PHASE EQUILIBRIA

Phase: A homogeneous part of a system is called a *phase.*

Homogeneous: If each *intensive macroscopic property* (property that do not depend on the amount of matter in the system and is measured at the molecular level) is constant throughout a system, the system is *homogeneous*.

Example: A saturated solution of AgCl containing solid AgCl in equilibrium with its aqueous solution, the system has two phases, namely solid AgCl and the saturated solution.

Gaseous system: Since gases are miscible with each other in all proportions, a mixture of gases will constitute a single phase,

Liquid system: For completely miscible liquids, the number of phase is one. A solution of water and ethanol will a one-phase system. If two or more liquids are not miscible with each other then number of liquids in the mixture will the number of phases. A mixture of water and chloroform will be a two-phase system.

Solid system: Every solid constitute a single phase except when a solid solution is formed.

Component: It is the smallest number of independent chemical constituents by means of which the composition of each and every phase can be expressed.

Example: (i) Consider the equilibrium between two phases of H_2O : ice $\rightleftharpoons$ liquid water. Here, composition of each phase can be expressed in terms of H_2O. Hence, it is one-component system (ii) An aqueous solution of sucrose is a two-component system. The composition of the solution phase can be expressed by specifying the amounts of sugar and water. (iii) Reactive system: consider the thermal decomposition of $CaCO_3$ in a closed vessel $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. It is a three-phase system, two solid phases and one gaseous phase. As a result of existence of equilibrium, the no of components is only two. If we choose them CaO and CO_2, then the composition of the solid $CaCO_3$ can be given by CaO + CO_2 (each one mole). If $CaCO_3$ and CO_2 are chosen as components, then the composition of solid CaO can be given by $CaCO_3 - CO_2$ and so on.

Degrees of freedom: It is defined as the number of independent intensive variables (pressure, temperature and composition) which must be specified in order to define the system completely. Consider the equilibrium ice $\rightleftharpoons$ liquid water, here either the temperature or the pressure of the system need to specify the system completely. Mole fraction of each phase (composition) is 1 and not at all a variable. If temperature is fixed, pressure of the system is fixed automatically and vice-versa. Hence the degrees of freedom of the system is one, univariant system.

Gibbs Phase Rule: The number of degrees of freedom (F) of the system is related to the number of components (C) and the number of phases (P) existing at equilibrium with one another by the equation $F = C - P + 2$

For one-component system the above equation becomes $F = 1 - P + 2 = 3 - P$ If there is only one phase exists in the system, say for example, H_2O (l) or H_2O (v), then for such a system $F = 3 - 1 = 2$, bivariant system. Both temperature and pressure of the system have to be specified in order to define the state of the system. If two phases of system are coexisting in the system as H_2O (l) $\rightleftharpoons$ H_2O (v), then $F = 3 - 2 = 1$, an univariant system as mentioned earlier. For three-phase coexistence H_2O (s) $\rightleftharpoons$ H_2O (l) $\rightleftharpoons$ H_2O (v), degrees of freedom $F = 3 - 3 = 0$. The system is non-variant. Both the temperature and pressure are fixed for such three-phase coexistence **(Triple point).**

Phase diagram of water: For one – component system the maximum number of degrees of freedom can be only 2 (when there is only one phase). So its phase diagram can be drawn in two dimensions by choosing rectangular axes representing pressure (p) and temperature (T) of the system.

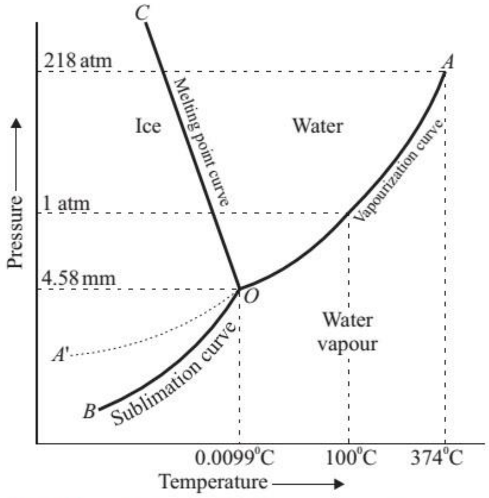


Fig. Phase diagram for the water system

- When P = 1, the three phases are shown in the diagram by three regions as shown in the figure (ice, water and water vapour). Where degrees of freedom F = 2.
- When P = 2, the three two - phase equilibria of the system are

(i) H_2O (s) ⇌ H_2O (l) (ii) H_2O (l) ⇌ H_2O (v) and (iii) H_2O (s) ⇌ H_2O (v) There are three lines shown in the figure to represent the above three two-phase coexistence. Melting point curve (or fusion curve) CO, vapourization curve, AO and the sublimation curve, BO for the above three equilibria respectively are shown in the figure. In each case F = 1.

