EXERCISES KJM5120

Chapter 5; Diffusion

1. Random (self) diffusion

a) The self-diffusion coefficient of a metal with cubic structure can be expressed as

$$D = \frac{1}{6}\frac{n}{t}s^2$$

where n/t represents the jump frequency (i.e. number of jumps n over a time t). Close to the melting point most fcc and bcc metals have $D \approx 10^{-8}$ cm^2/s.
i) If the jump distance is 3 Å, what is the jump frequency near the melting point?
ii) What is the relation between this frequency and the vibrational frequency?
iii) How far has one atom traveled after 1 hour?
iv) What is the root mean square displacement after one hour?
v) What is the root mean square displacement in one dimension after one hour?

b) For a metal with cubic structure the diffusion coefficient can also be expressed as

$$D = \alpha a_0^2 \varpi N_d$$

where α is a geometric factor, a_0 the lattice constant, ω is the jump frequency, and N_d is the defect concentration. Derive the value for α for vacancy diffusion in a metal with fcc structure.

Chapter 6; Electrical conductivity

1. Cobalt oxide: The electronic conductivity of $Co_{1-y}O$ at 1350°C and $p_{O2} = 0.1$ atm is 25 S/cm. Thermogravimetric measurements show that y = 0.008 under the same conditions. It is assumed that singly charged cobalt vacancies are the dominating point defects. Identify the charge carriers responsible for the conductivity and calculate their charge mobility. (Assume that the density of CoO at 1350°C equals that at room temperature, 6.4 g/cm^3. Atomic weights $M_{Co} = 58.93$, $M_O = 16.00$.)

2. Nickel oxide: Assume that doubly charged nickel vacancies and electron holes are the dominating defects in $Ni_{1-y}O$ under oxidising conditions. At 1245°C and $p_{O2} = 1$ atm we know the following for the compound:

The self diffusion coefficient for nickel: $D_{Ni} = 9*10^{-11}$ cm^2/s
Electrical conductivity: $\sigma = 1.4$ S/cm
(Data from M.L. Volpe and J. Reddy, *J. Chem. Phys.*, **53** (1970) 1117.)

Nickel vacancy concentration, in site or mole fraction: $[v_{Ni}''] = 2.5*10^{-4}$
(Data from W.C. Tripp and N.M. Tallan, *J. Am. Ceram. Soc.,* **53** (1970) 531.)

i) Calculate the concentration of electron holes under the given conditions, given as site fraction and as volume concentration (e.g. number/cm^3). (Atomic weights M_{Ni} = 58.71, M_O = 16.00, density of NiO = 6.67 g/cm^3.)

ii) Calculate the charge mobility of the electron holes.

iii) Calculate the diffusion coefficient of nickel vacancies.

iv) Calculate the charge mobility of the nickel vacancies and the ionic conductivity under the conditions referred to above.

3. Ca-stabilised ZrO_2 (CSZ)

We shall here consider a densely sintered ZrO_2 doped with 15 mol% CaO ($Zr_{0.85}Ca_{0.15}O_{1.85}$).

i) Assume that the oxide contains doubly charged oxygen vacancies compensating the Ca dopant. What are the site-fractions of dopants and of oxygen vacancies?

ii) Derive equations showing how the minority concentrations of defect electrons and electron holes vary with p_{O2} in this oxide under the given conditions.

iii) The conductivity of this oxide is independent of p_{O2} from oxidising to very reducing conditions. What can we deduce from this?

iv) Simpson and Carter (*J. Am. Ceram. Soc.* **49** (1966) 139) measured the self diffusion coefficient for oxygen in $Zr_{0.85}Ca_{0.15}O_{1.85}$ and found it to be $D_O = 2.0*10^{-7}$ cm^2/s at 1100°C. Calculate the electrical conductivity based on this.

v) Find also the diffusion coeffeicient and charge mobility for the oxygen vacancies.

Chapter 7; Electrochemical transport

1. Electrochemical cell with stabilised zirconias (YSZ and CSZ)

a) Consider an yttria-stabilised zirconia (YSZ) material with 90 mol% ZrO_2 and 10 mol% Y_2O_3. What is the site fraction of oxygen vacancies in the material? We often use and refer to the YSZ as an electrolyte. What is an electrolyte? What requirements does it put on a material?

b) We make ourselves a disk of YSZ, attach Pt electrodes to both faces, and place the disk in a cell where we can expose the two faces to different gases. If the gases have different partial pressures of oxygen, a voltage will be set up over the electrodes, and we can draw current from the cell. Write equations for the two half-cell-reactions that run when current is drawn. Write the expression for the voltage over the cell given that the material is a purely ionic conductor. Which (high or low pO_2) is the positive pole?

c) Smith, Meszaros and Amata (*J. Am. Ceram. Soc.,* **49** (1966) 240) found that the permeabilities at high temperatures of Ar and N_2 through calcium-stabilised zirconia (CSZ) were immeasureable, while that of O_2 was significant and proportional to

$p_{O2}^{1/4}$. Suggest an explanation for these observations.

