is the current multiplied with the voltage;

$$P = UI = -I^2 R + IE_N \quad (7.36)$$

and it goes through a maximum at $U = E_N/2$. Under these conditions, the power is split half-half between external work and internal loss, so the electrical efficiency is 50%. The efficiency increases as the power and current decrease, and commonly fuel cells are designed to run at ca. $U = 2/3 E_N$.

Mixed conducting oxygen permeable membrane

Now we will show how we obtain the flux of oxygen through a mixed conducting oxygen membrane material. As mentioned in the general section this is done by inserting the electrical potential gradient back into the flux equation for oxygen ions. Using e.g. Eqs. 7.21, 7.23, and 7.25 we get:

$$j_{O^{2-}} = -\frac{t_{O^{2-}} i_{tot}}{2e} - \frac{\sigma_{O^{2-}} t_{e^-}}{4e^2} \left[\frac{d\mu_{O^{2-}}}{dx} - 2 \frac{d\mu_{e^-}}{dx} \right] = -\frac{t_{O^{2-}} i_{tot}}{2e} - \frac{\sigma_{O^{2-}} t_{e^-}}{8e^2} \frac{d\mu_{O_2(g)}}{dx} \quad (7.37)$$

The steady state restriction is introduced by integrating over the thickness of the membrane:

$$\int_I^{II} j_{O^{2-}} dx = j_{O^{2-}} X = -\int_I^{II} \frac{t_{O^{2-}} i_{tot}}{2e} dx - \int_I^{II} \frac{\sigma_{O^{2-}} t_{e^-}}{8e^2} d\mu_{O_2(g)} \quad (7.38)$$

$$j_{O^{2-}} = -\frac{i_{tot}}{2eX} \int_I^{II} t_{O^{2-}} dx - \frac{kT}{8e^2 X} \int_I^{II} \sigma_{O^{2-}} t_e d \ln p_{O_2} \quad (7.39)$$

If i_{tot} is not zero, i.e., some external current is drawn, then the first term says that the oxygen ion flux is proportional to that current and to the oxygen ion transport number. If the latter is independent of x , then the integral is straightforward. The last term adds to the flux; it is driven by an oxygen pressure gradient, and it is proportional to the oxygen ion conductivity and the transport number of electrons. This term describes permeation of oxygen ions, requiring transport of both oxygen ions and electrons. Moreover, it is inversely proportional to the thickness of the sample, X . Under open circuit conditions we may simplify to get:

$$j_{O^{2-}} = -\frac{kT}{8e^2 X} \int_I^{II} \sigma_{O^{2-}} t_e d \ln p_{O_2} = -\frac{kT}{8e^2 X} \int_I^{II} \sigma_{tot} t_{O^{2-}} t_e d \ln p_{O_2} \quad (7.40)$$

We now apply our derived expression for the example case of an oxygen-deficient oxide MO_{1-x} . This contains oxygen vacancies compensated by electrons, and we have earlier shown that the defect concentrations are given by $n = 2[v_O^{**}] = (4K_{v_O}^{**})^{1/3} p_{O_2}^{-1/6}$. Since the mobility of electrons is usually much higher than that of ionic defect, and with similar concentrations of electrons and oxygen vacancies, we may assume that the material is mainly an n-type electronic conductor. Therefore $t_e \approx 1$. Furthermore, $\sigma_{O^{2-}} = \sigma_{v_O^{**}} = 2e[v_O^{**}]u_{v_O^{**}} = \sigma_0 p_{O_2}^{-1/6}$, and when we insert these in the flux expression we obtain

$$j_{O^{2-}} = -\frac{kT\sigma_0}{8e^2 X} \int_I^{II} p_{O_2}^{-1/6} d \ln p_{O_2} \quad (7.41)$$

We substitute $d \ln p_{O_2} = \frac{1}{p_{O_2}} dp_{O_2}$ and obtain

$$j_{O^{2-}} = -\frac{kT\sigma_0}{8e^2X} \int_I^{II} p_{O_2}^{-7/6} dp_{O_2} \quad (7.42)$$

which integrates into

$$j_{O^{2-}} = \frac{6kT\sigma_0}{8e^2X} \left\{ (p_{O_2}^{II})^{-1/6} - (p_{O_2}^I)^{-1/6} \right\} \quad (7.43)$$

One may note that we here have utilised the Wagner approach for electrochemical transport of two defect species and combined it with the solution of the defect chemical equilibria to obtain an accurate description of the flux of oxygen ions. Numerical values for the flux of course require that one knows σ_0 , which contains many parameters relating to formation and mobility of the defects. In the right-hand parenthesis the negative exponent $-1/6$ has the consequence that the smaller of the two partial pressures of oxygen has the biggest influence. The larger partial pressure makes a comparatively smaller difference and may be neglected to a first approximation for large gradients. For instance, consider a gas separation membrane exposed to air on the one side and a very reducing gas (e.g. methane) on the other. The flux would then be essentially proportional to $(p_{O_2}^{red})^{-1/6}$ while it would largely be independent of $p_{O_2}^{ox}$. It would thus not help much to compress the air to 100 atm, while removal of oxidised products like H₂O on the reducing side would lower $p_{O_2}^{red}$ and have a large effect.

Ambipolar diffusion and conduction

We have seen above that the transport coefficient term that enters in the flux of oxygen ions in a mixed oxygen ion conductor is a product which we may call the ambipolar conductivity

$$\sigma_{amb} = \sigma_{tot} t_{O^{2-}} t_{e^-} = \sigma_{O^{2-}} t_{e^-} = \frac{\sigma_{O^{2-}} \sigma_{e^-}}{\sigma_{O^{2-}} + \sigma_{e^-}} \quad (7.44)$$

This reflects the fact that so-called ambipolar conduction of two species is necessary (in this case for charge compensation).

The corresponding terms transformed to diffusivities are called the ambipolar diffusion coefficients for oxygen:

$$D_{amb} = D_{O^2} t_e \quad (7.45)$$

Such terms, like partial conductivity and self-diffusion, reflect thermal random mobility as before, but are restricted by the slower of the two ambipolar diffusing species (ions or electrons).

Many other cases of combined transport coefficients are in use, e.g. the combined (additive) transport of oxygen and metal ions commonly that we shall address later (and exemplify by the high temperature oxidation of metals), the combination of two diffusivities involved in interdiffusion (mixing) processes, and the mass transport in creep being rate limited by the smallest out of cation and anion diffusivities in a binary compound. As some of these sometimes are referred to as ambipolar or chemical diffusivities, we want to stress the above simple definition of ambipolar transport coefficients as relevant for membrane applications using mixed conductors.

Chemical diffusion and tracer diffusion

General case

The *chemical diffusion coefficient* is the *phenomenological* coefficient that enters a Fick's 1st law of diffusion in a concentration gradient:

$$j_i = -\tilde{D}_i \frac{dc_i}{dx} \quad (7.46)$$

Unlike our previous treatment in this chapter (which uses D_r , B , u or σ), Fick's 1st law and the chemical diffusion coefficient says in general nothing directly about the self-diffusion coefficient. Neither is, as we shall see, the chemical diffusion coefficient in general a constant in any sense. Only when the species i is an effectively neutral particle that moves independently of other species will the chemical diffusion coefficient be identical to the self-diffusion coefficient. If the flux and the concentration gradient are in terms of an isotope (tracer), the coefficient is the tracer diffusion coefficient, which is almost equal to the self-diffusion coefficient:

$$D_i = f D_r \quad (7.47)$$

where the correlation factor f is a number usually equal to or somewhat smaller than unity, depending on structure and diffusion mechanism, reflecting the difference of transport between distinguishable and indistinguishable diffusing species. For vacancy diffusion, f usually falls around 0.75 depending on structure.