- When P = 3 there is only one such equilibrium exists: H_2O (s) ⇌ H_2O (l) ⇌ H_2O (v) and one triple point O is shown in the figure for which F = 0.

Eutectic mixture:

A **eutectic system** is a homogeneous mixture of substances that melts or solidifies at a single temperature that is lower than the melting point of any of the constituents.

Clausius Clapeyron equation:

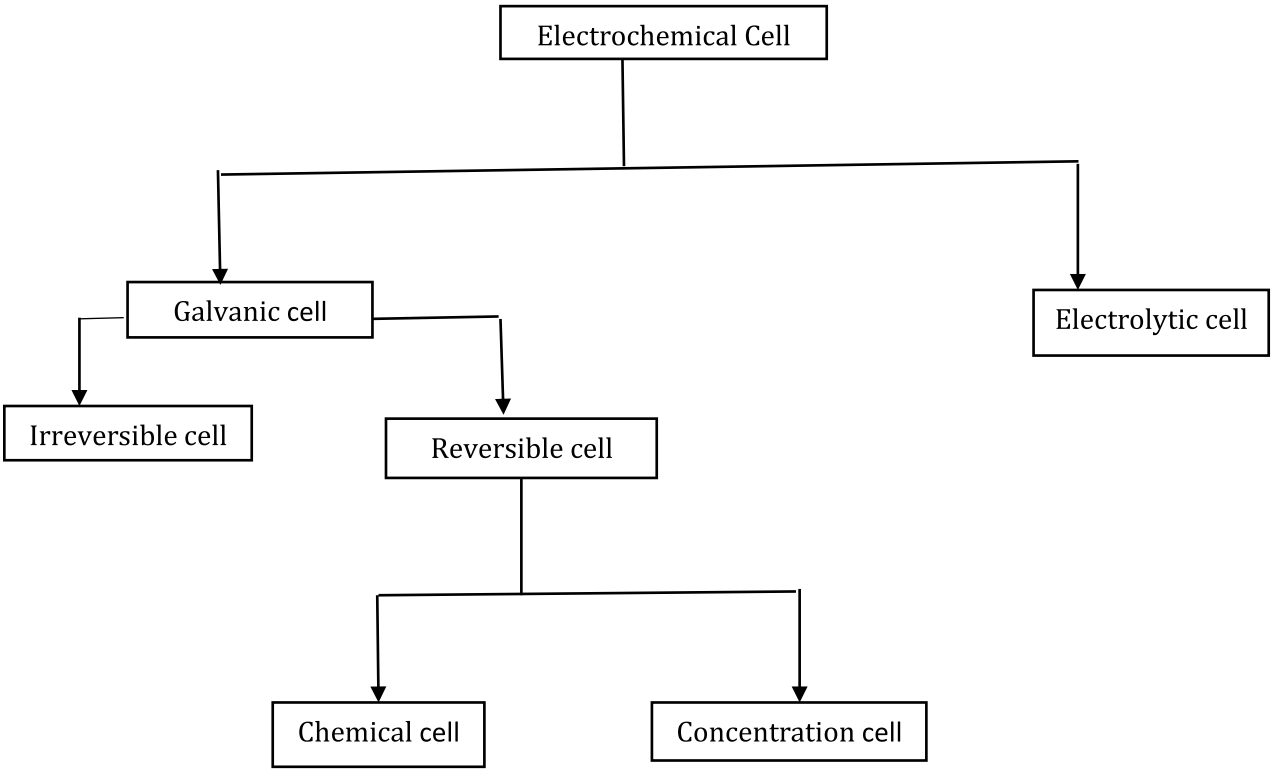
For solid – gas or liquid – gas equilibrium

