

Electrochemical Cells:

* Redox reactions are capable of producing an electrical current.

Ex: A piece of Zn is immersed in aqueous copper(II) sulphate

* After a while, the redox reaction will cause Zn to dissolve to form Zn^{2+} and copper solid forms. The solution will also lose its blue colour as all the Cu^{2+} is changed to Cu.

* Because it happens, we can assume the reaction is spontaneous.

Unfortunately, it does not work for us.

* when we separate the containers (now called half-cells), the electrons must travel through the wire to get to Cu^{2+} . We can then harness them to generate electricity.

BUT: It turns out that the current goes for a few seconds, but then quits.

* the problem is that the SO_4^{2-} from the copper(II) sulphate becomes a problem. On one side Cu^{+2} is converted to Cu, leaving SO_4^{2-} and only negative charge. On the other side Zn is converted to Zn^{2+} and giving an overall positive charge. There is a charge imbalance.

* we need some way of getting rid of the charge imbalance or POLARIZATION.

We use:

In General:

Electrodes are surfaces where electrons are transferred and occur in 2 types:

1/ Anode:

2/ Cathode:

The three requirements for an electrochemical cell:

1/

Read pages 215-217 and do questions # 34 & 35

Cell Potential:

* Just like a ball rolls downhill, electrons will flow from anode to cathode.

* The “force” that pushes electrons this way is called the electromotive force (emf) and it has to do with the electrical potential difference between the two electrode plates.

* The Cell Potential or Cell Voltage is the energy that is released when the electrons move from high potential energy plate to lower potential energy plate. It is this energy that we can use to do work.

* The Cell Potential will be different for each cell. It is easily measured and when it is measured at standard conditions (1 atm, 25°C, 1M ionic concentration), it is called the standard cell potential ($E^{\circ}\text{cell}$)

* Remember that $E^{\circ}\text{cell}$ is the difference between the potentials of the two plates (anode vs. cathode). What could we say about $E^{\circ}\text{cell}$ if the anode has a high electrical potential and the cathode has a low electrical potential?

* If $E^{\circ}\text{cell}$ is big, the cell has a large capacity to do work for us.

* $E^{\circ}\text{cell}$ depends on:

- 1)
- 2)
- 3)
- 4)

Finding $E^{\circ}\text{cell}$:

$$E^{\circ}\text{cell} = E^{\circ}\text{oxidation} + E^{\circ}\text{reduction}$$

We can get these values from the last table in our data booklet. BUT, these are all written as reduction reactions, so we have to do a little bit of work to get an $E^{\circ}\text{oxidation}$.

Ex:

If we switch the arrow direction, we switch the sign.
THEREFORE:

Calculating an E° cell:

Ex:

One more note:

***** Stoichiometry DOES NOT AFFECT E°

Using the table:

* The ones toward the top left reduce most strongly and the ones toward the bottom right oxidize more readily. However, there is another way we can do it.

* It turns out the ones with the more positive E°_{red} reduce most strongly and, when we switch the sign, the ones with the more positive E°_{ox} oxidize most strongly.

* When we mix a reactant that has a strong need to reduce with another that has a strong need to oxidize, the reaction is SPONTANEOUS.

* AND when we go to calculate E°_{cell} with 2 somewhat large numbers, the E°_{cell} will be positive.

Ex:

How did they come up with those E° values?

* If there was an electrode for which we did not know the E° value for, there is a way that we could get it.

* We could hook it up to another electrode that we know the E° value for, run the cell and get the E° cell value.

The Formula:

* The electrode E° that we use to compare all others is:

Ex:

Assignment: Read pages 218-228 and do questions #36 a, d, & g and #38 & 47

A few other points about E° :

1/ Equilibrium: Like any other equilibrium reaction, the forward reaction rate will decrease and the reverse reaction will increase and eventually they will become the same. What this means, is that E°_{red} will decrease and E°_{ox} will start to increase. Pretty soon, the difference between them will become minimal and E°_{cell} will approach zero

2/ Surface area of the electrodes: Will have no influence on the E° value for the electrode. However, it will affect the rate of the reaction and the length of its life.

