Non-equilibrium thermodynamics
Exercise 6
Transport of mass and charge

1

Electrochemical cells are systems with transport of mass and charge.

a) What are the flux equations for such systems?

b) What is the definition of the transference *coefficient*?

c) Derive the relation between the phenomenological coefficients and

   i) electric conductivity

   ii) diffusion coefficients (what will be the difference for the components CH_4, $AgNO_3$ and ZnI_2?)

   iii) transference coefficients

2

a) The following concentration cell is given:
$Ag(s)|AgCl(s)|NaCl(aq,c_1)||NaCl(aq,c_2)|AgCl(s)|Ag(s)$.

   i) What is the definition of a transference *number*? Express the transference number for Na^+ and Cl^- in this cell.

   ii) Assume constant transference numbers through the cell and account for all changes taking place when one mole of electrons passes from left to right in the outer circuit.

   iii) What is the relation between the transference numbers and the transference coefficient in this cell?

b) Consider the following concentration cell: $Zn(Hg)|ZnI_2(aq,c_1)||ZnI_2(aq,c_2)|Zn(Hg)$. Redo task ii) and iii) above for this concentration cell.

3

You have the following concentration cell: Ag(s)|AgCl(s)|KCl(aq,c_1)||KCl(aq,c_2)|AgCl(s)|Ag(s). Calculate the emf of a cell with $c_1 = 0.1$ kmol m^{-3} and $c_2 = 0.01$ kmol m^{-3} at 25 °C and transference numbers $t_{K^+} = t_{Cl^-} = 0.5$.

4

a) Consider the electrochemical cell Ag(s)|AgCl(s)|HCl(aq,c_1)|^C|HCl(aq,c_2)|AgCl(s)|Ag(s). The two half-cells are separated by a cation exchange membrane, |^C|, which does not allow any water transport. As there is a membrane present, it should be used as frame of reference. Assume ideal solutions and calculate the emf of the cell at 25 °C, when $c_1 = 0.1$ kmol m^{-3} and $c_2 = 0.01$ kmol m^{-3}. Neglect the contribution to the emf from transference of water.

b) Consider the same cell with the same conditions as in a), but the membrane allows some water transport, $t_{H_2O} = 5$. Calculate the emf of the cell in this case.

Hint: Use Gibbs-Duhem's equation.

5

Calculate the emf obtainable by moving water in an ion exchange membrane between two electrochemical half cells with hydrogen reversible electrodes and a pressure difference of 3 bar. Hydrogen reversible electrodes give a positive transference coefficient, in this case 2.6, and the molar volume of water is $18 \cdot 10^{-6}$ m^3/mol.

6

As we saw in exercise 1, work is lost where a river meets the ocean. One way to exploit this work is in an electrodialysis salt power plant. Calculate the emf of a single unit of an electrodialysis cell: Ag(s)|AgCl(s)|NaCl(aq,c_1)|^C|NaCl(aq,c_2)|^A|NaCl(aq,c_3)|AgCl(s)|Ag(s). Consider the ion exchange membranes to be perfect. Sea water enters compartment 1 and 3 while river water enters compartment 2. Electrodes are reversible to chloride. The salt concentration in sea water compartments are 0.55 mol/m^3. At that concentration and temperature 300 K, the mean activity coefficient is 0.681. The salt concentration in the river water compartment is 0.001 mol/m^3.