Chemical diffusion is sometimes referred to as diffusion under a chemical potential or concentration gradient. However, we have seen that self-diffusion properly describes this, and that all diffusion phenomena we consider here are merely minor perturbations of thermally induced self-diffusion. Why then do we need to be concerned with chemical diffusivity? We use it whenever we want to or have to relate our flux to the concentration gradient. Under steady state processes, our flux vs force equivalents provides sufficient description, and can be integrated to yield steady state fluxes through membranes, as we have shown; Thus, for this purpose, the self-diffusion coefficients and conductivities are useful since they behave in a simple manner vs defect concentrations, and since we in general know the chemical and/or electrical potential gradients applied. However, if we know the concentration gradients and how the chemical diffusivity varies with concentration, we *can* use chemical diffusivity.

In a transient experiment, however, parts of the material take up or give away matter (leading to changes in the concentration of species with time). This is sometimes referred to as a capacitive effect and is expressed in Fick's 2nd law:

$$\frac{dc}{dt} = - \frac{dj}{dx} = \frac{d(D \frac{dc}{dx})}{dx} \quad (7.48)$$

If D is independent of c and thus of x and t , then we can simplify to obtain:

$$\frac{dc}{dt} = -\frac{dj}{dx} = D\frac{d^2c}{dx^2} \quad (7.49)$$

Mathematical solutions for interpretation of transient tracer, thermogravimetric and electrical conductivity experiments are based on this. The diffusion coefficient obtained is the tracer diffusion coefficient in case of a transient in isotope composition (whether measured radiographically, mass spectrometrically, thermogravimetrically or electrically) or chemical diffusion coefficients in case of a transient in chemical composition (measured thermogravimetrically or electrically or by other means). The latter is usually executed by stepping the oxygen activity by gas composition, total pressure, or electrochemical means.

It may be noted that certain tracer experiments actually yield an interdiffusion coefficient between two tracers. The diffusion coefficient for oxygen in practice cannot and need not distinguish between the different isotopes in use (usually ^{18}O and ^{16}O , more rarely ^{17}O). However, for protons, the difference to deuteron (or triton) transport coefficients is considerable (e.g. a factor of 2) and should be taken into account when interpreting the results.

The multitude of transport coefficients collected can thus be divided into self-diffusion types (total or partial conductivities and mobilities obtained from equilibrium electrical measurements, ambipolar or self-diffusion data from steady state flux measurements through membranes), tracer-diffusivities, and chemical diffusivities from transient measurements. All but the last are fairly easily interrelated through definitions, the Nernst-Einstein relation, and the correlation factor. However, we need to look more closely at the chemical diffusion coefficient. We will do this next by a specific example, namely within the framework of oxygen ion and electron transport that we have restricted ourselves to at this stage.

Chemical diffusivity in the case of mixed oxygen vacancy and electronic conductor

In a system with oxygen vacancies as the only oxygen point defects, the concentration of oxygen ions is the concentration of oxygen sites *minus* the concentration of vacancies:

$$c_{O^{2-}} = c_{O^{2-}}^0 - c_{v\bar{O}} \quad (7.50)$$

such that

$$\frac{dc_{O^{2-}}}{dx} = -\frac{dc_{v\bar{O}}}{dx} \quad (7.51)$$

We manipulate this in the following manner:

$$\frac{dc_{O^{2-}}}{dx} = -\frac{dc_{v\bar{O}}}{dx} \frac{d \ln p_{O_2}}{d \ln p_{O_2}} = -\frac{dc_{v\bar{O}}}{d \ln p_{O_2}} \frac{d \ln p_{O_2}}{dx} \quad (7.52)$$

and insert the result into the flux equation for oxygen ions, Eq. 7.37 (open circuit, $i_{\text{tot}} = 0$):

$$j_{O^{2-}} = -\frac{\sigma_{O^{2-}} t_e}{8e^2} \frac{d\mu_{O_2(g)}}{dx} = -\frac{\sigma_{O^{2-}} t_e kT}{8e^2} \frac{d \ln p_{O_2}}{dx} = \frac{\sigma_{O^{2-}} t_e kT}{8e^2} \frac{d \ln p_{O_2}}{dc_{v\bar{O}}} \frac{dc_{O^{2-}}}{dx} \quad (7.53)$$

We have thus derived an expression for the flux that relates it to the concentration gradient of oxygen ions. We may now therefore compare this expression with that of the oxygen flux in terms of Fick's 1st law involving the concentration gradient in oxygen ions and the chemical diffusion coefficient:

$$j_{O^{2-}} = -\tilde{D}_{O^{2-}} \frac{dc_{O^{2-}}}{dx} \quad (7.54)$$

and we obtain

$$\tilde{D}_{O^{2-}} = -\frac{\sigma_{O^{2-}} t_{e^{-}} kT}{8e^2} \frac{d \ln p_{O_2}}{dc_{v_o^{\bullet\bullet}}} \quad (7.55)$$

Further, by using the Nernst-Einstein-relation and inserting the relation $D_{O^{2-}} c_{O^{2-}} = D_{V_o} c_{V_o}$ we get

$$\tilde{D}_{O^{2-}} = -\frac{D_{O^{2-}} c_{O^{2-}} t_{e^{-}}}{2} \frac{d \ln p_{O_2}}{dc_{v_o^{\bullet\bullet}}} = -\frac{D_{v_o^{\bullet\bullet}} c_{v_o^{\bullet\bullet}} t_{e^{-}}}{2} \frac{d \ln p_{O_2}}{dc_{v_o^{\bullet\bullet}}} = -\frac{D_{v_o^{\bullet\bullet}} t_{e^{-}}}{2} \frac{d \ln p_{O_2}}{d \ln c_{v_o^{\bullet\bullet}}} = -\frac{D_{v_o^{\bullet\bullet}} t_{e^{-}}}{2} \frac{d \ln c_{v_o^{\bullet\bullet}}}{d \ln p_{O_2}} \quad (7.56)$$

Thus, depending on the p_{O_2} -dependency of the vacancy concentration, the chemical diffusion coefficient becomes a varying function of the vacancy (defect) self diffusion coefficient. When the sample is mainly an electronic conductor and the transport number for electrons is unity, the collection of remaining terms (the enhancement factor) takes absolute values from 1 to 3 when the sample has a variable non-stoichiometry, while it increases beyond this (and can take on very large values) as the stoichiometry approaches a constant value, as in certain doped materials or materials with prevailing point defect (Schottky or Frenkel) disorder; the vacancy concentration is then close to independent of p_{O_2} .

The full range of aspects of chemical diffusion coefficients make them rather difficult to translate into other transport coefficients, and they tend to live their own lives in the literature. They can, as said before, be applied directly to calculate fluxes in membranes if the concentration gradients through the membranes are known. However, we note that the chemical diffusion coefficient (for oxygen ions) is

- *proportional* to the self diffusivity of the oxygen *defect* (here the vacancy),
- *proportional* to the electronic transport number (but which is often unity),
- *enhanced* by the term $d \ln p_{O_2} / 2d \ln c_{V_o}$, which for various limiting cases of simplified defect situations takes on values of 1, 3 or ∞ , and
- *fully forwards and backwards transformable into defect diffusivities* (and in turn self diffusivities) if we know the transport numbers and how defect concentrations vary with p_{O_2} .

Surface and interface kinetics limitations

The flux of matter through a fuel cell or electrolyser is limited by the electrolyte (ionic) resistance, the electrode kinetics, and the external electronic load resistance. We commonly express the steady state situation and the fact that the current is the same through the entire closed circuit in terms of the voltage drops around the circuit:

$$E = E_N - I R_i - (\eta_c + \eta_a) \quad (7.57)$$

where I is the current, E_N is the open circuit (Nernst) voltage, R_i is the ionic electrolyte resistance, and η_c and η_a are the cathode and anode overpotentials, respectively. (The conventions and practices on measuring and reporting the sign of various voltages may vary, so that the equation may take various forms with respect to signs).