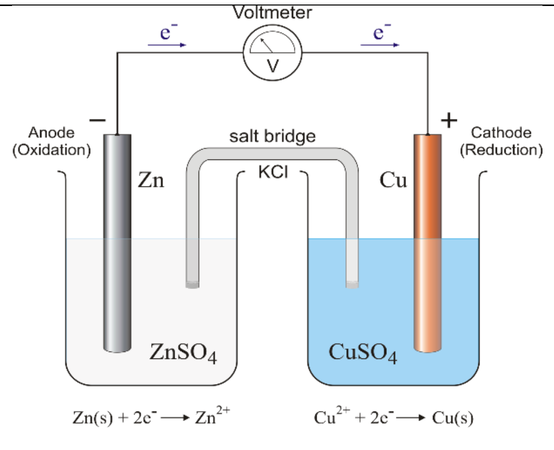
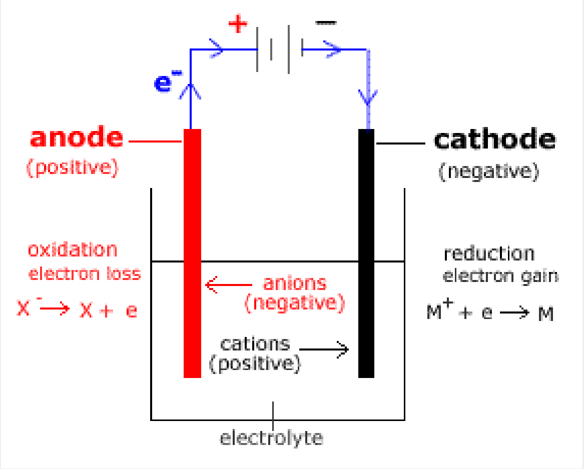
$\frac{d\ln P}{dT} = \frac{\Delta H_m}{RT^2}$ where P is the equilibrium pressure, T is the transition temperature in Kelvin and ΔH_m is the corresponding molar enthalpy of transition.
If ΔH_m is assumed to be constant then the above equation on integration yield

$$\ln\frac{P_2}{P_1} = -\frac{\Delta H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Electrochemical Cell

Electrochemical cell is a device which converts electrical energy to chemical energy and vice versa



No.	Galvanic cell	Electrolytic cell
1	Converts chemical to electrical energy	Converts electrical to chemical energy
2	Energy produced within cell is supplied outside the cell	Energy from outside is supplied within the cell
3	Energy producer	Substance producer
4	Cell rection spontaneous	Cell reaction non spontaneous
5	Oxidation occurs at negative electrode and reduction at positive electrode	Oxidation occurs at positive electrode and reduction at negative elcectrode
6	Eg. Daniel cell $Zn(s)/Zn^{+2}(aq)/Cu^{+2}(aq)/Cu(s)$	Eg. Electrolysis of acidulated water
7	 $Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$	

Galvanic cell: It is an electrochemical cell which converts chemical energy to electrical energy. It utilizes chemical reaction within the cell to produce electric current.

It is of two types: reversible cell and irreversible cell

Reversible cell	Irreversible cell
No reactions occur unless electrodes are connected by external circuit	Reaction occur even in absence of current flow in external circuit
Reversing direction of current reverses cell reaction	Reversing direction of current does not reverse cell reaction
Example: $Zn(s)/Zn^{+2}(aq)/Cu^{+2}(aq)/Cu(s)$	Example: $Zn/H_2SO_4/Cu$

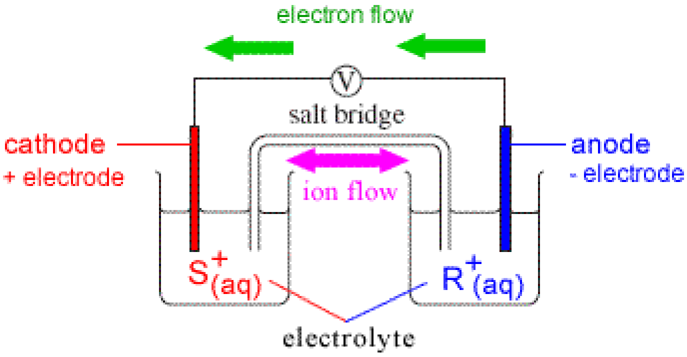
To maintain reversibility of cell open circuit condition [i.e. I(current) =0] condition is to be maintained,

Cell components:

A cell is composed of two **electrodes** (usually metals) and one or more **electrolytic** solutions.

The electrodes conduct electricity by the help of electrons. Hence it is called an electronic conductor.

The electrolytic solution conducts electricity by the help of ions. Hence it is called an ionic conductor.



