

ELECTROCHEMICAL CELLS

These are devices used for changing chemical energy into electrical energy.

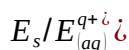
There are two types of cells namely:

1. Primary cells: These are cells whose reactions (through which electric current is generated) are irreversible. They cannot be recharged after they have been used. They have high resistances and hence generate low currents. They are affected by local action and polarisation. Examples include Leclanche cell (also called dry cell) and the Daniel cell
2. Secondary cells: These are also called accumulators. They are the opposite of primary cells.

An electrochemical cell consists of two electrodes of which each has its own electrolyte. The two electrodes are connected by a salt bridge or a porous partition.

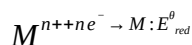
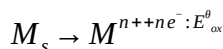
One electrode with its electrolyte is called a half-cell. The electrode is an element (mostly metals although it may be non-metals) and the electrolyte is a salt of the element. The element is said to be in contact with its own ions.

A half-cell can be represented as



An electrode has a quantitative property called the electrode potential.

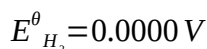
Electrode potential is a measure in volts of the tendency of an atom of an element of the electrode to undergo oxidation and reduction.



E_{ox}^θ & E_{red}^θ of an electrode have the same value but different signs (one is negative while the other is positive).

When all the concentrations of aqueous solutions are 1mol dm^{-3} , all gases taking part in the reactions are at 1atm and the temperature is 25°C (Room temp), the electrode potential is called the standard electrode potential.

The standard hydrogen electrode was assigned a standard electrode potential of 0.000Volts



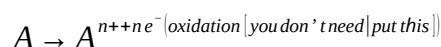
The standard electrode potentials of other elements can be determined using the standard hydrogen electrode as a reference.

The standard electrode potential of an element is the potential difference set up between a standard hydrogen electrode and a half-cell.

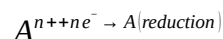
It is called the electromotive force (emf) when a standard hydrogen electrode is coupled to the electrode of the element.

NB:

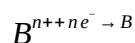
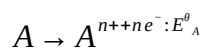
1. A/A^{n+} is represented as



2. A^{n+}/A is represented as



3. $A/A^{n+}/B^{n+}/B$



$$E_{cell}^\theta = E_A^\theta + E_B^\theta$$

E.g.

Zn/Zn^{2+} is represented as



When calculating the emf of a cell,

- Write the anodic reaction (Oxidation)
- Write the cathode reaction (Reduction)
- Make electrons gain equal to electrons lost.
- Add the two electrode potentials i.e.

$$E_{cell}^\theta = E_A^\theta + E_B^\theta$$

If the emf of a cell (after calculation) is positive, then the reaction is spontaneous and the Gibbs free energy is negative.

If the emf is negative, the reaction will not take place.

The table below shows the standard potentials of elements.

Element	Half-cell reaction (Reduction)	Half-cell reaction (Oxidation)	Standard reduction potential	Standard oxidation potential	Reducing ability	Oxidising ability
K			-2.93		Highest reducing ability (but can be easily oxidised)	Lowest oxidising ability
Na			-2.87			
Ca			-2.71			

Mg			-2.37			
Al			-1.67			
Zn			-0.76			
Fe			-0.44			
Sn			-0.14			
Pb			-0.13			
H			0.00			
Cu			0.34			
Hg			0.79 0.85			
Ag			0.80			
Au			1.5			
OH			Not an element			
I			0.54			
Br			1.09			
Cl			1.36			
NO			Not an element			
SO			Not an element			
F			2.87		Lowest reducing ability	Highest oxidising ability

DEFECTS OF PRIMARY CELLS

1. Local action: This is caused by the presence of impurities on the zinc plate electrode. The impurities on the electrode prevent the free flow of current. Local action can be prevented by Amalgamation. Amalgamation is the process of coating the zinc electrode with mercury. Local action can also be prevented by using a pure zinc electrode (which can be gotten from electrolytic process).
2. Polarization: This is defined as the process whereby hydrogen bubbles produced at the zinc electrode prevent free flow of current. The hydrogen bubbles also increase the resistance of the electrode. The bubbles produce what is known as Hydrogen Electrode. These bubbles also create a back emf.