Similarly, the current of matter through an electrodeless gas separation, mixed conducting membrane will be limited by ionic conduction, the surface kinetics, and by the *internal* electronic resistance, the latter replacing the external circuit in the previous case.

However, we may need to express the loss of potential in terms of the chemical potential of oxygen.

If we look at the system without any gradients or currents applied, there will be equilibrium at both the electrodes and the surfaces. Depending on the application and the side of the membrane, the electrochemical processes in operation on an oxygen ion conductor may be:

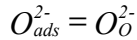
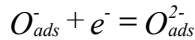
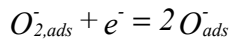
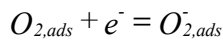
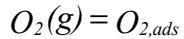


and



In all of these the electrons can be supplied to or from an electrode or a mixed conductor surface. Thus, basically, the reactions are the same in the electrolyte/electrode as in the mixed conductor, although the physical presence of the electrode can promote (by catalysis) or obstruct the reaction.

Most surface reactions are believed to be made up of a sequence of reactions steps. Some possible step reactions in the case of the reduction of oxygen gas are given by the following reaction sequence;



The last of these steps may involve bulk defects (e.g. a vacancy that the adsorbed ion may occupy) but we will not attempt here an analysis of surface or electrode kinetics in terms of defect chemistry. Determination of the nature of the rate limiting step of a reaction is a difficult task. Studies of surface exchange kinetics using ^{18}O or by relaxation methods can give information about the temperature and pressure dependence of the rate determining step. However, it should be pointed out that information from such methods do not give direct information about the exact mechanism and which intermediate species that are involved. Each step will have its own specific rate and resistance to the mass transport across the membrane. In lack of detailed knowledge of the rate limiting step(s) we normally have to relate to the overall reaction.

At equilibrium the overall reaction takes place forth and back at equal rates r_0 as a result of thermal energy. The activation process forth and back may not be symmetrical in this case, but that will not affect us at present. Similarly to the random diffusion coefficient connected with these thermal disorders in bulk ($D_r = 1/6 r_0 s^2$) we introduce an exchange coefficient for interfaces; $k_i = r_0 s_i$ which says something about the thermal fluctuations of the reaction across the interface of thickness s_i . We can alternatively express this as an exchange flux density

$$j_0 = k_i c = r_0 s_i c \tag{7.60}$$

or an exchange current density

$$i_0 = j_0 ne = k_i nec = r_0 s_i nec \quad (7.61)$$

where n is the number of electrons involved in the reaction. If we now apply a small force over the interface, we get a perturbation and a net flux, given by

$$j = -c k_i \frac{dP}{kT} \quad (7.62)$$

where c is the volume concentration of species in the interface, and dP is the potential step over the interface. The net current density is

$$i = jne = cne k_i \frac{dP}{kT} = i_0 \frac{dP}{kT} \quad (7.63)$$

If dP is taken as the electrical (over-)potential energy step affecting the reaction, $dP = \eta ne$ and the overpotential becomes

$$\eta = \frac{kT}{ne} \frac{i}{i_0} \quad (7.64)$$

This is the linear or ohmic (small overpotential) form of the kinetics expression, as we expect from our specification of small forces and perturbations. We note that the interface thickness s_i has dropped out and is mostly not an interesting parameter at this level.

By measuring the overvoltage vs current density by voltammetric DC or impedance spectroscopy AC methods, we may obtain the charge transfer resistance

$$R_e = \frac{\eta}{i} = \frac{kT}{ne i_0} = \frac{kT}{n^2 e^2 k_i c} \quad (7.65)$$

The overpotential enters directly into the sum of voltages over the fuel cell or electrolyser circuit, and we can solve the system in terms of current and voltage. As the force and perturbations of the reaction becomes larger, the full so-called Butler-Volmer exponential dependence of current and flux on overpotential (and force) must be taken into account:

$$\eta = \frac{kT}{ne} \ln\left(\frac{i}{i_0}\right) \quad (7.66)$$

, but we will not elaborate on this here.

In order to approach an interpretation of transport measurements, we take as starting point that the flux(es) through the interface must be the same as that in the bulk of the membrane next to the interface in all cases (and in the entire membrane in the steady state cases). This is done in reality and in the mathematical solutions by adjusting the potential at the border between the interface and the bulk so as to equalise the two fluxes. However, this soon becomes difficult, as it is not trivial to choose the proper set of potentials to apply for different interface processes.

We resort first to chemical diffusion and assume that the interface process is one which can be described as species flowing from a high to a lower concentration. Then

$$-D\left(\frac{dc}{dx}\right)_{bulk} = -k\Delta c_{interface} \quad (7.67)$$

, and D as well as k must refer to chemical coefficients. This requirement can be included in the solution of Fick's 2nd law for transients, and D and k can in principle be found independently by fitting transient data to this solution. The k 's obtained in this way can be used to predict steady state fluxes if they are measured as a function of e.g. p_{O_2} or at the p_{O_2} extremes which the membrane is going to be subjected to. Otherwise, the k values are not immediately easy to relate to other data.

In a tracer experiment, we obtain D_t which is close to the self diffusivity ($D_t = f D_r$) and then the exchange coefficient should also reflect the tracer exchange coefficient $k_t \approx k_i$ and this should be comparable to that calculated as above from measurements of R_e ; the difference should say to what extent the presence of an electrode has changed the kinetics of the rate limiting step of the surface reaction.

In order to analyse the effect of interface kinetics on fluxes through a membrane under steady state conditions, we may take an approach similar to that for fuel cells and electrolyzers. Principally, no electrodes are involved, and voltages are therefore not directly appropriate as in the other cases. Instead we may sum up chemical potential changes of oxygen (or hydrogen) through the membrane and its interfaces. We start out with the membrane interior, and from earlier we have for a mixed oxygen ion and electron conductor of thickness L (earlier also referred to as X or Δx):

$$j_{O^{2-}} = -\frac{1}{L} \int_I^II \frac{\sigma_{O^{2-}} t_{e^-}}{8e^2} d\mu_{O_2(g)} \quad (7.68)$$

If we introduce ambipolar diffusivities and conductivities and assume these constant, the equation may be integrated to obtain

$$j_{O^{2-}} = \frac{D_{amb} c_{O^{2-}}}{2kT} \frac{\Delta\mu_{O_2}}{L} = \frac{\sigma_{amb}}{8e^2} \frac{\Delta\mu_{O_2}}{L} \quad (7.69)$$

and, by rearrangement, the chemical potential drop over the bulk of the membrane is

$$\Delta\mu_{O_2} = \frac{-2j_{O^{2-}}kTL}{D_{amb}c_{O^{2-}}} = \frac{-j_{O^{2-}}8e^2L}{\sigma_{amb}} \quad (7.70)$$

This drop over the membrane bulk is given by the external full gradient minus the losses at the interfaces. In the present terms, the flux through an interface is, from Eqs. 7.62 and 7.65 given by

$$j_{O^{2-}} = \frac{-c_{O^{2-}}k_i\Delta\mu_{O_2}^{interface}}{2kT} = \frac{-\Delta\mu_{O_2}^{interface}}{8e^2R_e} \quad (7.71)$$

such that, by rearrangement,

$$\Delta \mu_{O_2}^{interface} = \frac{-2 j_{O_2} kT}{k_i c_{O_2}} = -j_{O_2} 8 e^2 R_e \quad (7.72)$$

Now, we sum up the total gradient in chemical potential of oxygen over the bulk of the membrane and the two interfaces

$$\Delta \mu_{O_2}^{tot} = \Delta \mu_{O_2}^{bulk} + 2\Delta \mu_{O_2}^{interface} \quad (7.73)$$

and after insertion of the above expressions for bulk and interface, we can solve for the flux of oxygen ions through a membrane with two equally contributing interfaces under the conditions given:

$$j_{O_2} = \frac{-\Delta \mu_{O_2}^{tot} c_{O_2} / 2kT}{\frac{L}{D_{amb}} + \frac{2}{k_i}} = \frac{-\Delta \mu_{O_2}^{tot} / 8 e^2}{\frac{L}{\sigma_{amb}} + 2 R_e} \quad (7.74)$$

This result simply states that the flux is given by the driving force (which easily transforms to Nernst voltage) divided by the total ambipolar resistance, in our case namely that of the bulk and twice that of one interface.

