CHEM1612 Worksheet 11: Concentration and Electrochemistry

Model 1: The Effect of Concentration on the Cell Potential

In worksheet 9, you set up a **voltaic cell** to harness the electrical energy in a redox reaction, such as that below, to make a battery:

$$Zn(s) + Sn^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Sn(s) \qquad E^0_{\text{cell}} = +0.62 \text{ V} \qquad (1)$$

During the reaction, tin ions are consumed and zinc ions are produced. The driving force becomes weaker and the cell potential becomes smaller. Eventually, equilibrium is established and the battery is dead.

The *standard* cell potential refers to the reaction in which the reactants are present at 1 M concentrations.

In Model 2 of worksheet 9, you calculated the standard cell potential for the oxidation of nicotine adenine dinucleotide (NADH) by O_2:

$$\tfrac{1}{2} O_2 + H^+ + \text{NADH} \rightarrow H_2O + \text{NAD}^+ \qquad E° = +1.335 \text{ V} \qquad (2)$$

Critical thinking questions

1. What pH does the standard cell potential refer to?

2. If the reaction is performed at a pH of 7.4, will the cell potential be higher or lower?

Model 2: The Nernst Equation

The actual cell potential, E_{cell}, can be calculated from the standard cell potential using the Nernst equation:

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF} \ln Q$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the temperature (in Kelvin), n is the number of electrons transferred in the reaction, F is Faraday's constant (96485 C mol^{-1}) and Q is the reaction quotient. For the reactions in Model 1:

$$(1) \qquad Q = \frac{[Zn^{2+}(aq)]}{[Sn^{2+}(aq)]} \qquad\qquad (2) \qquad Q = \frac{[H_2O][NAD^+]}{[O_2]^{1/2}[H^+][NADH]}$$

Critical thinking questions

1. What is the value of n in these reactions? (*Hint*: how many electrons in total are required to change the oxidation number of Zn in (1) and of the two O atoms in O_2 in (2)?)

2. In the biochemical literature, the biological standard state is used. This has all concentrations as 1 M, except [H^+] which is taken to be 10^{-7} as this is closer to its value in the body. Use the Nernst equation to calculate the *biological* standard cell potential for the oxidation of NADH by O_2 at the typical body temperature of 37 °C.

3. Is your numerical answer to Q2 in Model 2 consistent with your answer to Q2 in Model 1?

Model 3: Concentration Cells

In Model 2, you investigated the effect of the concentrations of the chemicals in a redox reaction on the cell potential. It is also possible to generate a cell potential using differences in concentrations alone.

Critical thinking questions

1. A pair of copper(II) sulfate solutions, one concentrated and dark blue and the other dilute and light blue, are separated by a removable barrier.

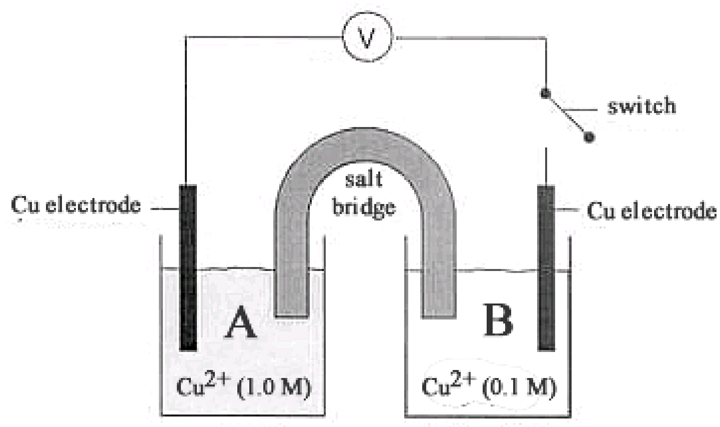
   (a) What will happen when the barrier is removed?

   (b) What will happen to the entropy of the system?

   (c) What will happen to the enthalpy of the system?

2. The cell opposite consists of two half cells connected together by a wire and a salt bridge. Each cell is made from a copper electrode in a solution of $Cu^{2+}(aq)$ ions.

   - Cell A has $[Cu^{2+}(aq)] = 1.0$ M.
   - Cell B has $[Cu^{2+}(aq)] = 0.1$ M.



   (a) Is the system at equilibrium?

   (b) If not, what must happen to the concentrations in each cell to reach equilibrium?

   - Cell A:
   - Cell B:

   (c) Unlike the situation in Q1, equilibrium must be achieved *without* Cu^{2+} ions being able to move.

   What *redox* processes can occur in each cell to change the concentrations in the required direction to achieve equilibrium?

