## Electrochemical cells.

We are concerned however the overall chemical process that occurs, when electricity is passed through a conducting solution

Electrochemical cells

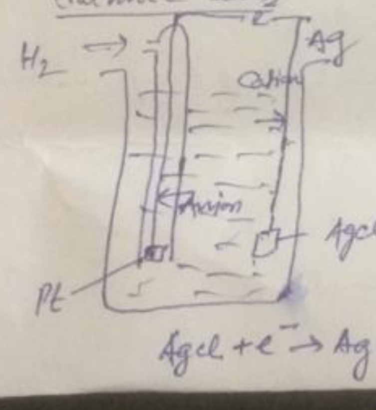
**Electrolytic cells**

An electrolytic cells is a device in which the external supply of electrical energy is necessary in order to bring about a physical or Chemical change in the cells.

**Galvanic Cells.**

In a galvanic cell, the free energy released by a physical or Chemical change is transformed into electrical. Therefore a galvanic cell serves as a source of electricity whereas an electrolytic cell cannot.

### Galvanic cells



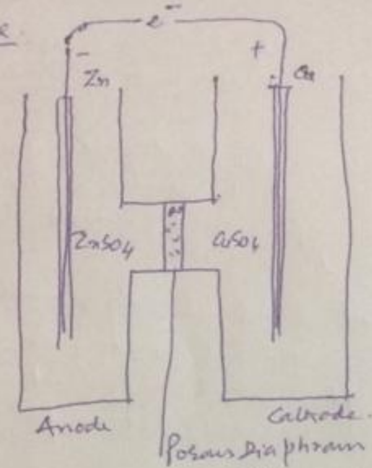

$$AgCl + e^- \rightarrow Ag + Cl^-$$

At anode: $\frac{1}{2}H_2(1\,Atm) = H^+(m) + e^-$ — (1)

At cathode: $AgCl + e^- = Ag + Cl^-(m)$ — (2)

Net: $\frac{1}{2}H_2(1\,Atm) + AgCl = Ag + H^+(m) + Cl^-(m)$ (3)

Daniell cell.




Cell Diagram

$Zn/ZnSO_4(m_1) \vdots CuSO_4(m_2)|Cu$

At anode : $\frac{1}{2}Zn = \frac{1}{2}Zn^{2+}(m_1) + e^-$

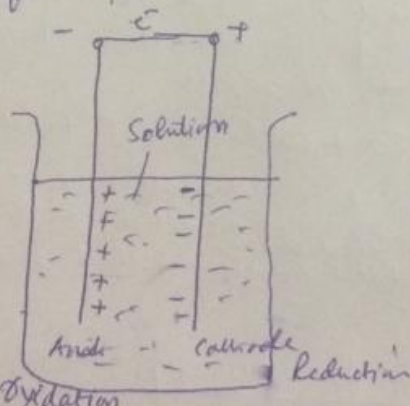
At Cathode : $\frac{1}{2}Cu^{2+}(m_2) + e^- = Cu$

Net $\frac{1}{2}Zn + \frac{1}{2}Cu^{2+}(m_2) = \frac{1}{2}Zn^{2+}(m_1) + \frac{1}{2}Cu$.

Tendencies of electrode to liberate electrons.

$Zn > H_2 > Cu > Ag$

Direction of flow of electrons.




Reversible and irreversible cells.

In Thermodynamics sense a cell is said to be reversible if it fulfils the following conditions

1) If the e.m.f (exactly) equal to its own) is applied by some external source the cell reaction

2) If the external e.m.f. is slightly greater to its own, is applied to it, the current will begin to flow in opposite direction and the cell reaction is reversed.

3) If the external emf slightly smaller than that of the cell itself is applied, a very small amount of the current will flow and a corresponding small amount of chemical reaction takes places in the cell.

$$Zn/ZnSO_4 || CuSO_4 / Cu$$

Net cell reaction.

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

The e.m.f is 1.09 volts. If the emf is increased infinitesimally beyond 1.09 V, the external flows in opposite direction and the cell reaction is reversed

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

If the e.m.f. is less than 1.09 volts, the cell reaction remains.

