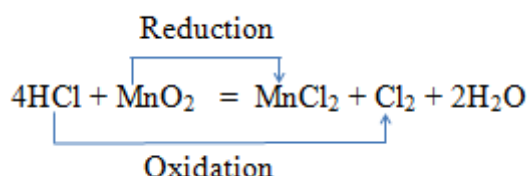# Redox Chemistry

The reactions which involve oxidation & reduction are called redox reaction.

e . g .

$$\overset{\text{Reduction}}{4HCl + MnO_2} = \overset{}{MnCl_2 + Cl_2} + 2H_2O$$

Oxidation

In here HCl has been oxidised to Cl_2 and MnO_2 has been reduced to $MnCl_2$.

Oxidation number : It's the charge which an atom of an element has in its ion or appear to have when present in the combined state. It is also known as oxidation state.

Rules for calculation of oxidation number:

1. Oxidation number of any atom in the elementary state is zero.

    e . g . in O_2 , H_2 , Na, He and Fe the oxidation state of each atom equal to zero.

2. Oxidation number of mono atomic ion is equal to the charge on it.
3. Oxidation number of H is +1 when combined with non metal and -1 when combined with active metal like Na, Ca etc. *e . g .* NaH, CaH_2 .
4. Oxidation number of oxygen is -2 except in peroxides like H_2O_2 , Na_2O_2 etc where it is -1 and OF_2 where it is +2.
5. Oxidation number of alkali and alkaline earth metals is +1 and +2 respectively.
6. Oxidation number of halogens is in -1 in metal halides.
7. In compounds of metal with non-metal, metal have positive oxidation numbers whereas non-metals have negative Oxidation numbers.
8. In compound of two different elements, the more electronegative has negative Oxidation number and the other has positive oxidation number.
9. In complex ions, the sum of the oxidation numbers of all atoms is equal to the charge on the ion.

    Oxidation (de-electronation): loss of electron or result in the increase in oxidation number of its atom/s.

    Oxidising agent: acceptor of electron/s.

    Reduction (Electronation): Gain of electron/s or decrease in oxidation number of its atom/s.

    Reducing agent: Donor of electron/s.

    Redox potential:

    Any oxidation -reduction (redox) reaction can be divided into two half reactions: one in which a chemical species undergoes oxidation and one in which another chemical species undergoes reduction. If a half-reaction is written as a reduction, the driving force is the reduction potential. If the half-reaction is written as oxidation , the driving force is the oxidation potential related to the reduction potential by a sign

change. So the redox potential is the reduction/ oxidation potential of a compound measured under standards conditions against a standard reference half-cell.

In biological systems the standard redox potential is defined at pH − 7.0 versus the hydrogen electrode and partial pressure of hydrogen = 1 bar .

e . g . $2Ag + Cl_2 = 2AgCl$

The above redox reaction can be split into two half reactions

2 Ag = 2Ag⁺ + 2e or Ag = Ag⁺ + e - (I)

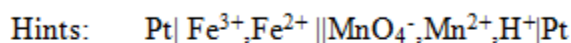Cl_2 + 2e = 2Cl⁻ or ½ Cl_2 + e = Cl⁻ - (II)

Reaction (I) is a oxidation process & the potential of this reaction is oxidation potential whereas potential of reaction (II) is reduction potential.
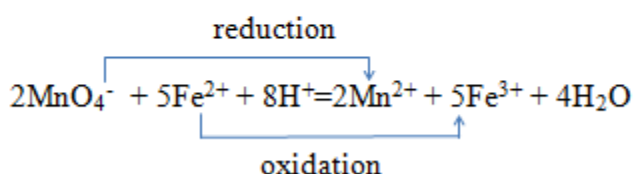
Analysis of redox cycle:

The half-cell potential of two half cells is given below. What is the redox reaction happened when they are combined in a favourable condition?