2. Electrochemical cell for determination of thermodynamic properties

a) Indicate how you can use a YSZ cell with Pt electrodes to determine the thermodynamic parameters for formation of a binary oxide (e.g. NiO).

b) J.J. Egan (J. Phys. Chem. **68** (1964) 1978) studied an electrochemical cell built up as follows:

- (Mo)Th(s),ThF_4(s)|CaF_2(s)|ThF_4(s),ThC_2(s),C(s)(Mo) +

in order to measure the thermodynamic properties of ThC_2. The Mo serves as inert electrodes. The cell was kept under an inert atmosphere. The CaF_2(s) is a solid electrolyte – a fluoride ion conductor – in the temperature range of operation of the cell (700-900°C). The signs indicate the polarity of the cell. Write the reactions at each electrode when current is drawn from the cell. Also, express the voltage of the cell as a function of the Gibbs energy, enthalpy and entropy of formation of ThC_2.

3. Wagner's oxidation theory

Wagner's equation for the oxidation rate of a metal, forming the oxide M_aO_b, can in one form be written

$$\frac{dn}{dt} = \frac{RT}{8bF^2}\int_1^2 \sigma(t_{cat} + t_{an})t_{el} d\ln p_{O_2} \frac{1}{\Delta x}$$

a) Specify what the different symbols denote in this equation.
b) Examine the equality of units on both sides of the equation.
c) What are the model and requirements for the theory. Why do the different terms enter the equation as they do?
d) This type of behaviour is called parabolic. What does it reflect? Identify the parabolic rate constant.
e) Which deviations from the requirements of the theory may give rise to non-parabolic (e.g. linear) behaviour?
f) Assume that the oxide has formula MO and is a p-type semiconductor with doubly charged metal vacancies as dominating point defects ($D_M >> D_O$). Assume that $pO_2^o >> pO_2^i$ and find how the oxidation rate varies with the outer oxygen pressure pO_2^o.
g) Assume that the oxide has formula M_aO_b and that it is an n-type semiconductor with $M_i^{\cdots}$ as dominating point defects and that $D_M >> D_O$. How does the oxidation rate in this case vary with the outer oxygen partial pressure (assuming also now that $pO_2^o >> pO_2^i$)?
h) The tracer self-diffusion coefficient for Co in CoO in air at 1200°C is $9*10^{-9}$

cm^2/s. Calculate the parabolic rate constant in cm^2/s (which is k_p in $dx/dt = k_p/x$) when cobalt oxidizes to CoO under the same conditions. The dominating point defects in CoO are assumed to be singly charged metal vacancies v_{Co}'.

4. Sintering

a) What happens during sintering? What are the driving forces? What are the contributing mechanisms and what may be the rate limiting factors?

b) Powders of CoO can be sintered to dense samples. The defect structure of CoO is characterized by the following: There is a deficiency of metal and the dominating point defects are singly charged metal vacancies. $D_{Co} >> D_O$.Assume that the oxygen defects are interstitials with one negative effective charge. Draw a Brouwer-diagram for the oxide. Under what conditions should the oxide be sintered to achieve the highest sintering rate?

5. Creep

a) What is creep? What are the driving forces, mechanisms, and rate limiting factors?

b) TiO_2 is an n-type electronic conductor with oxygen deficiency, dominated by doubly charged oxygen vacancies and triply charged titanium interstitials. Assume that the concentration of oxygen vacancies is 1000 times higher than that of titanium interstitials at $pO_2 = 1$ atm. Draw a Brouwer diagram for the oxide from $pO_2 = 10^{-20}$ to 1 atm. How would you qualitatively expect that the creep of TiO_2 single crystals varies with pO_2?

6. General considerations

a. The expression "uphill diffusion" is used for diffusion against a concentration gradient, referring to Fick's 1st law. From what you know about electrochemical transport, what might cause uphill diffusion?

b. Eq. 7.4 is written with conductivity as the transport coefficient. Flux of a neutral species is not affected by the electrical potential gradient and can not be expressed by conductivity. It is therefore meaningful to express the equation using the random diffusion coefficient for the chemical potential gradient and the conductivity for the electrical potential gradient. Do this splitting/substitution. (This is mainly a simple exercise in the Nernst-Einstein relation). Check that both parts of the resulting equation will have units that confer with flux density.