Types of reversible electrodes:

1. **Metal/Metal ion electrode[M/M^{n+}]:** Consists of metal as the electrode and its corresponding ion as the electrolytic solution. $M^{n+}(aq) + ne \rightleftharpoons M(s)$ reversible to metal ion (M^{n+})
   e.g. $Zn(s)/Zn^{+2}(aq)$
   Reaction in terms of reduction $Zn^{+2} + 2e \rightleftharpoons Zn$
   Reaction in terms of oxidation $Zn - 2e \rightleftharpoons Zn^{+2}$

2. **Metal/metal Insoluble salt electrode[$M/MX(s)/X^-(aq)$]:** Consists of metal coated with layer of insoluble salt of the metal and is immersed in an electrolyte solution containing the anion(negative) of the salt. $MX(s)+e \rightleftharpoons M + X^-(aq)$ reversible to X^-.
   e.g. $Hg(l)/Hg_2Cl_2(s)/Cl^-(aq)$(calomel)
   Reaction in terms of reduction $Hg_2Cl_2+2e \rightleftharpoons 2Hg+ 2Cl^-$
   Reaction in terms of oxidation $2Hg +2Cl^- -2e \rightleftharpoons Hg_2Cl_2$

3. **Gas electrode :** It is of two types
   (i) Cation reversible electrode e.g. $H^+(aq)/H_2(g)/Pt$
   Reaction in terms of reduction $2H^+ + 2e \rightleftharpoons H_2$
   Reaction in terms of oxidation $H_2 - 2e \rightleftharpoons 2H^+$

   (ii) Anion reversible electrode e.g. $Cl^-(aq)/Cl_2(g)/Pt$
   Reaction in terms of reduction $Cl_2+2e \rightleftharpoons 2Cl^-$
   Reaction in terms of oxidation $2Cl^- -2e \rightleftharpoons Cl_2$

4. **Redox electrode:** Both oxidized and reduced form of species is present in the solution and an inert metal like Pt is used as an electronic conductor.
   E.g. $Pt/Fe^{+2},Fe^{+3}(aq)$
   Reaction in terms of reduction $Fe^{+3} + e \rightleftharpoons Fe^{+2}$
   Reaction in terms of oxidation $Fe^{+2} - e \rightleftharpoons Fe^{+3}$

Cell representation: By convention the oxidation reaction species are written on the left hand side of the cell and the reduction reaction species on the right hand side.

E.g. For the cell reaction $Zn(s) + Cu^{+2}(aq) \rightleftharpoons Zn^{+2}(aq) + Cu(s)$
LHS (oxidation reaction) at the negative electrode (anode) $Zn(s) - 2e \rightleftharpoons Zn^{+2}(aq)$
RHS (reduction reaction) at the positive electrode (cathode) $Cu^{+2}(aq) + 2e \rightleftharpoons Cu(s)$
Cell representation: **$Zn(s)/Zn^{+2}(aq)//Cu^{+2}(aq)/Cu(s)$**
The // sign represents a salt bridge.

Electrode potential of a reversible electrode: It is the potential difference between the electronic and ionic conductor of the half cell.

Electromotive force (EMF) of a galvanic cell: The difference in electrode potentials of the two half cell comprising the galvanic cell at a particular temperature. $E_{cell} = E_R - E_L$ (both half cell potentials written in terms of reduction). It is calculated by the help of **Nernst equation** and measured by **Poggendorff's compensation method**.

Standard electrode potential (E°) : It is the potential of the electrode when all the species involved in the given half cell are in their standard state of unit activity at a particular temperature. It is measured by coupling it with SHE (standard hydrogen electrode) as a oxidation electrode .

Standard hydrogen electrode (SHE): It is a reversible hydrogen electrode with H2 gas at 1 bar pressure in equilibrium with an acid solution containing hydrogen ion of unit activity.
E° of SHE is taken to be zero at all temperatures.