$E°_{Fe3+,Fe2+|Pt} = 0.771$ V and $E°_{MnO4-,Mn2+,H+|Pt} = 1.51$ v

Hints: $Pt| Fe^{3+},Fe^{2+} ||MnO_4^-,Mn^{2+},H^+|Pt$

Reaction happened   reduction

$$2MnO_4^- + 5Fe^{2+} + 8H^+ = 2Mn^{2+} + 5Fe^{3+} + 4H_2O$$

oxidation
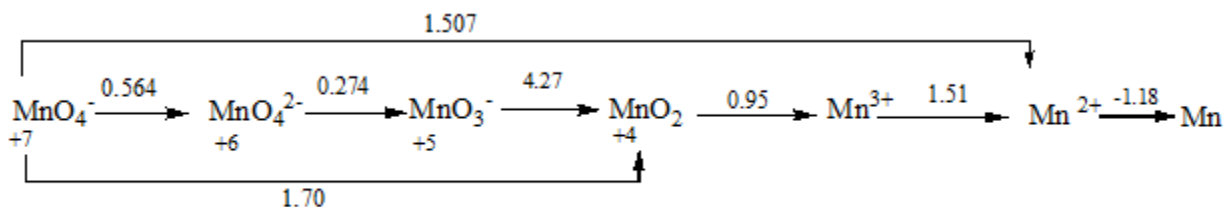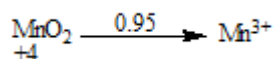
Latimer diagram:

Latimer or reduction potential diagrams show the standard reduction potentials connecting various oxidation states of an element. The Latimer diagram for a series of manganese species in acidic solution is shown below.


Latimer diagram for a series of manganese species in acidic solution

Utility of the diagram: The standard reduction potential for the reduction half-reaction involving the two species joined by the arrow is shown above the arrow. Latimer diagrams show the redox information about a series of species in a very condensed form. From these diagrams you can predict the redox behaviour of a given species. The more positive the standard reduction potential, the more readily the species on the left is reduced to the species on the right side of the arrow. Thus, highly positive standard reduction potentials indicate that the species at the left is a good oxidizing agent. Negative standard reduction potentials indicate that the species to the right behaves as a reducing agent.

Construction: In a Latimer diagram of an element, oxidation numbers of the element decrease from left to right and the numerical values of $E°$ in volts) are written above the line joining the species involved in the couple.
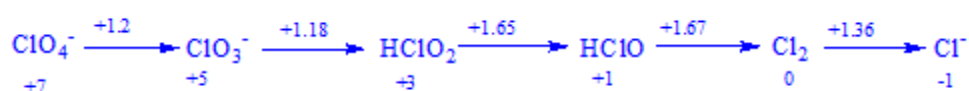
$$MnO_2 \xrightarrow{0.95} Mn^{3+}$$
$$\text{+4}$$

In the above example, the notation denotes the half-cell reaction with E° = +0.95 volt

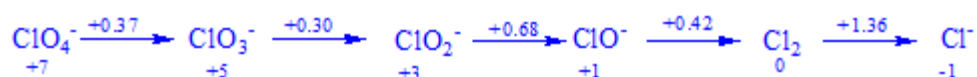$$MnO_2 + 4H^+ + e \longrightarrow Mn^{3+} + 2H_2O$$
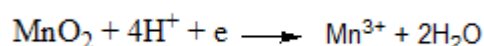
Note that both of these half-reactions involve hydrogen ions, and therefore the potentials depend on pH.

$e.g.$ The Latimer diagram for chlorine in acidic solution, for instance, is

$$ClO_4^- \xrightarrow{+1.2} ClO_3^- \xrightarrow{+1.18} HClO_2 \xrightarrow{+1.65} HClO \xrightarrow{+1.67} Cl_2 \xrightarrow{+1.36} Cl^-$$
$$\quad +7 \qquad\qquad +5 \qquad\qquad +3 \qquad\qquad +1 \qquad\quad 0 \qquad\qquad -1$$