In lack of full understanding of the relations involved in interface kinetics of membranes, we may refer to a critical thickness; the thickness of the bulk membrane where the interface and bulk impose equally large restrictions on the flux. In any membrane application, going much below this thickness is not of much use. We see from the above that this thickness is $L_{crit}=D/k$ for the thickness of the part of a membrane relating to one interface, or $L_{crit}=2D/k$ for thickness of a membrane with two equally limiting interfaces, typically the two surfaces.

Experimentally the value of L_{crit} has been found to be of the order of 100 μm for many polished samples of different fluorite and perovskite materials, indicating that there is a close relationship between e.g. vacancy concentration in bulk and the surface exchange. Roughing the surface should increase relatively the surface flux, and this has been shown to work.

Ionic transport of both anions and cations

General expressions

We have in the previous section considered ionic transport by oxygen ions (anions) only. This was done for simplicity, because it represents many real applications, and because oxygen ions relate most directly to the oxygen (non-metal) activity which we may control most conveniently.

Now we will include cation (metal ion) transport. Some systems have predominant transport of cations, and we thus need to see how this relates this to the non-metal activity. Some systems have both anion and cation transport so we need to take both into account. In some cases we may not know which one is dominating and as we shall see it is not always easy or necessary to distinguish them.

In an inorganic compound the total ionic current density, i_{ion} , is given by the sum of the current densities of anions, i_{an} , and the cations, i_{cat} . From our previously derived expressions for partial current densities we thus obtain

$$i_{ion} = i_{an} + i_{cat} = z_{an} e j_{an} + z_{cat} e j_{cat} = \frac{-\sigma_{an}}{z_{an} e} \frac{d\eta_{an}}{dx} + \frac{-\sigma_{cat}}{z_{cat} e} \frac{d\eta_{cat}}{dx} \quad (7.75)$$

where z_{an} and z_{cat} represent the valences and thus ionic charges of the anions and cations, respectively.

In order to relate the current density of the cations and anions let us consider the equilibrium involving the formation of the compound $M_a O_b$ from its ions:



Through the Gibbs-Duhem relation, equilibrium in this reaction may be expressed as

$$a d\mu_{M^{z_{cat}}} + b d\mu_{O^{z_{an}}} = d\mu_{M_a O_b(s)} \quad (7.77)$$

The fact that $d\mu_{M_aO_b(s)} = 0$ arises from $M_aO_b(s)$ being a pure condensed phase. It may further be noted that

$$az_{cat} = -bz_{an} \quad (7.78)$$

so that we obtain the very important expression

$$\frac{d\mu_{cat}}{dx} = -\frac{b}{a} \frac{d\mu_{an}}{dx} = \frac{z_{cat}}{z_{an}} \frac{d\mu_{an}}{dx} \quad (7.79)$$

From this we note that the cation and anion chemical potential gradients are the negative of each other in a binary compound, a relation that is used extensively, mathematically or by intuition.

By adding $z_{cat}e \frac{d\phi}{dx}$ to both sides of the equation and rearranging on the right hand side we obtain

$$\frac{d\eta_{cat}}{dx} = \frac{z_{cat}}{z_{an}} \frac{d\eta_{an}}{dx} \quad (7.80)$$

By combining Eqs 7.75. and 7.80 the total ionic conductivity may be expressed by

$$i_{ion} = \frac{\sigma_{ion}}{z_{cat}e} \frac{d\eta_{cat}}{dx} = \frac{\sigma_{ion}}{-z_{an}e} \frac{d\eta_{an}}{dx} \quad (7.81)$$

Thus, the ionic current density can be expressed in terms of the ionic conductivity (sum of cationic *and* anionic conductivities) and the gradient in the chemical potential of cations *or* anions.

From this it becomes clear that the derivations of oxygen ion fluxes and currents in various situations done earlier could have been done for the case of ions (sum of cations and

anions) simply by inserting σ_{ion} instead of $\sigma_{O^{2-}}$, but with for instance the oxygen activity gradient as the driving force.

Membrane "walk-out"

Metal ions are transported from the low oxygen pressure to the high oxygen pressure side of the membrane while metal vacancies are transported in the opposite direction. During the process oxygen is liberated and oxygen and metal sites are annihilated at the low oxygen pressure side, e.g. for a metal deficient oxide $M_{1-\delta}O$ with doubly charged metal vacancies:



while equivalent number of lattice sites are formed at the high oxygen pressure side:



In this way the oxide membrane is actually moving in laboratory space in the direction of the higher oxygen potential.

From this we see that even a very minor transport of metal ions may be detrimental to the operation of an oxygen separation membrane or fuel cell: Over the many years of operation the electrolyte or membrane will simply "walk out" of its housing, towards the high oxygen pressure.

Demixing of oxide solid solutions

An additional important aspect of diffusional transport of metal ions in a chemical potential gradient is that in a homogeneous crystal of an oxide solution, e.g. $(A,B)_{1-\delta}O$ such as for instance $(Co,Ni)_{1-\delta}O$, a demixing process begins to take place. Both cations move by vacancy diffusion. When one of the cations in $(A,B)_{1-\delta}O$, e.g. A^{2+} , has a higher mobility than the other, the A^{2+} ions will move faster to the side of the higher oxygen potential. The solid solution is enriched in AO at this side and thus becomes kinetically demixed. After extended time a steady state concentration profile is reached. This can be formulated through the use of the appropriate

transport equations and by taking into account the conditions of electroneutrality and of local thermodynamic equilibrium. The process is schematically illustrated below.

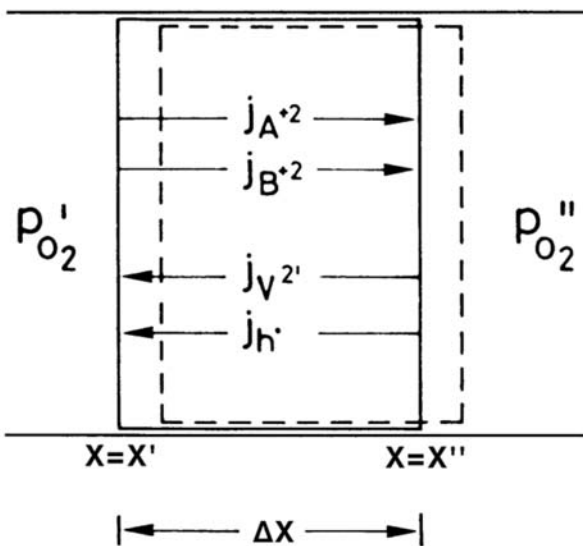


Figure 7-1. Schematic illustration of kinetic demixing of the oxide solid solution $(A,B)_{1-\delta}O$ in an oxygen potential gradient.

Multicomponent compounds, e.g. ABO_3 and AB_2O_4 , can similarly be demixed in an oxygen potential gradient. In this case defects are formed due to the nonstoichiometric A/B ratio. Both in the case of the solid solution and in the case of a ternary oxide, new phases may be precipitated as soon as the concentration of solute or defects exceeds the solubility limit. We may in fact end up in the peculiar situation that the starting oxide is stable in both the low and the high oxygen activities separately, but unstable in the gradient between them.

The decomposition and precipitation of new phases may violate the functional or mechanical properties of the material. These types of phenomena are not only of importance in oxide membranes, but also in oxidation of alloys where solid solutions of two or more oxides or multicomponent compounds may be formed in the oxide scales.

