Electrochemistry extras for Matric

You have finished revising the galvanic and electrolytic cells covered in Grade 11. There are still a few extra details that we need to cover to complete this section. All this work can be found from pg 176-214 in your Chemistry printed notes.

Galvanic cells:

Galvanic cells are made up of TWO vessels connected by a .
The function of this is:

- to maintain electrical neutrality in the cell
- to complete the circuit.

The salt bridge contains a neutral solution like KNO_3, $NaNO_3$ or Na_2SO_4 that will not react with any of the substance used in the two half cells, and thus not form a precipitate that can clog up the salt bridge.

Each vessel contains an (substance that contains free ions and can conduct electricity).

The purpose of a galvanic cell is to convert chemical / electrical energy into chemical / electrical energy. The emf (voltage / potential difference) produced by the cell is calculated according to the formula:

$$E_{cell} = E_{red} - E_{ox}$$

Remember that the **standard conditions** for every galvanic cell are:

Temperature: °C

Electrolyte concentration: $mol.dm^{-3}$

Pressure of any gases present: atm

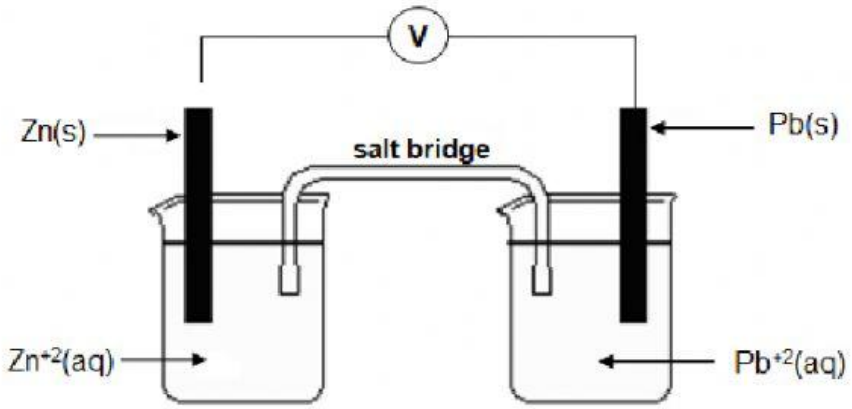
NB

What this means is that the cell potentials that are listed on the half reaction table are only accurate if the galvanic cell is at that specific temp and concentration.

So what can affect the E_{cell} value and make it DIFFERENT from the value calculated from the half reaction table?

- The size of the electrodes do not affect the emf of the cell.
- However the concentration of the electrolytes do affect the value of the emf:
  - If the concentration of the **reactants** is increased the emf will **increase**.
  - If the concentration of the **products** is increased the emf will **decrease**.

For example:



$Zn + Pb^{+2} \rightarrow Pb + Zn^{+2}$

- If the Pb^{+2} concentration in the above example increases then the emf will increase / decrease .

- If the Pb^{+2} concentration decreases then the emf will increase / decrease .

- If the Zn^{+2} concentration increases / decreases the emf will decrease.

- If the Zn^{+2} concentration increases / decreases the emf will increase.

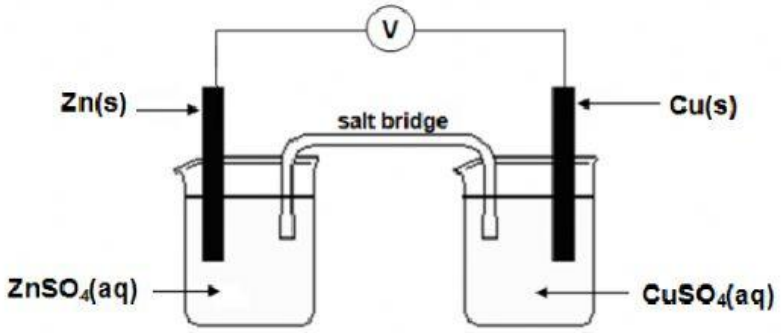
Over time there is a gradual drop in the emf – because the concentration of the Pb^{+2} ions is decreasing as they are gaining electrons to become Pb(s). So the calculated value for E_{cell} is only true at the BEGINNING of the reaction when the cell is first set up.

Note:
We have not yet covered the section on reaction EQUILIBRIUM so some of this will make more sense once we have completed that section...