Polarization can be prevented using chemical substances called Depolarizers.

Cell Name	Anode	Cathode	Electrolyte	Depolarizer	EMF value
Leclanche cell	Carbon (C)	Zinc (Zn)	Ammonium Chloride (NH_4Cl)	Manganese (IV) oxide(MnO_2)	1.5 V
Daniel Cell	Copper (Cu)	Zinc (Zn)	Tetraoxosulfate (VI) acid (H_2SO_4)	$CuSO_4$	1.1 V
Lead-acid accumulator	Lead oxide	Lead (Pb)	H_2SO_4	None	2.2 V
Alkaline accumulator	Nickel Hydroxide	Cadmium (Cd) or Iron (Fe)	Potassium Hydroxide	None	1.25 V

DIFFERENCE BETWEEN THE ELECTROLYTIC CELL AND THE ELECTROCHEMICAL CELL

Electrolytic cell	Electrochemical cell
Converts electrical energy to chemical energy	Converts chemical energy to electrical energy
Electrons are pushed by an outside force such as a battery	Electrons are generated by oxidation at the electrode (anode)
Cathode is negative electrode	Cathode is the positive electrode
Anode is the positive electrode	Anode is the negative electrode
Electrodes are in the same compartment	Electrodes are in separate compartments
Salt bridge is not needed	Salt bridge is needed
Only one electrolyte is used	Two electrolytes are used

ARRANGEMENT OF CELLS

Series Arrangement: Cells are arranged in series in order to increase their effective emf

$$E = E_1 \pm E_2 \pm E_3$$

The reason it is plus or minus is because, some times if two terminals of the same sign are put together, there will be a minus

Cells are connected positive negative to positive negative to positive negative. However, if there is an error in connection and one gets connected negative to negative, there will be a loss of emf.

The effective internal resistance of the combined cells in series is expressed

$$r = r_1 + r_2 + r_3$$

Parallel Arrangement: Cells are arranged in parallel in order to reduce their effective internal resistance and hence increasing the amount of current

The effective emf of all the cells have is value in a parallel arrangement in the circuit.

$$\text{Effective emf} = E$$

EMF: The electromotive force of a circuit or cell is the work done in moving a unit charge round the entire circuit. It is also defined as the voltage across on an open circuit (i.e. when it is not delivering any current).

The emf can also be defined as the work done per unit charge.

$$\text{Emf} = \frac{\text{Work done}}{\text{Charge}}$$

$$E = \frac{W}{q}$$

$$W = Eq$$

It is seen above that the formula from electric fields has been repeated

$$W = qV$$

So it can be understood that the electric potential (V) is actually a potential difference (E)

The emf of a cell is mathematically the sum of the terminal voltage (V) and the lost volt (L)

$$E = V + L$$

$$E = IR + Ir$$

$$E = I(R + r)$$

$$I = \frac{E}{R + r}$$

If there is no energy loss in the circuit

The lost volt equals zero

Therefore, for an ideal circuit,

$$L = 0$$

$$E = V + L$$

$$E = V + 0$$

$$E = V$$

$$E = IR$$

EFFICIENCY OF A CELL

This is defined as the (percentage) ratio of the power output to the power input

$$\text{Efficiency} = \frac{\text{Power output}}{\text{Power input}} \times 100$$

$$\text{Eff} = \frac{VI}{(Emf) \times I} \times 100$$

$$\text{Eff} = \frac{V}{Emf} \times 100$$

$$\text{Eff} = \frac{IR}{I(R+r)} \times 100$$

$$\text{Eff} = \frac{R}{R+r} \times 100$$

The maximum power is transferred by the battery when load resistance (R) is equal to the internal resistance (r) of the battery.

However, the efficiency at that point will only be 50%.