High temperature oxidation of metals; the Wagner oxidation theory

When high temperature oxidation of metals results in the formation of compact scales and sufficient oxygen is available at the oxide surface, the rate of reaction is governed by the solid

state diffusion of the reactants or transport of electrons through the scale. As the diffusion distance increases as the oxide grows in thickness, the rate of reaction decreases with time. When the diffusion takes place homogeneously through the scale, the rate of growth of the oxide thickness, x , is inversely proportional to the oxide thickness:

$$\frac{dx}{dt} = k_p^* \frac{1}{x} \quad (7.84)$$

In the integrated form this becomes

$$x^2 = 2k_p^* t + C_0 = k_p t + C_0 \quad (7.85)$$

where $k_p (= 2k_p^*)$ and k_p^* are expressions for the rate constants and C_0 is an integration constant.

The oxide thickness may alternatively be measured in terms of the oxygen uptake by the metal specimen during oxidation by using, for instance, thermogravimetry. The oxide thickness or oxygen uptake is parabolic with time, and the oxidation is termed parabolic. Accordingly k_p and k_p^* are termed parabolic rate constants. The figure below illustrates the variation in the oxide thickness or oxygen uptake as a function of time.

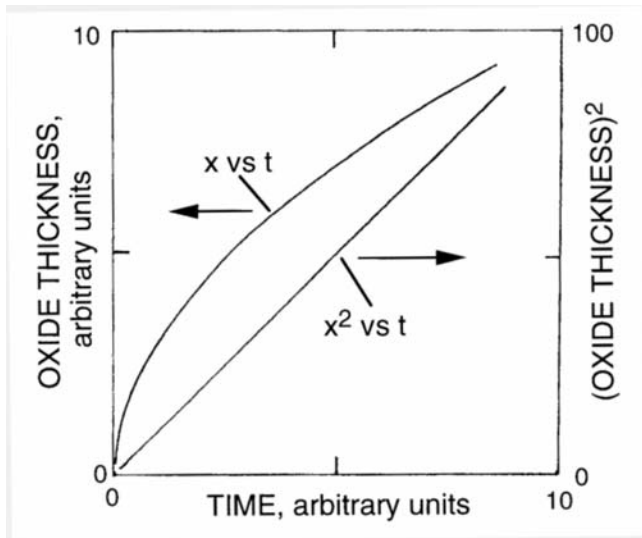


Figure 7-2. The variation in oxide thickness as a function of time (x vs t and x^2 vs t) during parabolic oxidation of metals

Carl Wagner developed the theory for parabolic oxidation assuming that the reaction is governed by lattice diffusion of the reacting ions (metal and oxygen ions) or transport of electrons. The important aspect of the Wagner oxidation theory is that the parabolic rate constant is expressed in terms of independently measurable properties, i.e. the electronic and ionic conductivity of the oxide or alternatively in terms of the self-diffusion coefficients of the reacting ions. This thus provides an interpretation of the reaction mechanism and a theoretical basis for changing and improving the oxidation resistance of metals and alloys. The Wagner theory has been one of the most important contributions to our understanding of the high temperature oxidation of metals.

The basic assumption of the theory is that the lattice diffusion of the reacting ions or the transport of electrons through the dense scale is rate-determining for the overall reaction. Lattice diffusion is assumed to take place because of the presence of point defects, and the migrating species may alternatively be considered to constitute lattice and electronic defects. Wagner further assumed that ions and electrons migrate independently of each other and that local equilibria exist within the oxide. Such transport processes through a dense, single-phase scale growing by lattice diffusion is illustrated in the figure below. One part (a) illustrates the transport of metal and oxygen ions and electrons, while the other (b) illustrates the transport processes when the predominant diffusion processes involve metal vacancies and interstitials.

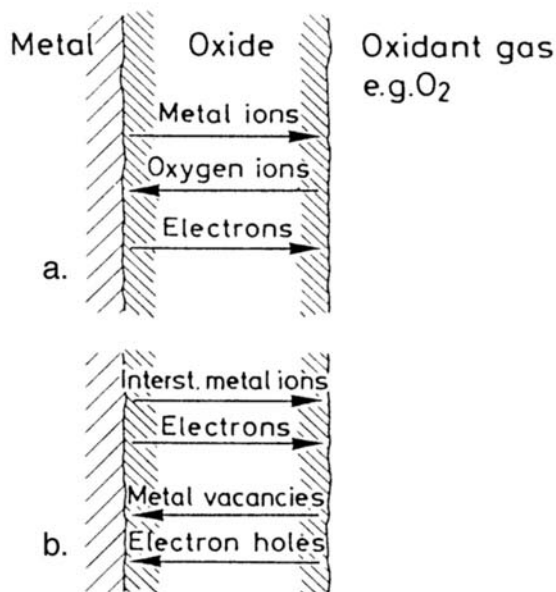


Figure 7-3. Transport processes during growth of a dense, single phase scale growing by lattice diffusion. a) transport processes illustrated by transport of reacting ions, b) transport processes illustrated by transport of diffusion of important point defects (in this case assumed to be metal vacancies and interstitials).

As diffusion through the scale is rate-determining, reactions at the phase boundaries are considered to be rapid, and it is assumed that thermodynamic equilibria are established between the oxide and oxygen gas at the oxide/oxygen interface and between the metal and the oxide at the metal/oxide interface.

The overall "driving energy" of the reaction is the Gibbs free energy change associated with the formation of the oxide, e.g. M_aO_b , from the metal M and the oxygen gas. Correspondingly, a gradient in the partial pressure (activity) of oxygen exists across the scale from the partial pressure of oxygen in the ambient atmosphere at the outer surface to the partial pressure of oxygen at the metal/oxide interface. The latter partial pressure is the decomposition pressure of the oxide in equilibrium with its metal.

The main driving force for the transport through the plane is the chemical potential gradient. But when one considers the transport of the reacting ions and of the electrons through the scale, it may also be noted that the mobilities of the cations, anions and electrons are not equal. Because of this difference, a separation of charges takes place in a growing scale. This creates a space charge (diffusion potential) that opposes a further separation of charges, and a stationary state is reached for which no net electric current flows through the scale. In describing the transport of ions and electrons through the scale, it is thus necessary to take into account both the transport due to the gradient of the chemical potential and that due to the gradient of the electrical potential, i.e. the electrochemical potential gradient. Thus, the treatment of the transport through the oxide scale is identical to that done earlier for electrochemical transport through a mixed conducting oxide.

The net ionic current is from earlier given by

$$i_{ion} = -\frac{\sigma_{ion}}{z_{an}e} \frac{d\eta_{an}}{dx} = \frac{\sigma_{ion}}{2e} \frac{d\eta_{O^{2-}}}{dx} \quad (7.86)$$

and the electronic current is given by

$$i_{el} = -\frac{\sigma_{el}}{-1e} \frac{d\eta_{el}}{dx} = \frac{\sigma_{el}}{e} \frac{d\eta_{el}}{dx} \quad (7.87)$$

As no net current flows through the scale during the scale growth, then $i_{tot} = i_{ion} + i_{el} = 0$. By solving this system in the usual manner (solving for the electrical potential gradient, inserting into the expression for the ionic current density and inserting the equilibrium condition between oxygen ions, oxygen molecules and electrons) we obtain

$$i_{ion} = \frac{\sigma_{ion} t_{el}}{4e} \frac{d\mu_{O_2(g)}}{dx} = \frac{\sigma_{ion} t_{el} kT}{4e} \frac{d \ln p_{O_2}}{dx} \quad (7.88)$$

The rate of oxygen ions reacting per unit area is obtained by dividing the ionic current density by the charge of the oxygen ions. Moreover, the rate dn/dt of oxide molecular units M_aO_b formed per unit area is obtained by further division by b :

$$\frac{dn}{dt} = \frac{1}{b} \frac{dn_{O_2}}{dt} = \frac{i_{ion}}{-2eb} = -\frac{\sigma_{ion} t_{el}}{8e^2 b} \frac{d\mu_{O_2(g)}}{dx} = -\frac{\sigma_{ion} t_{el} kT}{8e^2 b} \frac{d \ln p_{O_2}}{dx} \quad (7.89)$$