3/ Cells not at standard conditions: Use Le Chatelier's Principle to determine what the stress will do to the reduction reaction.

Electrochemical Applications (Spontaneous):

1/ Corrosion:

- * metals spontaneously go to oxides.
- * many metals form an oxide "skin" to prevent further oxidation (corrosion).
- * oxidation means that the metal DISSOLVES.

Ex:

- * During corrosion, the metal acts as an anode (oxidizes)
- * The cathode reaction could be:
 - a)
 - b)
 - c)
- * Also need a salt. WHY?

* Corrosion will occur in cracks in the metal oxide "skin"

Now let us draw:

* the electrons migrate through the metal to the surface where oxidation can occur (where O_2 can be reduced).

* Oxidation happens where the surface of the metal meets water and oxygen.

Protection from Corrosion:

a)

b)

c)

a) Anodic Inhibition:

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b) Cathodic Protection: (force the metal to become the cathode)

2/ Bleaching:

- * used to eliminate unwanted colour from fabrics, etc.
- * colour is caused by the movement of electrons through energy levels.
- * OCl^- in bleach, in its need to reduce, rips the electrons away from the coloured dyes
- * Cl_2 and H_2O_2 do the same thing
- * H_2O_2 kills bacteria by oxidizing the cell wall.

3/ Fuels and explosives:

- * Fuels release energy when they are oxidized

Ex:

- * explosives often contain both oxidizing and reducing agents (TNT)
- * the rapid formation and expansion of gases cause the shockwave.

4/ Batteries: read the text book and fill in the spaces beside each battery with a letter.

5/ Silver Tarnish:

Assignment: Read pages 228-236

Electrolysis:

* It is like an electrochemical cell but, THE ELECTRODES PRODUCE A NON-SPONTANEOUS REACTION

* this means that when we measure E°_{cell} , it will be negative and we will have to SUPPLY at least that much energy to make the cell work.

* Reactions of this type are called electrolysis and take place in electrolytic cells.

* It consists of a battery, which acts as an electron pump (pulls electrons from the anode and pushes them into the cathode), an external wire, and 2 electrodes that are immersed in a melted or aqueous salt solution. A salt bridge is not necessary.

* The battery sucks electrons out of the ANODE making it POSITIVE, and pushes them into the CATHODE making it NEGATIVE.

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* In many electrolytic cells, the electrodes are INERT. They only serve as a source of electrons and do not appear in the overall reaction of interest. Examples of inert electrodes are:

Electrolysis in Aqueous Solutions:

* when the salt is in an aqueous solution (when the question says anything about molarity OR if it doesn't say molten), water becomes a possible player.

* In an aqueous solution water OR the ions may react and which one does is a function of where the reactions are in the table. The highest one will reduce (look for your reactant on the left side) and the lowest one will oxidize (look for your reactant on the right side).

Ex: Electrolysis of 1M NaCl

Ex: Electrolysis of CuCl_2

BUT WAIT! THERE'S MORE!!

The Overpotential Effect:

The half-reactions of H_2O involve mechanisms that may not allow for them to react at the E° values given in the table. The E°_{red} may be lower and the E°_{ox} may be higher (see arrows in table)

THEREFORE:

In example 1:

Oxidation:

Reduction:

In example 2:

Oxidation:

Reduction:

** From now on, we will pretend they will react where the arrows point DUE TO THE OVERPOTENTIAL EFFECT (yes, you have to say that)

Applications of Electrolysis:

1/ Electroplating:

- * object to be plated needs to be the cathode
- * solution contains ions of the coating metal
- * anode is a bar of the coating metal OR an inert electrode (Pt/C)
- * voltage must be controlled so that water does not react

Ex: plating with silver:

2/ Electrorefining: Read text and make notes (what is the anode, cathode, solution, for example)

Assignment: Read pages 237 –end and do questions 60, 65, 66, 69, 74, 75, 77, & 80