Nernst equation: Gives a relationship between emf of cell or electrode potential of hal cell with concentration of chemical species of the cell/half-cell.
For half-cell $M^{n+}(aq) + ne \rightleftharpoons M(s)$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

where E = electrode potential of half-cell in volts, E° = Standard electrode potential of half-cell in volts, R = universal gas constant = 8.314 J/K/mole, T = temperature in K, n = no. of electrons involved in the half cell reaction, F = Faraday = 96500 coulomb/volt

For the cell reaction $M(s) + N^{+n}(aq) \rightleftharpoons M^{+n}(aq) + N(s)$

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[M^{n+}]}{[N^{n+}]}$$

EMF and thermodynamic relations:

1. $\Delta G = -nFE$, where ΔG = Gibbs free energy of the ell reaction in J/mole
2. $\Delta G^0 = -nFE^0$ where ΔG^0 = Standard Gibbs free energy of the ell reaction in J/mole
3. $\Delta G^0 = -RT \ln K$ where K = equilibrium constant of the cell reaction
4. $\Delta S = nF\left(\frac{\delta E}{\delta T}\right)_P$ where ΔS = entropy change of the cell reaction
5. $\Delta H = -nFE + nFT\left(\frac{\delta E}{\delta T}\right)_P$ where ΔH = enthalpy change of the cell reaction

Faradays laws of electrolysis:

1. The amount of any substance deposited or dissolved is proportional to the quantity of electricity passing through the electrolytic solution. m(mass deposited or dissolved) α Q (charge)
   M =ZQ= ZIt where Z = electrochemical equivalent = E/96500, Q charge in coulombs, I = current in amperes, t = time in seconds
2. The amount of different substances deposited or dissolved by the same quantity of electricity are proportional to their chemical equivalent weights W α E (equivalent weight in gms)
3. The quantity of electricity required to liberate 1 equivalent of any substance is independent of its nature and is called Faraday. 1 F = 96500 coulombs.

Chemical cell: A galvanic reversible cell where emf is produced due to chemical reaction within the cell. E.g. $Zn(s)/Zn^{+2}(aq)/Cu^{+2}(aq)/Cu(s)$ with chemical reaction $Zn(s) + Cu^{+2}(aq) \rightleftharpoons Zn^{+2}(aq) + Cu(s)$.

Concentration cell: A cell in both half-cells are similar but the concentration of either the electrolytes or electrodes are different. E.g. (i) $Pt(s)/H_2(g)(P_1)/HCl(aq)/H_2(g)(P_2)/Pt(s)$ electrode concentration cell, where hydrogen electrode have different pressure P_1 and P_2.
(ii) $Ag(s)/AgCl(s)/HCl(aq, c_1)//HCl(aq, c_2)/AgCl(s)/Ag(s)$ electrolyte concentration cell, where electrolyte HCl has different concentrations c_1 and c_2.

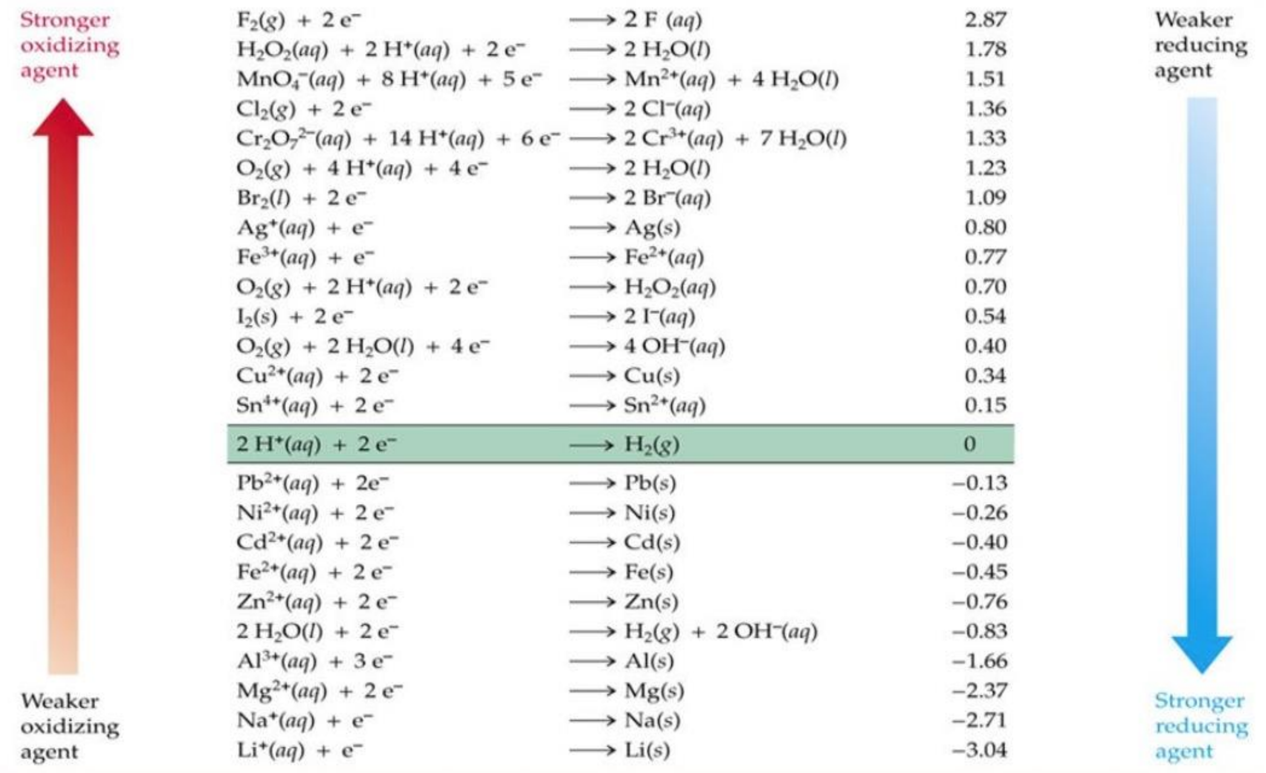
Liquid Junction Potential: It is a potential which arises at the junction of the two half cells where two electrolytic solutions are in contact due to difference in ionic mobility.
It is eliminated by the help of a device called **salt bridge**.