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

Electrical energy. In the Daniell cell e.m.f. is 1.10 V
The cell reaction involves liberation as well as taking up of two electrons.
Electrical energy generated $= 2 \times 96500 \times 1.1 =$ 213,300 Joules

Relation between free energy and electrical energy

If the e.m.f. of a particular cell is E volts and the process taking place in it is accompanied by the passage of n faradays i.e. nF Coulombs where F represents 96500 Coulombs or Joules. If the cell is reversible one, this represents the maximum work.

Since electrical work does not involve mechanical work resulting from a volume change, it may be taken as equal to the change of free energy accompanying in the cell reaction.

$\therefore$ Decrease in the free energy of the system, $-\Delta G = nFE$ — (1)

According to the Gibbs Helmholtz equation, which is applied to reversible changes

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \quad -(2)$$

On introducing the equation 1

$$-nFE = \Delta H + T\left(\frac{\partial(-nFE)}{\partial T}\right)_P$$

$$-nFE = \Delta H - TnF\left(\frac{\partial E}{\partial T}\right)_P$$

$$nFE = -\Delta H + TnF\left(\frac{\partial E}{\partial T}\right)_P \quad -(3)$$

The equation 3 permits the calculation of the heat of reaction from the measured e.m.f and temperature coefficient of emf of the reaction. Evidently whether the electrical energy $nFE$ is equal to or greater or less than the heat of reaction (i.e. $-\Delta H$) depends upon the sign of the value $\left(\frac{\partial E}{\partial T}\right)_P$, the temperature coefficient.

(1) If $\left(\frac{\partial E}{\partial T}\right)_P$ is positive if the emf of the cell increases with the rise in temperature, the electrical energy will be greater than ~~that of~~ the heat of reaction i.e $nFE > \Delta H$

(2) If $\left(\frac{\partial E}{\partial T}\right)_P$ is negative i.e. if the emf of the cell decreases with increase in temperature the electrical energy will be smaller than the heat of the reaction, i.e

$$nFE < \Delta H$$

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(3) If $\left(\frac{\partial E}{\partial T}\right)_P$ is equal to zero, the electrical energy will be equal to heat of reaction i.e.

$$nFE = \Delta H$$

From eqn 3.

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_P \quad (4)$$

$$\because \quad \Delta G = \Delta H - T\Delta S \quad (5)$$

and writing equation 3 as

$$-\Delta G = -\Delta H + TnF\left(\frac{\partial E}{\partial T}\right)_P$$

$$\text{or} \quad \Delta G = \Delta H - TnF\left(\frac{\partial E}{\partial T}\right)_P \quad (\because -\Delta G = -nFE) \quad (6)$$

From eq 5 & 6.

$$-T\Delta S = -TnF\left(\frac{\partial E}{\partial T}\right)_P$$

$$\text{or} \quad \Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P \quad (7)$$

with the aid of eq 7 the entropy change of a reaction can readily be calculated from the temperature coefficient of e.m.f

__Numerical 1.__ The e.m.f. of the cell $Pb/PbCl_2(s)/KCl(m)/Hg_2Cl_2(s)/Hg$ is 0.5357 V at 298 K and increases with temperature by $1.45 \times 10^{-4}\,VK^{-1}$. Calculate $\Delta G$, $\Delta H$, $\Delta S$.

__Sol.__ The cell reaction is

$$Pb + Hg_2Cl_2 = PbCl_2 + 2Hg(l)$$

1. Free energy change $\Delta G^\circ$

The above reaction requires 2 Faradays of electricity for its completion i.e. $n=2$

Free energy change is given by the reaction

$$\Delta G = -nFE = -2 \times 96500 \times 0.5357 \text{ Joules}$$
$$= -103.39\,KJ$$

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2. Enthalpy change $\Delta H$

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_P$$

$$0.5357 = -\frac{\Delta H}{2\times96500} + 298 \times 1.45\times10^{-4}$$

$$= -95.050 \text{ KJ/mol}$$

3. Entropy change $\Delta S$

$$\Delta G = \Delta H - T\Delta S$$

$$-103.39 = -95.05 - 298 \times \Delta S$$

$$\Delta S = \frac{+103.39 - 95.05}{298}$$

$$= 27.98 \text{ J/K/mol.}$$