   - Cell A:
   - Cell B:

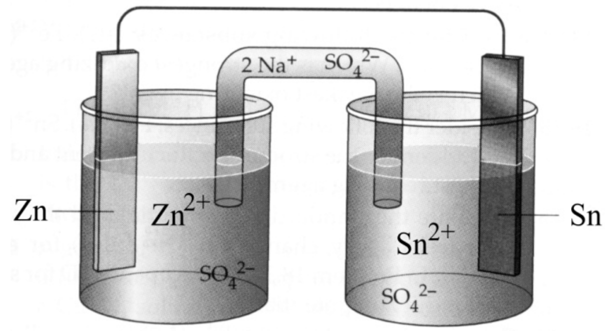
   (d) In which direction must electrons flow for these redox processes to occur?

   (e) Label the cathode and anode in the diagram.

   (f) What is the *standard* electrode potential for this cell?

   (g) Use the Nernst equation to work out the electrode potential of the cell when the switch is connected at 298 K. (*Hint*: remember that $E_{cell} > 0$ for a spontaneous process.)

Model 4: Voltaic Cells



In worksheet 9, you saw how the electrical energy in a redox reaction can be harnessed to make a battery, by setting up the **voltaic cell** opposite. The potentials for the two reactions are:

$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \qquad E^0_{red} = -0.14\ V$$
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad E^0_{ox} = +0.76\ V$$

The overall reaction is spontaneous as the reaction has a positive E^0_{cell} value:

$$E^0_{cell} = E^0_{ox} + E^0_{red} = +0.62\ V.$$

Critical thinking questions

1. Which electrode (Zn or Sn) will *lose* mass and which one will *gain* mass?

2. What is the overall reaction that occurs when the cells are connected?

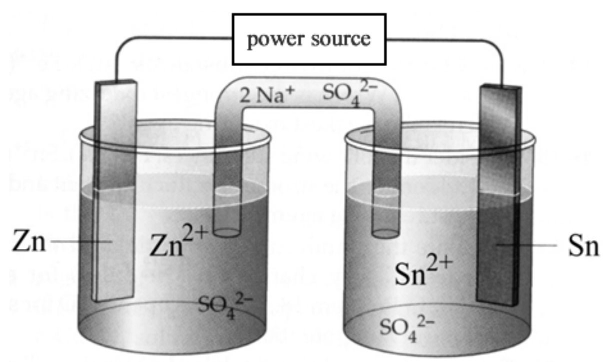
3. Oxidation always occurs at the anode. Label the anode and cathode on the cell.

4. Which way do the electrons flow? Draw an arrow on the diagram to show this.

5. Electrons flow from the *negative* electrode to the *positive* electrode. Which is positive, the anode or the cathode? Label the electrodes as positive or negative.

6. The salt bridge contains $Na^+(aq)$ and $SO_4^{2-}(aq)$. In which direction(s) do these ions move?

Model 5: Electrolytic Cells



The *reverse* reaction can be made to happen if power from an external source with potential *greater* than E^0_{cell} is applied.

Critical thinking questions

1. Which electrode (Zn or Sn) will now *lose* mass and which one will *gain* mass?

2. What is the overall reaction that now occurs when the cells are connected?

3. Oxidation always occurs at the anode. Label the anode and cathode on the cell.

4. Which way do the electrons flow? Draw an arrow on the diagram to show this.

5. The power source supplies electrons to the electrode where reduction occurs, so it becomes negative. The power source removes electrons from the electrode where oxidation occurs, so it becomes positive. Which is positive, the anode or the cathode? Label the electrodes as positive or negative.

6. The salt bridge contains $Na^+(aq)$ and $SO_4^{2-}(aq)$. In which direction(s) do these ions move?

Model 6: Electrolysis of Water

Electrolytic cells can be used to perform many useful tasks. A particular useful one is the electrolysis of water as this has the potential to convert electricity generated using solar energy into hydrogen gas, a combustible fuel. The reactions at the cathode and anode are:

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^0_{red} = -0.83$ V

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^0_{ox} = -1.23$ V

The amount of a substance produced in an electrolytic cell is directly proportional to the amount of electricity that passes through the cell. The number of moles of electrons that pass when a current I is applied for a time t is given by:

number of moles of electrons = $I \times t / F$

Critical thinking questions

1. What is the overall reaction for the electrolysis of water?

2. F is Faraday's constant. It is the charge of one mole of electrons. The charge of one electron is 1.602×10^{-19} C. What is the charge of one mole?

3. If a current of 10.0 A is applied for 2.00 hours, how many moles of electrons are supplied? (*Hint*: remember to convert t into seconds).

4. How many moles of $H_2(g)$ will be generated from this amount? (*Hint*: look at the stoichiometry of the reaction at the cathode.)

5. How many moles of $O_2(g)$ will be generated from this amount?

6. Water is a poor conductor so a salt is usually added to increase the conductivity. The salt must contain ions that are harder to reduce or oxidise than water. Using the standard reduction potentials, select a suitable salt.