In basic aqueous solution, the Latimer diagram for chlorine is

$$ClO_4^- \xrightarrow{+0.37} ClO_3^- \xrightarrow{+0.30} ClO_2^- \xrightarrow{+0.68} ClO^- \xrightarrow{+0.42} Cl_2 \xrightarrow{+1.36} Cl^-$$
$$\quad +7 \qquad\qquad +5 \qquad\qquad +3 \qquad\qquad +1 \qquad\quad 0 \qquad\qquad -1$$
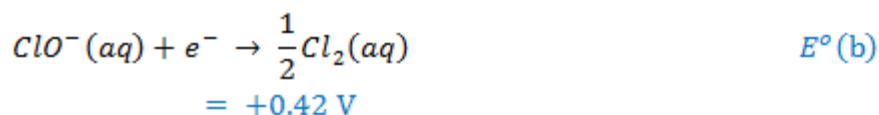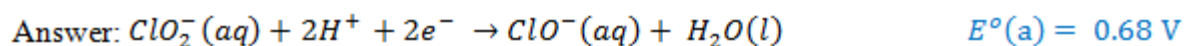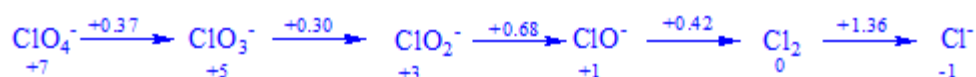
Nonadjacent species: For the nonadjacent species the standard potential of a couple that is the combination of two other couples is obtained by combining the standard Gibbs energies, not the standard potentials, of the half-reactions.

$$\Delta G°(a+b) = \Delta G°(a) + \Delta G°(b)$$

And as $G = -nFE°$, hence

$$E°(a+b) = \frac{n(a)E°(a) + n(b)E°(b)}{n(a) + n(b)} \qquad\qquad \text{...... ... ... (L1)}$$

Q. From the Latimer diagram for chlorine in basic aqueous solution find out the reduction potential value for ClO_2^-/Cl_2 couple.

$$CO_4^- \xrightarrow{+0.37} ClO_3^- \xrightarrow{+0.30} ClO_2^- \xrightarrow{+0.68} ClO^- \xrightarrow{+0.42} Cl_2 \xrightarrow{+1.36} Cl^-$$
$${+7}{+5}{+3}{+1}{0}{-1}$$

Answer: $ClO_2^- (aq) + 2H^+ + 2e^- \rightarrow ClO^- (aq) + H_2O(l)$ $\qquad\qquad$ $E^\circ(a) = 0.68$ V

$ClO^- (aq) + e^- \rightarrow \dfrac{1}{2} Cl_2(aq)$ $\qquad\qquad\qquad\qquad\qquad$ $E^\circ(b)$

$\qquad\qquad = +0.42$ V

Their sum is the half-reaction for the couple we require.

$$ClO_2^- (aq) + 2H^+ (aq) + 3e^- \rightarrow \frac{1}{2} Cl_2(gas) + H_2O(l)$$
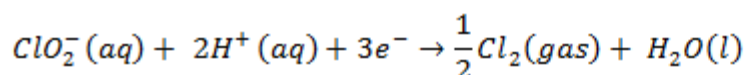
We see that $n(a) = 2$ and $n(b) = 1$. It follows from equation $L1$ that the standard potential of the ClO_2^- / Cl_2 couple is
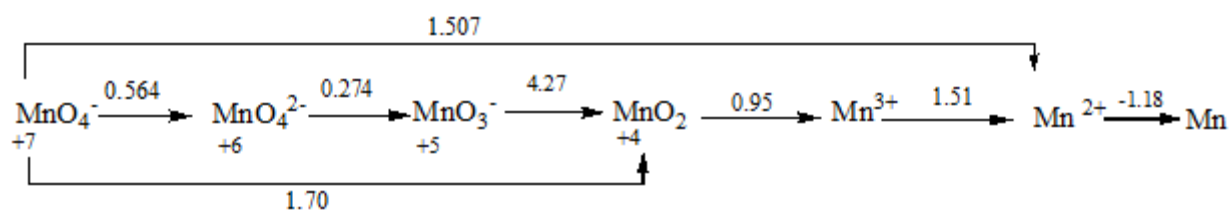
$$E^\circ = \frac{(2)(0.68v) + (1)(0.42)}{3} = +0.59 \; V$$