Similar to the integrations we have done earlier over the thickness of the oxide, we now integrate over the instantaneous thickness Δx and from the ambient oxygen pressure, $p_{O_2}^0$, to the partial pressure at the metal/oxide interface, $p_{O_2}^i$. The growth rate $\frac{dn}{dt}$ then takes the form

$$\frac{dn}{dt} = \left\{ \frac{kT}{8e^2 b} \int_{p_{O_2}^i}^{p_{O_2}^0} \sigma_{ion} t_{el} d \ln p_{O_2} \right\} \frac{1}{\Delta x} \quad (7.90)$$

We have chosen to organize the equation and direction of integration such that the rate is positive if $p_{O_2}^0 > p_{O_2}^i$. In general the directionalities and signs of the fluxes and processes that go on pose a problem for us. One may most often neglect this issue because the output, namely growth (increase in amount of oxide or thickness of scale) is intuitively positive. However, it may not be just that easy, since there is nothing preventing scale reduction (reverse of growth) if the outer oxygen partial pressure is smaller than the activity at the metal/oxide.

Many readers will probably wonder about another small apparent problem: We integrate over the scale to take into account the steady state condition, namely that the fluxes are constant throughout the scale. Still, the scale grows, so how can it be steady state? The answer is that it is

steady state (constant fluxes) for that moment of time with that instantaneous thickness of the scale. So our integration is for a given moment in time. At another moment the integration will give a different flux.

The expression in the parentheses, $\left\{ \frac{kT}{8e^2b} \int_{p_{O_2}^i}^{p_{O_2}^o} \sigma_{ion} t_{el} d \ln p_{O_2} \right\}$, can be considered to be one

form of the parabolic rate constant and is in the following written k_t :

$$\frac{dn}{dt} = k_t \frac{1}{\Delta x} \quad (7.91)$$

k_t thus represents a time-independent coefficient, while the flux and thickness of the scale vary according to the parabolic relation above.

As written in this form $\frac{dn}{dt}$ is expressed in number of molecular units of M_aO_b per cm^2sec and Δx in cm. The derivation of Wagner's equation that we here have done for growth of oxide scales, may be applied to many other gas-metal reactions.

It may be noted that although the total particle current is equal to the rate of growth of the scale, the rate-determining process may either be diffusion of ions or transport of electrons depending on the properties of the scales. If the scale is an electronic conductor, $t_{el} \approx 1$, the diffusion of the reacting ions through the scale is rate-determining, while the transport of electrons through the scales is rate-determining if the scale is an ionic conductor, $t_{ion} \approx 1$. The oxygen pressure dependence of the reaction will depend on whether the scale is an ionic or electronic conductor and in the latter case on the type of nonstoichiometry that prevails in the oxide scale.

In our derivation, the growth rate is proportional to $\sigma_{ion} t_{el} = \sigma_{tot} t_{ion} t_{el} = (\sigma_{an} + \sigma_{cat}) t_{el}$. However, the conductivity of the metal and oxygen ions in M_aO_b can be expressed in terms of the self-diffusion coefficients of the metal and oxygen ions in M_aO_b through the Nernst-Einstein relation ($z_i^2 e^2 D_i c_i = kT \sigma_i$). Let us insert this relationship in Eq. 7.89 and assume that the oxide is an electronic conductor ($t_{el} \approx 1$). Let us furthermore take into account that concentrations of metal ions (cations), c_M , and oxygen ions, c_O , in an oxide M_aO_b with relatively small deviation from stoichiometry are related through $c_M/c_O = a/b = |z_{an}|/z_{cat}$. The expressions for the flux through the growing scale (expressed in terms of the number of M_aO_b units per cm^2sec .) and for k_t then become

$$\frac{dn}{dt} = -\frac{c_O z_{an}^2}{8b} \left(\frac{z_{cat}}{|z_{an}|} D_M + D_O \right) \frac{d \ln p_{O_2}}{dx} = -\frac{c_O}{2b} \left(\frac{z_{cat}}{2} D_M + D_O \right) \frac{d \ln p_{O_2}}{dx} \quad (7.92)$$

$$\frac{dn}{dt} = \left\{ \frac{c_0}{2b} \int_{p_{O_2}}^{p_{O_2}^0} \left(\frac{z_{cat}}{2} D_M + D_O \right) d \ln p_{O_2} \right\} \frac{1}{\Delta x} = k_t \frac{1}{\Delta x} \quad (7.93)$$

c_O denotes the number of oxygen ions in M_aO_b per cm^3 and D_M and D_O are respectively the self-diffusion coefficients of the metal and oxygen ions in M_aO_b . It should be noted that D_M and D_O are the self-diffusion coefficients for random diffusion of the respective ions.

In Eqs. 7.92 and 7.93, k_t represents the rate of formation of M_aO_b units per cm^2 per second for an M_aO_b scale of thickness 1 cm. One may as said before alternatively express the parabolic rate constant in terms of the rate of growth of the oxide thickness

$$\frac{dx}{dt} = k_p^* \frac{1}{x} \quad (7.94)$$

The dimensions of k_p^* are then $\text{cm}^2\text{sec}^{-1}$, and Eq. 7.93 then takes the form

$$\frac{dx}{dt} = \frac{b}{c_0} \frac{dn}{dt} = \left\{ \frac{1}{2} \int_{p_{O_2}}^{p_{O_2}^0} \left(\frac{z_{cat}}{2} D_M + D_O \right) d \ln p_{O_2} \right\} \frac{1}{\Delta x} = k_p^* \frac{1}{\Delta x} \quad (7.95)$$

Growth of metal-deficient $M_{a-y}O_b$ on M

Let us make use of Eq. 7.95 to illustrate the temperature and oxygen pressure dependence of the parabolic rate constant. Consider the growth of the metal deficient oxide $M_{a-y}O_b$ on high purity M. Let us assume that the predominant defects throughout the entire scale are metal vacancies with an effective charge α , i.e. $V_M^{\alpha'}$. Let us further assume that the metal ion diffusion is much faster than the oxygen diffusion, i.e. $D_M \gg D_O$. Eq. 7.95 then reduces to

$$\frac{dx}{dt} = \left\{ \frac{z_{cat}}{4} \int_{p_{O_2}}^{p_{O_2}^0} D_M d \ln p_{O_2} \right\} \frac{1}{\Delta x} = k_p^* \frac{1}{\Delta x} \quad (7.96)$$

In order to integrate this we need to analyse the defect structure of the oxide. The formation of the metal vacancies may be written as



If other defects may be neglected and the electroneutrality condition is given by $\alpha[V_M^{\alpha'}] = p$, the concentration of metal vacancies is given by

$$\alpha[v_M^{\alpha'}]^{\alpha+1} = K_{V_M^{\alpha'}} p_{O_2}^{b/2a} \quad (7.98)$$

where $K_{V_M^{\alpha'}}$ is the equilibrium constant for the formation of the metal vacancies (Eq. 7.97) and $[v_M^{\alpha'}]$ denotes the fraction of the metal ion sites that are vacant. On the basis of this relation, $d \ln p_{O_2}$ may be written

$$d \ln p_{O_2} = \frac{2a(\alpha+1)}{b} d \ln[v_M^{\alpha'}] \quad (7.99)$$

When this expression for $d \ln p_{O_2}$ is introduced in Eq. 7.96, the expression for k_p^* becomes

$$k_p^* = (\alpha+1) D_{v_M^{\alpha'}} \{ [v_M^{\alpha'}]^0 - [v_M^{\alpha'}]^i \} \quad (7.100)$$

If the concentration of metal vacancies at the oxide/oxygen interface is much larger than at the metal/oxide interface, i.e. $[v_M^{\alpha'}]^0 \gg [v_M^{\alpha'}]^i$ then

$$k_p^* = (\alpha + 1)D_{v_M^{\alpha'}} [v_M^{\alpha'}]^0 = (\alpha + 1)D_M^o \quad (7.101)$$

where $D_M^o = D_{v_M^{\alpha'}} [v_M^{\alpha'}]^0$ is the self-diffusion coefficient of the metal ions in $M_{a-y}O_b$ at the oxide/oxygen interface. Thus under these conditions the parabolic rate constant and the self-diffusion coefficient of M in $M_{a-y}O_b$ has the same temperature and oxygen pressure dependences.