7. Transport number and partial conductivity measurements

a. A membrane of a mixed oxygen ion and electron conducting oxide is equipped with Pt electrodes and exposed to two different oxygen partial pressures: On one side is dry air ($p_{O2} = 0.21$ atm) and on the other is pure oxygen ($p_{O2} = 1.00$ atm). What is the Nernst voltage of this cell at 1000°C?

b. A voltage of 0.10 V is read over the cell at 1000°C using a high impedance voltmeter. What is the average ionic transport number of the oxide under these conditions?

c. Make a sketch of the sample and gases and external circuitry during the voltage measurement. Indicate internal and external fluxes and currents (with directions).
d. The total conductivity of the sample is measured and the result is 0.01 S/cm. What are the partial ionic and electronic conductivities?
e. Assuming that the sample is 0.5 mm thick, what is the flux of oxygen gas through the sample during the voltage measurements?
f. If you had measured this flux in some way, and used this as your (only) transport measurement, what would be the transport parameter that you find?

8. Sensor

a. A sensor is made out of a membrane of yttria.stabilized zirconia (YSZ) with Pt electrodes and is operated at 700°C. As reference is used pure oxygen at 1 atm. A voltage of -950 mV is read over the sensor (measuring on the "unknown" side vs the reference side). What is p_{O2} at the "unknown" side?
b. If you assume that the "unknown" side is hydrogen gas at 1 atm, what does the sensor voltage say about the water vapour content of that hydrogen gas?

9. Fuel cell

a. A fuel cell made of YSZ electrolyte with Pt electrodes is operated at 700°C and runs on hydrogen as fuel and air as oxidant, both at atmospheric pressure. Both gases contain 2% water vapour. What is the open circuit voltage of the fuel cell?
b. Assuming that the electrolyte has a conductivity of 0.1 S/cm and is 100 μm thick, calculate the short-circuit current density, the maximum power density and the current and power densities at a voltage of 2/3 of the open circuit voltage. (Assume in all cases that the gas compositions remain unaffected by the current in the cell, and that electrode polarization is insignificant).
c. Assuming the operation at 2/3 of the OCV voltage, what is the area of electrolyte needed for a power plant of 300 MW capacity?
d. The assumption that the gas compositions are unaffected is not realistic for a real power plant; what would it mean in terms of fuel utilization?
e. The system we have described can be operated at other temperatures. Still neglecting electrode polarization, what are the factors and processes that enter into the temperature dependency of the power density of the fuel cell? (Hint: refers to defects and transport.)

10. Gas separation membranes

a. A gas separation membrane that can separate oxygen from air is constructed from La_2NiO_{4+d}, a material where we for simplicity may assume that the defect structure is dominated by doubly ionized oxygen interstitials compensated by electron holes. In the following assume further that the cell is operated at 1000°C and that the membrane is 100 μm thick and has no surface kinetics limitations. Assume also that the oxygen ion conductivity (by interstitials) is 1 S/cm at 1 atm O_2 and that the electronic (hole) conductivity is 200 S/cm at 1 atm O_2. The membrane is operated with atmospheric air on one

side and pumped to effectively 0.1 atm at the other side. What is the area-specific flux of oxygen?
b. What would increase the flux more: Compress the air to 10 atm or pump the vacuum side to 0.01 atm?
c. Find an expression for the chemical diffusion coefficient for oxygen ions.
d. During operation the membrane may possibly suffer from both membrane “walk-out” and decomposition. Explain both phenomena qualitatively.

11. Solid –solid reactions

a. La_2NiO_4 may be synthesized by solid-state reaction between La_2O_3 and NiO. Imagine that you investigate this reaction by making tablets of the two reactants and holding them together at high temperature. Sketch how the product La_2NiO_4 is formed as a phase between the reactants and what diffusion process (or processes) that take place to constitute the reaction.
b. Suggest how you might use a marker (e.g. a Pt wire) to identify the rate limiting diffusion process.
c. The reaction rate can be measured as the thickness of the product layer. It would be expected to grow parabolically. Explain.

12. High temperature oxidation of metals

a. Zr metal is used at high temperatures in nuclear installations. It is protected by an oxide layer of ZrO_{2-y}, dominated by oxygen vacancies and electrons.
b. What is rate limiting for the parabolic oxidation process in your opinion?
c. Nb is often used as allyoing element in Zr in order to reduce oxidation of the metal. Explain how this dopant might work when it ends up in the oxide scale.
d. In nuclear reactors it is a problem that hydrogen diffuses as protons through the oxide scale, dissolves in the Zr alloy and makes it brittle. How would you expect Nb alloying to affect the proton transport through the oxide scale?
e. Ni oxidizes to $Ni_{1-y}O$, i.e. an oxide dominated with Ni vacancies and electron holes. How would you suggest to dope this oxide to reduce oxidation?