$$E^\circ(a+b) = \frac{n(a)E^\circ(a) + n(b)E^\circ(b)}{n(a) + n(b)}$$

Disproportionation: It is a specific type of redox reaction in which a species simultaneously reduced and oxidized to form two different species with lower and higher oxidation sate.
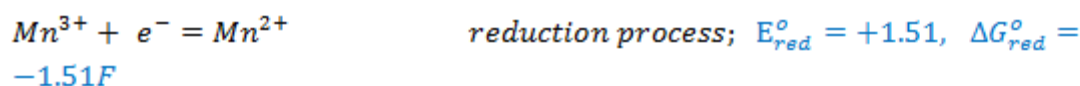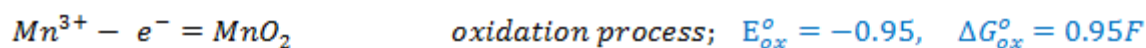
$$e.g. \; 2Mn^{3+} = Mn^{2+} + MnO_2$$
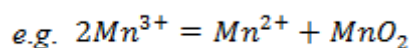
A species has a tendency to disproportionate into its two neighbours if the potential on the right of the species in a Latimer diagram is higher than that on the left.

$$1.507$$

$$\underset{+7}{MnO_4^-} \xrightarrow{0.564} \underset{+6}{MnO_4^{2-}} \xrightarrow{0.274} \underset{+5}{MnO_3^-} \xrightarrow{4.27} \underset{+4}{MnO_2} \xrightarrow{0.95} Mn^{3+} \xrightarrow{1.51} Mn^{2+} \xrightarrow{-1.18} Mn$$

$$1.70$$

Latimer diagram for a series of manganese species in acidic solution

For the given example,

$Mn^{3+} - e^- = MnO_2$ $\qquad$ oxidation process; $E^o_{ox} = -0.95, \quad \Delta G^o_{ox} = 0.95F$

$Mn^{3+} + e^- = Mn^{2+}$ $\qquad$ reduction process; $E^o_{red} = +1.51, \quad \Delta G^o_{red} = -1.51F$

$\Delta G^o_{total} = \Delta G^o_{ox} + \Delta G^o_{red} = -0.56F$ $\quad$ a negative value, spontaneous process

Q. MnO_4^{2-} undergoes disproportionation reaction. Find out the change in free energy for the disproportionation process and find out the equilibrium constant (k)?

Hints: Find out ΔG^o_{total} from the Latimer diagram shown above ($\Delta G^o_{total} = -3.40\ F$) and then from the equation $\Delta G^o = -RTlnk$ find out k at $298° K$.

$$k = 3.2\ X\ 10^9$$

Q. A part of Latimer diagram is,

$$O_2 \xrightarrow{+0.70\ V} H_2O_2 \xrightarrow{+1.76\ V} H_2O$$
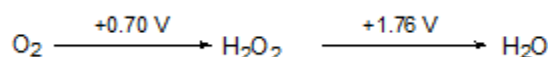
Does hydrogen peroxide have a tendency to disproportionate in acid solution?

Frost Diagrams:

Frost or oxidation state diagrams plot the relative free energy of a species versus oxidation state. These diagrams visually show quite a bit about the properties of the different oxidation states of a species. Frost diagrams can be constructed from Latimer diagrams. The values to be plotted on the y-axis are obtained by multiplying the number of electrons transferred during an oxidation state change by the standard reduction potential for that change.
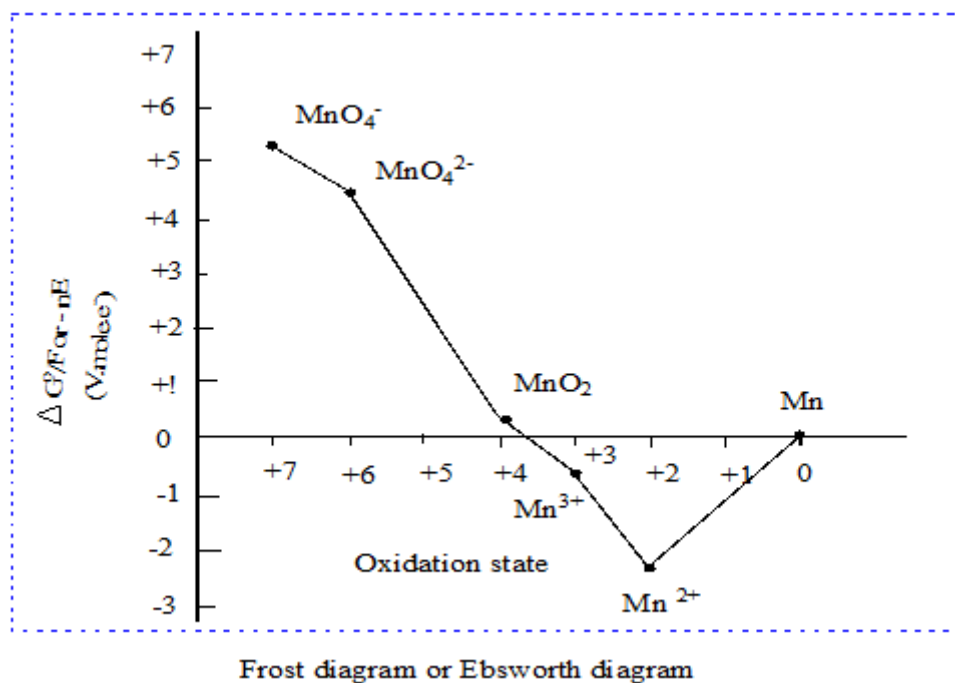
Figure 5.1. Frost diagram for MnO_4^- to Mn system.

Utility and limitation of Frost Diagram:

- Thermodynamic stability is found at the bottom of the diagram. Thus, the lower a species is positioned on the diagram, the more thermodynamically stable it is (from a oxidation-reduction perspective) Mn (II) is the most stable species.
- A species located on a convex curve can undergo disproportionation
  MnO_4^{2-} and Mn (III) tends to disproportionate.
- Those species on a concave curve do not typically disproportionate. MnO_2 does not disproportionate
- Any species located on the upper left side of the diagram will be a strong oxidizing agent.
  MnO_4^- is a strong oxidizer.
- Any species located on the upper rignt side of the diagram will be a reducing agent.
  manganese metal is a moderate reducing agent
- These diagrams describe the thermodynamic stability of the various species.
  Although a given species might be thermodynamically unstable toward reduction, the kinetics of such a reaction might be very slow.
  Although it is thermodynamically favourable for permanganate ion to be reduced to Mn (II) ion, the reaction is slow except in the presence of a catalyst. Thus, solutions of permanganate can be stored and used in the laboratory
- The information obtained from a Frost diagram is for species under standard conditions (pH=0 for acidic solution and pH=14 for basic solution).
  Changes in pH may change the relative stabilities of the species. The potential of any process involving the hydrogen ion will change with pH because the concentration of this species is changing. Under basic conditions aqueous Mn^{2+} does not exist. Instead Insoluble $Mn(OH)_2$ forms
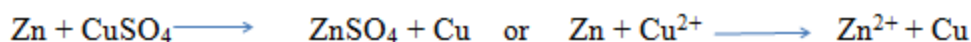
Redox principles involved in extraction of elements:

Electrochemical cells:

A device producing an electric current from a chemical reaction (Redox reaction) is called electrochemical cell i.e. it converts chemical energy to electrical energy.
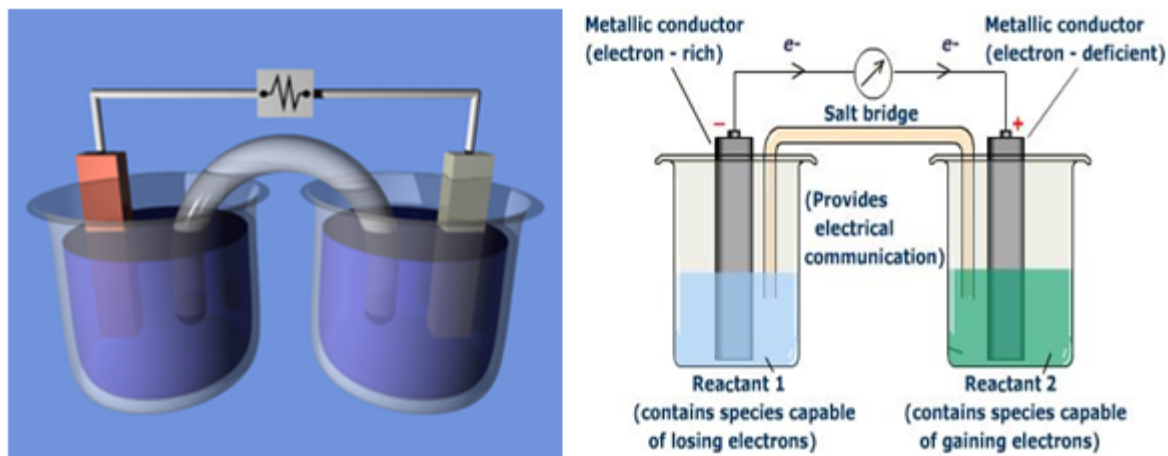
Figure 5.2. A demonstration electrochemical cell setup resembling the Daniell cell. The two half-cells are linked by a salt bridge carrying ions between them. Electrons flow in the external circuit.

A redox reaction consists of two half reactions called oxidation half reaction and reduction half reaction.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu \quad \text{or} \quad Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

Two half redox reactions are

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad \text{oxidation half reaction}$$

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \text{reduction half reaction}$$

Electrochemical cell based on this reaction is called Daniel cell.

In electrochemical cell those two half reactions are used as two half cells joined together by salt bridge.

Salt bridge: A U-shaped tube containing a concentrated solution of an inert electrolyte like K_2SO_4 , KCl, KNO_3 etc. The function of salt bridge is to complete inert circuit by flow of ions and to maintain the electrical neutrality in the solution of two half cells.

For making the salt bridge only those electrolytes are used for which cations and anions have nearly same ionic mobility.

In electrochemical cell, the electrode at which oxidation takes place is called anode or negative pole and the electrode at which reduction takes place is called anode or positive pole.

Electrochemical cell is represented as electron flow from anode to cathode in the external circuit while current flows from cathode to anode.

Electrode potential or half-cell potential:

The tendency of an electrode to lose electrons is called oxidation potential, while tendency of an electrode to gain electrons is called reduction potential. Electrode potential depends upon concentration of metal ion and temperature. At standard condition i.e. 1 molar concentration and 298k are called standard electrode potential.

The absolute value of electrode potential cannot be measured directly because half reaction cannot take place independently. Electrode potential is measured against reference electrode i.e. standard hydrogen electrode (S.H.E) and the standard electrode potential of S.H.E is taken as zero. S.H.E is represented as

$$\text{Pt,H}_2(\text{gas,1 atm})|\text{H}^+(1\text{M})$$
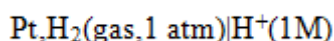
Standard electrode potential (E°) is given a positive sign if reduction occurs at that electrode with respect to the S.H.E and is given a negative sign, if oxidation occurs at the electrode with respect to the S.H.E.

EMF of cell and Electrode potential

The electromotive force or EMF of a cell is expressed in term of potential difference established between the half cells when no current passes through the cell. Under standard condition of temperature and concentration EMF is known as standard EMF and abbreviated as E° . This is expressed in volts.

$$E^\circ = [\text{standard reduction potential of cathode}] - [\text{standard oxidation potential of anode}]$$

$$= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

Nernst Equation: Dependence of electrode potential and EMF on concentration and temperature.