Growth of oxygen-deficient M_aO_{b-y} on M

The same procedure may be used to derive the parabolic rate constant for the growth of oxygen deficient M_aO_{b-y} on M. let us assume that the oxygen vacancies have α charge α , i.e. $V_O^{\alpha'}$, and the formation of the oxygen vacancies may then be written



If $D_O \gg D_M$ and $(p_{O_2}^i \ll p_{O_2}^o)$ then k_p^* becomes

$$k_p^* = (\alpha + 1)D_{v_O^{\alpha'}} [v_O^{\alpha'}]^i = (\alpha + 1)D_O^i = (\alpha + 1)D_O^0 (p_{O_2}^i)^{\frac{-1}{2(\alpha+1)}} \quad (7.103)$$

where $D_{v_O^{\alpha'}}$ is the self-diffusion coefficient of the oxygen vacancies, $[v_O^{\alpha'}]^i$ the concentration of oxygen vacancies and D_O^i the self-diffusion coefficient of oxygen in M_aO_{b-y} at the metal/oxide interface. D_O^0 is the oxygen self-diffusion coefficient at 1 atm. O_2 , and $p_{O_2}^i$ is the oxygen activity at the metal/oxide interface. For this case the parabolic rate constant is independent of the ambient oxygen pressure, and the temperature dependence is given by that of the oxygen self-diffusion coefficient in M_aO_{b-y} at the metal/oxide interface. In this respect it may be further noted that the oxygen self-diffusion coefficient at the metal/oxide interface is given by that the product of the self-diffusion coefficient of oxygen at constant oxygen pressure (at 1 atm O_2) and $(p_{O_2}^i)^{-1/2(\alpha+1)}$, i.e. $D_O^i = D_O^0 (p_{O_2}^i)^{-1/2(\alpha+1)}$. In these terms the activation energy of the parabolic rate constant is under these conditions given by the activation energy associated with

D_{O^0} and the enthalpy term associated with $(p_{O_2}^i)^{-1/2(\alpha+1)}$. Similar treatments may be given for oxide scales growing by interstitial metals ions or interstitial oxygen ions.

Scales with ionic conductivity predominant.

Most oxides encountered in high temperature oxidation of metals are electronic conductors. In the literature there are no examples of high temperature metal-oxygen reactions involving conventional metals or alloys with essentially pure ionic conductivity over the entire existence range of the oxide. Such type of reactions are, however, found in metal-halogen reactions, e.g. $Ag+Br_2$ to form $AgBr$. The same treatment as given above may be applied to reactions involving formation of ionically conducting scales, and the important feature of these reactions is that it is the electronic transport through the scale that is rate-determining.

Varying defect structure situations through the scale.

In the preceding examples it has been assumed that the same defect structure prevails throughout the entire scale from the scale/gas to the metal oxide interfaces. This is an oversimplified model for many systems. The charge on the defects, or even the predominant defects may change with changing oxygen activity. Furthermore, the presence of impurities and dopants may significantly affect the defect structure situation. Thus, following the discussion in Ch.4 one part of the scale may possibly have intrinsic properties and another part extrinsic properties. As part of such behaviour one part of the scale may have significant ionic conductivity while the rest has electronic conductivity.

In the presence of water vapour, hydrogen defects may affect the diffusional behaviour in growing oxide scales in many different ways.

Diffusion–limited creep

General terms and mechanisms

Creep represents plastic deformation of solids under an applied stress. At high temperatures and under constant applied stress, a steady state is reached (secondary creep stage) where the rate of deformation remains constant. The steady state creep rates of crystalline solids can be expressed by the equation

$$\varepsilon = f(s) \sigma_{\text{str}}^n \exp(-Q/RT) \quad (7.104)$$

where $f(s)$ is a function which is dependent upon the structure, σ_{str} is the applied stress, n is a constant and Q the activation energy.

Several mechanisms based on diffusion controlled processes have been proposed to explain experimentally observed creep behaviour: the Nabarro-Herring and Coble mechanisms, grain boundary sliding, and dislocation movements. The Nabarro-Herring mechanism applies to low stress levels at high temperatures. It is based on the assumption of stress-directed lattice diffusion of solids. If this takes place by the vacancy mechanism, the vacancies diffuse from regions under tension to regions under compressive stress. This is illustrated schematically in the figure below. If the diffusion takes place by interstitial defects, the defects move in the opposite direction.

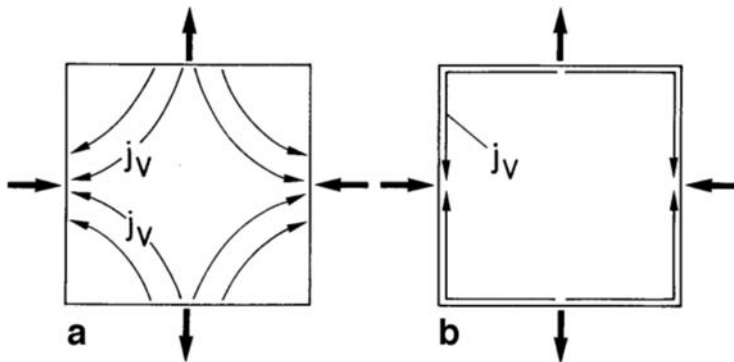


Figure 7-4. Vacancy fluxes in single grains due to imposed stresses: a) through vacancy lattice diffusion (Nabarro-Herring creep; b) through diffusion along grain boundaries (Coble creep)

Creep in an elemental solid

The theory predicts that the tensile strain rate due to creep under a tensile stress σ is given by

$$\varepsilon = K \frac{\Omega D_1 \sigma}{kT g^2} \quad (7.105)$$

where K is a geometrical constant, Ω is the atomic volume, D_l is the lattice self-diffusion coefficient, g is the length of the diffusion path (i.e. the average grain size), k is the Boltzmann constant and T the absolute temperature. The Nabarro-Herring creep rate is thus proportional to the stress and the activation energy is equal to that for the self-diffusion.

In polycrystalline solids the defects (or atoms) can migrate by both lattice and grain boundary diffusion and as discussed in Chapter 5 the effective diffusion coefficient may be written

$$D_{\text{eff}} = D_l + \frac{3\delta D_{\text{gb}}}{g} \quad (7.106)$$

If this value for D_{eff} is substituted for the lattice diffusion coefficient, D_l , the creep rate becomes

$$\varepsilon = K \frac{W s}{kT g^2} \left(D_l + \frac{3\delta}{g} D_{\text{gb}} \right) \quad (7.107)$$

If lattice diffusion is negligible compared with grain boundary diffusion, this reduces to

$$\varepsilon = K \frac{3\Omega \sigma}{kT g^3} \delta D_{\text{gb}} \quad (7.108)$$

This mechanism was first proposed by Coble, and it is illustrated schematically in Fig.7.8b. Also in this case the strain rate is proportional to the stress. Both the Nabarro-Herring and Coble mechanisms are favoured by small grain sizes.