Cell potential and equilibrium:

- At the beginning of the reaction, the cell potential will equal E_{red} - E_{ox}
- When the cell has reached equilibrium, the cell potential will be equal to **O V**
- Cell potential is not a constant value, and it will be at its highest when the reactant concentration is high and the product concentration is low - at the beginning of the reaction.
- As the reaction progresses and the reactants are used up, the potential difference will decrease.
- The reaction will continue until equilibrium is reached. The reaction in the cell reaches equilibrium when the cell is completely discharged ("flat"), and electrons no longer flow.

Example:



$$Zn + Cu^{+2} \leftrightarrows Zn^{+2} + Cu$$

- The cell will continue to function until all the zinc has dissolved (in the Zn half cell) or until there are no more copper ions left (in the Cu half cell)

- The voltmeter reading can be increased / decreased by increasing the concentration of the reactants e.g. by adding Cu^{+2} ($CuSO_4$) to the Cu half cell.

- Reason: adding Cu^{+2} will favour the forward reaction according to Le Chatelier and that will increase the emf.

- A **positive E_{cell}** value shows that the forward reaction is **spontaneous** and that the reaction must shift to the right (forward) to reach equilibrium.

- A **negative E_{cell}** value is an indication of a **non-spontaneous** reaction and the reverse reaction is favoured.

Change in mass of electrodes:

$$Zn(s) + Cu^{+2}(aq) \rightarrow Zn^{+2}(aq) + Cu(s)$$

- In a galvanic cell, the cathode INCREASES in mass as reduction occurs and the oxidising agent is deposited onto the cathode.

$$\text{Red:} \quad Cu^{+2}(aq) + 2e^{-} \rightarrow Cu(s)$$

- At the same time, the anode will DECREASE in mass as the reducing agent loses electrons and becomes an ion.

$$\text{Ox:} \quad Zn(s) \rightarrow Zn^{+2}(aq) + 2e^{-}$$

- The mass loss at anode will NOT be the same as the mass gain at cathode, but using mole ratios it is possible to calculate the expected mass gain / loss.

Example:

The cell notation for a standard electrochemical cell is given as follow:

$$\mathbf{Al(s)/Al^{+3}(aq)(1\ mol.dm^{-3}) \,//\, Cu^{+2}(aq)(1\ mol.dm^{-3})/\ Cu(s)}$$

The volume of the electrolyte in each standard half cell is 60 cm^3.

1. Calculate the maximum mass loss that can occur at the anode.

   First you need to work out the BALANCED net cell reaction:

   (s) + (aq) → (aq) + (s)

   Then calculate how many moles of Cu(s) can form at the cathode based on the amount in solution:

   n = C x V = $mol.dm^{-3}$ x dm^3 = mol

Now calculate the no of moles Al that can react, using mole ratios:

n (Al) = n (Cu) x ÷ = mol

Now convert this no of moles to a mass of Al:

m = n x M = mol x $g.mol^{-1}$ = g

2. How would an increase in $Cu^{+2}(aq)$ influence the cell's emf?
   INCREASE, DECREASE or REMAIN THE SAME.

3. Which electrode is positive? Al or Cu

Try another similar example – do the workings in your books and fill in the answers below to check your results:

The cell notation for a standard electrochemical cell is given as follow:

$Mg(s)/Mg^{+2}(aq)(1\ mol.dm^{-3})\ //\ Ag^{+1}(aq)(1\ mol.dm^{-3})/\ Ag(s)$

The volume of the electrolyte in each standard half cell is 40 cm^3.

1. Calculate the maximum mass loss that can occur at the anode.

   m = g

2. How will an increase in $Ag^{+1}(aq)$ influence the cell's emf?

   INCREASE, DECREASE or REMAIN THE SAME.

3. Which electrode is positive? Mg or Ag

Electrolytic cells:

Remember that electrolytic cells are converting chemical / electrical energy to chemical / electrical energy. So how can we increase the rate of the chemical reaction?

Relationship between current and rate of reaction

The stronger the current the faster the reactions at the anode and cathode. Thus the amount of chemical change that takes place in an electrolytic cell is directly proportional to the amount of electricity passing through the cell.

Questions to complete from Chemistry notes:

Pg 182-187: 1.10, 2.8, 3.8, 4.8, 5.8, 6.8, 7.8

Pg 206: 2.8