Use of salt bridge:

1. It is a device connecting the oxidation and reduction half cells i.e. it maintains electrical connection between two half cells.
2. It eliminates liquid junction potential

Composition of salt bridge: It is composed of saturated (highly concentrated) solution of salts having ions of equal mobility. E.g. KCl salt bridge, NH_4NO_3 salt bridge.

Electrochemical Series: The arrangement of elements in order of their standard reduction potentials is called an electrochemical series.



$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

- Substances higher on the electrochemical series, with high reduction potential can be reduced easily and hence act as better oxidising agents.
- Down the series, reduction potential decreases, substance cannot be easily reduced, i.e. they are easily oxidized and hence act as better reducing agents.

pH determination using electrochemical cell: pH = -log $[H^+]$ (for dilute solutions)

3 types of electrochemical half cells can be used for pH determination of a solution.

1. **Hydrogen electrode:** Pt (s) / H_2(g) (1 atm)/H^+ (aq) It is a gas electrode reversible to hydrogen ion. Reaction : $2H^+ + 2e \rightleftharpoons H_2$.

   According to Nernst equation:

   $$E_{H^+/H_2} = E° - \frac{RT}{2F} \ln \frac{p_{H_2}}{[H^+]^2} = \frac{RT}{F} \ln[H^+] = 2.303 \frac{RT}{F} \log[H^+] = -0.059\text{pH}$$

   E° =0 for SHE, $2.303 \frac{RT}{F} = 0.059$ volts at 25°C, $p_{H_2} = 1\ atm$

2. **Quinhydrone electrode:** Q, QH_2, H^+(aq)/Pt(s) It is a redox electrode reversible to hydrogen ion containing equimolar mixture of quinone and hydroquinone. Reaction: $Q + 2H^+ + 2e \rightleftharpoons QH_2$.

   According to Nernst equation:

   $$E_{Q/QH_2} = E^0_{Q/QH_2} - \frac{RT}{2F} \ln \frac{[QH_2]}{[Q][H^+]^2} = E^0_{Q/QH_2} + \frac{RT}{F} \ln[H^+] = E^0_{Q/QH_2} + 2.303 \frac{RT}{F} \log[H^+] = 0.699 - 0.059\text{pH}$$

   Where [Q] =$[QH_2]$ as equimolar mixture of quinone and hydroquinone taken. E^0_{Q/QH_2} =0.699V at 25°C.

3. **Glass electrode:**
   - It is an ion selective membrane electrode reversible to hydrogen ion.
   - It allows exchange of hydrogen ions across a glass membrane.
   - The E° glass depends on type of glass membrane , hence it is used in measuring unknown pH by calibrating the glass electrode with solution of known pH.
   - It cannot be used at high pH values (>10)
   - $E_{glass} = E^0_{glass} - 0.059\text{pH}$ (at 25°C)
   - Ag(s)/AgCl(s)/HCl (0.1N)/glass/unknown solution