Hence, the ratio, $E^\circ_{cell} = \frac{-\Delta G^\circ}{nF} = \frac{-\Delta G^\circ}{nF}$

$$E^\circ = -\frac{\Delta G^\circ}{nF}$$

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{\Delta G^\circ}{Nf}$$

Thus, E° remains constant. Electrical potential is an intensive property which does not depend on the amount of substance.

Standard cell potentials and equilibrium constants :

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$\Delta G^\circ = -RT \log_e K$$

L.H.S. same $\therefore$ equating R.H.S.

$$\therefore -nFE^\circ_{cell} = -RT \log_e K$$

$$E^\circ_{cell} = \frac{RT}{nF} \log_e K$$

OR

$$E^\circ_{cell} = \frac{2.303\,RT}{nF} \log_{10} K$$

$$E^\circ_{cell} = \frac{0.0592}{n} \log_{10} K \quad \text{(at 25° C)}$$

ΔG° = std Gibbs energy change

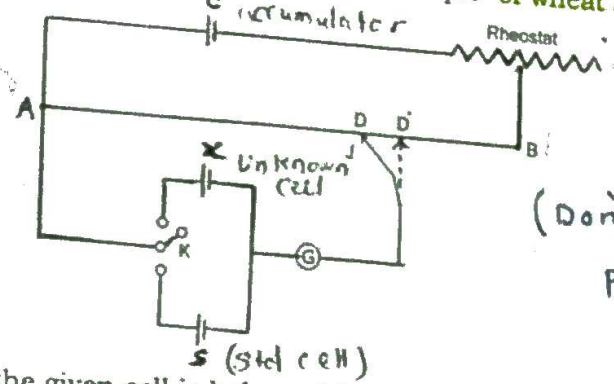
E°_{cell} = std emf of the cell.

K = equilibrium const.

Measurement of cell potential : (EMF)

(Poggendorff's compensation method)

[Using potentiometer which works on principle of wheat stone's bridge circuit.]



(Don't draw Physics diagram)

The emf of the given cell is balanced by an equal and opposite external potential so that no current flows through the circuit.

The potentiometer consists of a thin conduction wire AB made up of platinum, Cu alloy of uniform cross section.

Secondary Voltaic cells

Definition :

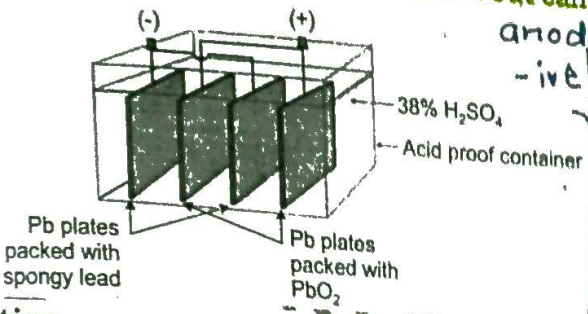
The voltaic cells that can be recharged by reversing the direction of current flow and thereby regenerating the original reactants are called secondary voltaic cells.

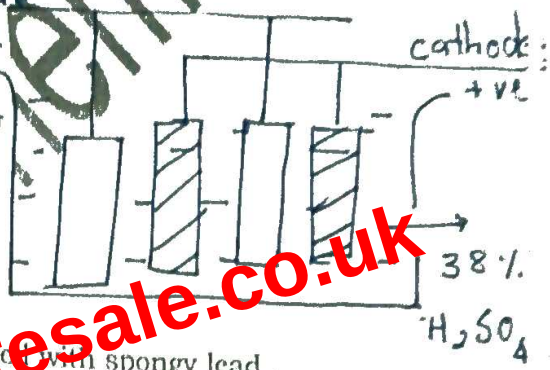
When a potential slightly greater than that generated by the cell is imposed across the electrodes, the direction of current flow is reversed.
All the reactions occurring in the cell during discharge are then reversed.
The cell is thus recharged.

Eg :**Lead accumulators (Lead storage battery)**

Storage cell :

Electrical energy is not generated with in the cell but can be stored from ext. source.





Construction

(-ve electrode) anode is a group of lead plates packed with spongy lead .
(+ve electrode) cathode A group of lead plates containing lead dioxide (PbO_2) .
The two types of plates are alternately arranged.
To provide large reacting surface each cell contains several plates of each type,
The electrodes are immersed in electrolyte which is an aqueous solution of 38% (by mass) H_2SO_4 of density around about 1.2 g/ml.