Creep in compounds

In a compound, e.g. an oxide M_aO_b , the creep process is more complicated in that both metal and oxygen atoms (or ions) must migrate in order to conserve electroneutrality and

maintain local composition of the oxide. Thus the fluxes of the metal and oxygen ions are coupled, and one must consider the flow of "molecular units" of M_aO_b . The molecular diffusion coefficient D_{mol} is a composite value of the self-diffusion of the metal and oxygen ions and is given by

$$D_{mol} = \frac{D_M D_O}{aD_O + bD_M} \quad (7.109)$$

In the expressions for the creep rates, the molecular volume must be substituted for the atomic volume:

$$\Omega_{mol} = a\Omega_M + b\Omega_O \quad (7.110)$$

The value of D_{mol} may be expressed either in terms of the lattice self-diffusion coefficients for metal and oxygen ions for Nabarro-Herring creep or in terms of D_{eff} for creep taking place by simultaneous lattice and grain boundary diffusion.

From Eq. 7.109 it is seen that the creep rate is governed by the diffusion of the slower moving species. Thus, if metal ions diffuse much faster than the oxygen ions, $D_M \gg D_O$, then

$$D_{mol} = \frac{1}{b} D_O \quad (7.111)$$

and accordingly the creep rate is determined by the diffusion of oxygen atoms in M_aO_b . A meaningful interpretation of the creep behaviour in terms of the diffusion processes thus requires knowledge of the self-diffusion of both components in the binary compound.

In addition to the above models other creep mechanism have been advanced based on dislocation movements in the material.

Sintering

Stages of the sintering process

Sintering is the process whereby powders and small particles agglomerate and grow together to form a continuous polycrystalline body. As a rule of thumb the material must be heated to $2/3$ of the melting temperature to achieve considerable sintering.

The overall sintering process may conveniently be divided into different stages. The principal stages involved is illustrated schematically below.

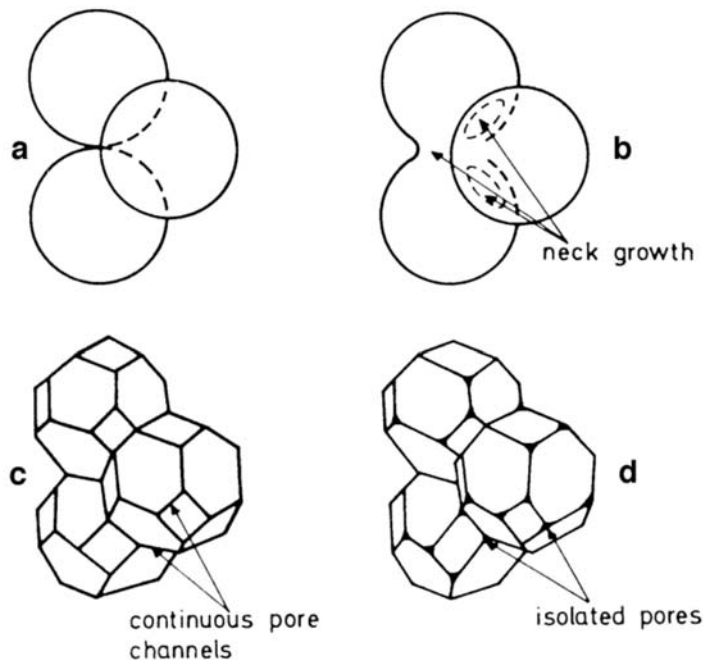


Figure 7-5. Principle stages during the sintering process: a) particles in contact prior to sintering; b) neck growth between particles during initial stage of sintering; c) further neck growth and formation of continuous pore channels along grain boundaries; and d) further sintering in closing channels and formation of closed pores at grain corners.

During an initial stage the surface roughness is decreased and the particles begin to adhere and grow together. At the end of this stage grain growth begins to occur and grain boundaries and metastable pore phase is established. Only modest shrinkage of a few percent takes place during the initial stage.

During an intermediate stage grain growth continues, and the cross-sectional area of the pore phase decreases. The final stage begins when the body achieves 90-95% theoretical density. At this point the pore phase becomes discontinuous, and the closed pores usually remain at grain

boundaries. The final stage may involve complete removal of the remaining pores, leading to a completely dense material. Alternatively, it may involve discontinuous growth of the large grains at the expense of the small ones, and closed pores may as a consequence be isolated inside the grains. If the latter process occurs, complete densification becomes extremely difficult.

Driving force for sintering

During sintering, as for other spontaneous processes, the total free energy of the system decreases. For elemental solids and homogeneous compounds the only free energy change involved in sintering is that of the surface free energy or surface tension, γ , of the particles.

Any surface atom or molecule is subjected to a resultant inward attraction because of the unsaturated chemical bonds at the surface. The surface therefore tends to contract to the smallest possible area. In the case of a spherical particle with radius r , the interior is subjected to an excess force of $\pi r^2 p$, where p is the pressure. This is counteracted by the surface tension acting along the circumference: $2\pi r\gamma$. When equating these opposing forces, the pressure is given by

$$p = \frac{2\pi r\gamma}{\pi r^2} = \frac{2\gamma}{r} \quad (7.112)$$

From this it is seen that the vapour pressure of a sphere is larger the smaller the radius and as a result a large sphere will grow at the expense of a neighbouring small sphere. This type of grain growth in polycrystalline solids is termed Ostwald's law. Similarly the vapour pressure of convex surfaces is larger than the vapour pressure of a concave surface and as a result surface roughness of particles is reduced during the initial stage of sintering.

Transport processes during sintering

As for creep, sintering of oxides implies that molecular units of the oxide are transported from areas from high to low surface free energies, e.g. from convex to concave surfaces. Generally it is concluded that transport of the slower moving species determines the overall sintering rate. Thus, in a binary oxide where oxygen ions diffuse much more slowly than the metal ions, it is generally to be expected that the sintering rate is determined by the transport, e.g. lattice or grain boundary diffusion of oxygen.

Sintering governed by lattice diffusion will be dependent upon the concentration of point defects in oxides. Accordingly, sintering rates of an oxide can be optimised by close control of impurities or dopants and the ambient partial pressures of oxygen and of water vapour in cases where proton defects affect the defect structure of the oxide.

Oxides with additional transport of protons

If an oxidic material conducts protons in addition to oxygen ions and electrons we need to introduce electrochemical equilibria between neutral and charged species of both oxygen and hydrogen:



for which equilibria can be expressed by

$$d\mu_{O_2(g)} + 4d\mu_{e^-} = 2d\mu_{O^{2-}} \quad (7.115)$$

$$d\mu_{H_2(g)} = 2d\mu_{H^+} + 2d\mu_{e^-} \quad (7.116)$$

We insert these into the flux equations for the species and utilise that the sum of all transport numbers equals unity. We furthermore use that $d\mu = kT d \ln a \approx kT d \ln p$, where a and p are activity and partial pressure, respectively, and obtain

$$\frac{d\phi}{dx} = -\frac{i_{tot}}{\sigma_{tot}} + \frac{t_{O^{2-}} kT}{4e} \frac{d \ln p_{O_2}}{dx} - \frac{t_{H^+} kT}{2e} \frac{d \ln p_{H_2}}{dx} + \frac{1}{e} \frac{d \mu_e}{dx} \quad (7.117)$$

This can now be integrated to obtain the voltage of a cell, or inserted into a flux equation of a species of interest in the usual manner. We now have a system with two chemical driving forces for electrochemical transport; that of oxygen activity and that of hydrogen activity.

Other cases

We have in the present version of the treatment of electrochemical transport omitted many cases. These include a more full coverage of proton transport in oxides and transport by other hydrogen species and other foreign species. Moreover, we have left out the case of solid-solid reactions. Also, creep and sintering were given more phenomenological than defect-chemical treatments.

We have throughout assumed isothermal conditions. If we instead of (or in addition to) chemical driving forces considered a temperature gradient, our integrations over membranes would have been from one temperature to another. The voltage we would have obtained would be the thermoelectric voltage. It has several contributions, but in general it is related to the transport numbers and the gradients in concentrations of defects. The variations of concentration is in turn given by the entropy of the defects.

More on these themes will be included in future updates.