Representation :

Pb(s) | $PbSO_4$(s)| 38%H_2SO_4 (aq) | $PbSO_4$(s) | PbO_2(s) | Pb (No salt bridge)

Working of the cell

(I) Cell reactions during discharging (cell functions as galvanic cell)

Chemical energy ⟶ electrical energy

Oxidation reaction at anode (negative electrode) When the cell provides current, spongy lead is oxidized to Pb^{2+} and negative charge (electrons) accumulates on lead plates. The Pb^{2+} ions formed combine with SO_4^{2-} ions from H_2SO_4 to form insoluble $PbSO_4$.

$$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^- \quad \text{(oxidation)}$$

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) \quad \text{(precipitation)}$$

$$Pb_{(s)} + SO_4^{2-}(aq) \rightarrow PbSO_{4(s)} + 2e^- \quad \text{(overall oxidation at anode)}$$

The standard aqueous electrode potentials at 298 K.

Electrochemical series

Electrode	Half reaction			E°/V
	Left side species (oxidizing agents)		Right side species (reducing agents)	
$F^- \mid F_2 \mid Pt$	$F_2 + 2e^-$	Reduction rate →	$2F^-$	+ 2.87
$Au^+ \mid Au$	$Au^+ + e^-$	⟶	Au	+1.68
$Ce^{4+}, Ce^{3+} \mid Pt$	$Ce^{4+} + e^-$	⟶	Ce^{3+}	+ 1.61
$Au^{3+} \mid Au$	$Au^{3+} + 3e^-$	⟶	Au	+ 1.50
$Cl^- \mid Cl_2 \mid Pt$	$Cl_2 + 2e^-$	⟶	$2Cl^-$	+1.36
$Pt^{2+} \mid Pt$	$Pt^{2+} + 2e^-$	⟶	Pt	+1.20
$Br^- \mid Br_2 \mid Pt$	$Br_2 + 2e^-$	⟶	$2Br^-$	+1.08
$Hg^{2+} \mid Hg$	$Hg^{2+} + 2e^-$	⟶	Hg	+0.854
$Ag^+ \mid Ag$	$Ag^+ + e^-$	⟶	Ag	+0.799
$Hg_2^{2+} \mid Hg$	$Hg_2^{2+} + 2e^-$	⟶	Hg_2	+0.79
$Fe^{3+}, Fe^{2+} \mid Pt$	$Fe^{3+} + e^-$	⟶	Fe^{2+}	+0.771
$I^- \mid I_2(s) \mid Pt$	$I_2 + 2e^-$	⟶	$2I^-$	+0.535
$Cu^{2+} \mid Cu$	$Cu^{2+} + 2e^-$	⟶	Cu	+0.337
$Ag \mid AgCl(s) \mid Cl^-$	$AgCl(s) + e^-$	⟶	$Ag + Cl^-$	+0.222
$Cu^{2+}, Cu^+ \mid Pt$	$Cu^{2+} + e^-$	⟶	Cu^+	+0.15
$Sn^{4+}, Sn^{2+} \mid Pt$	$Sn^{4+} + 2e^-$	⟶	Sn^{2+}	+0.15
$H^+ \mid H_2 \mid Pt$	$2H^+ + 2e^-$	⟶	H_2	0.00
$Pb^{2+} \mid Pb$	$Pb^{2+} + 2e^-$	⟶	Pb	−0.126
$Sn^{2+} \mid Sn$	$Sn^{2+} + 2e^-$	⟶	Sn	−0.136
$Ni^{2+} \mid Ni$	$Ni^{2+} + 2e^-$	⟶	Ni	−0.257
$Co^{2+} \mid Co$	$Co^{2+} + 2e^-$	⟶	Co	−0.280
$Cd^{2+} \mid Cd$	$Cd^{2+} + 2e^-$	⟶	Cd	−0.403
$Fe^{2+} \mid Fe$	$Fe^{2+} + 2e^-$	⟶	Fe	−0.440
$Cr^{3+} \mid Cr$	$Cr^{3+} + 3e^-$	⟶	Cr	−0.740
$Zn^{2+} \mid Zn$	$Zn^{2+} + 2e^-$	⟶	Zn	−0.763
$Al^{3+} \mid Al$	$Al^{3+} + 3e^-$	⟶	Al	−1.66
$Mg^{2+} \mid Mg$	$Mg^{2+} + 2e^-$	⟶	Mg	−2.37
$Na^+ \mid Na$	$Na^+ + e^-$	⟶	Na	−2.714
$Ca^{2+} \mid Ca$	$Ca^{2+} + 2e^-$	⟶	Ca	−2.866
$K^+ \mid K$	$K^+ + e^-$	⟶	K	−2.925
$Li^+ \mid Li$	$Li^+ + e^-$	⟶	Li	−3.045

INCREASING STRENGTH AS OXIDISING AGENT

INCREASING STRENGTH AS REDUCING AGENT

Note the following points:

* All ions are at 1M concentration in water. * All gases are at 1 atm pressure

* $Fe^{3+}, Fe^{2+} \mid Pt$, $Cu^2, Cu^+ \mid Pt$, $Sn^{4+}, Sn^{2+} \mid Pt$, the order of writing ions in solution is immaterial.

2) **Relative strength of reducing agents in terms of E° values : Selecting elements as reducing agent**

- The strongest reducing agents are located in the bottom right half of the reactions., examples Li, K, Ca etc.
- The half reactions at the bottom of the series with large negative E° values have little or no tendency to take place in the forward direction as written. On the contrary they tend to occur in the reverse direction.
- The species in the bottom right side of reactions are most effective electron donors. They are, stronger reducing agents.
- Their strength as reducing agent decreases from bottom to top as the E° values become more positive.

3) **Identifying the spontaneous direction of reaction:**

- The standard electrode potentials can be used to determine the spontaneity of redox reactions.
- E°_{cell} for the overall cell reaction can be calculated.
- **Any overall cell reaction, for which E°_{cell} is positive, is spontaneous whereas that for which E°_{cell} is negative is nonspontaneous.**

Example : $Mg + 2Ag^+ \longrightarrow Mg^{2+} + 2Ag$,

Whether Mg is oxidized by Ag^+ ? whether the reaction is spontaneous ?

(i) $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^\circ = 0.8V$ (Reduction potential)

(ii) $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $E^\circ = -2.37V$ (Red. pot.)

Reverse the reaction of Mg^{2+} / Mg electrode with changing the sign of E°

(iii) $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ $E^\circ = -(-2.37V) = 2.37V$

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{red}$ (cathode) (anode)

Ag Mg

Add the equations (i) and (iii). While adding, multiply equation (i) by 2 to cancel the electrons. Do not multiply E° value by 2

$2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$ $E^\circ = 0.8V$ (reduction)

$Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^-$ $E^\circ = 2.37V$ (oxidation)

$2Ag^+_{(aq)} + Mg_{(s)} \longrightarrow 2Ag_{(s)} + Mg^{2+}_{(aq)}$ $E^\circ_{cell} = 3.17V$ (overall)

- The overall cell reaction is the oxidation of Mg by Ag^+.
- E°_{cell} for the reaction is positive , the reaction is spontaneous.

- **Diagonal rule** : **Any oxidizing agent** (the species on the left of half reaction) can oxidize **any reducing agent** (the species on the right of half reaction) that appears **below it in the electrochemical series.**
- The elements which is having lower position will spontaneously displace other metal having higher position in emf series.

$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu$ from its salt

Fe is below Cu ∴ can displace Cu metal. Sol.

Ag above (oxidising ag.)

↓

Mg below (reducing agent)

$FeSO_4 + Cu \longrightarrow CuSO_4 + Fe$ X

Cu above

↓

Fe below

$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu$ ✓

$Mg + 2Ag^+ \longrightarrow Mg^{2+} + 2Ag$

$Mg \rightarrow Mg^{2+}$ (oxidation reac.)

According to Wheatstone bridge principle
The resistance of a conductor is proportional to its length.

$$\therefore \quad \frac{R\ (solution)}{l\ (AC)} = \frac{R\,x}{l\ (BC)}$$

Or

$$\boxed{R\ (solution) = R\ x\ \frac{l\ (AC)}{l\ (BC)}}$$

By measuring the lengths AC and BC and knowing Rx, the resistance of KCl solution can be calculated.

$$\boxed{\text{Cell constant} \quad b = k\ .\ R\ (solution)}$$

The conductivity (k) of KCl solution is known. Hence, b, the cell constant can be calculated.

Step II : Determination of conductivity of the given solution :→

KCl solution is replaced by the given solution and its resistance is measured by Wheatstone bridge principle as described earlier. The conductivity of the given solution is calculated.

$$\text{Conductivity of given solution} = k = \frac{\text{Cell const.}}{R} = \frac{b}{R}$$

The molar conductivity of the given solution is calculated as

$$\boxed{\Lambda = \frac{k}{c}}$$

THE END