For electrode potential:

$$M^{n+} + ne^- \longrightarrow M(s)$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}(aq)]} \qquad \text{or} \qquad E = E^\circ - \frac{2.303\ RT}{nF} \log \frac{[M(s)]}{[M^{n+}(aq)]}$$

For solid, liquid or gases at 1 atm, $[M(s)] = 1$, $R = 8.314\ \text{JK}^{-1}\text{mol}^{-1}$, $T = 298\ \text{K}$, $F = 96500\ \text{C}$

$$E = E^\circ - \frac{0.059}{n} \log \frac{1}{[M^{n+}(aq)]}$$

For EMF of a cell involving the redox reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Q. What is the EMF of the following Denial cell? How can you calculate the equilibrium constant value for this cell?

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$$

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$$

LHE — Oxidation happened at half cell
RHE — Reduction happened at half cell

$$Zn(s) - 2e^- = Zn^{2+}(aq) \qquad Cu^{2+}(aq) + 2e^- = Cu(s)$$

total cell reaction

$$Zn(s) + Cu^{2+}(aq) = Zn^{2+}(aq) + Cu(s)$$

For this reaction n = 2 (no.s of electron transfer)

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

At equilibrium $E_{cell} = 0$ and $\dfrac{[Zn^{2+}]}{[Cu^{2+}]} = K_c$

$$0 = E^\circ_{cell} - \frac{0.059}{2} \log K_c$$

$$\log K_c = nE^\circ_{cell}/0.059 \text{ at } 298 \text{ K}$$

$$\log K_c = 2E^\circ_{cell}/0.059 \text{ at } 298 \text{ K}$$

<div align="center">Relation free energy change and EMF:</div>

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

When the EMF i.e. E_{cell} or E°_{cell} is positive then the redox reaction is spontaneous ($\Delta\Delta$ ΔG negative) and at negative E_{cell} or E°_{cell} value the redox reaction is not spontaneous (ΔG positive)

Relation between ΔG° and the equilibrium constant:

$\Delta G^\circ = -RT \ln K_c = -2.303RT \log K_c$

Some applications:

Purification of water: Ozone is a strong oxidizing agent and it is capable of destroying organic pollutants and bacteria present in water. Hence, oxidation reaction can be utilize for water purification process.

Electroplating: In this process electrical current is employed to reduce dissolved metal cation followed by deposition on a metal plate. This techniques is high in use to prevent corrosion in metals and its matalic machines.

Metallurgy: Metal ores are obtained in their complex form mainly as oxides, sulfides. Reduction of those ores provides pure metal, e.g. Hematite (Fe_2O_3), magnetite (Fe_3O_4) are reduced in the presence of carbon to have metallic iron.

Redox dependence :

Concentration dependence: The concentration of the reacting species in a half-cell greatly influences the potential of a system. A half-cell reaction is generally expressed as

<div align="center">Oxidized form + ne⁻ = Reduced form</div>

For this reaction, the Nernst reaction is

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[Reduced\ form]}{[Oxidized\ form]}$$

This shows that a tenfold increase in the concentration of the oxidized form will raise the half-cell potential by 0.059/n volts at *298°K* .

pH dependence: Many redox reactions in aqueous solution involve transfer of proton as well as electrons and the electrode potential or Value of E° therefore depends on the pH.

When hydrogen or hydroxyl ion or electron are involved in a reaction(half-cell reaction), there concentration appear in the Nertnst equation & accordingly the potential is influenced by the pH of the medium.

A reaction of this type should be represented through this way;

$$Ox + ne^- + mH^+ = Red$$

For this reaction, E = E° − (RT/nF)lnQ ....(i)

Where n = numbers of electron transfer

$$Q = \frac{[Red]}{[Ox][H^+]^m}$$

Ultimately at 25° C, equation (i) can be expressed as

$$E = E^o - \frac{RT}{nF}\ln\frac{[Red]}{[Ox]} + \frac{mRT}{nF}\ln[H^+]$$

As we know that $\ln[H^+] = 2.303\log[H^+]$ and $pH = -\log[H^+]$, hence

$$E = E' - \frac{mRT}{nF}pH, \qquad where\ E' = E^o - \frac{RT}{nF}\ln\frac{[Red]}{[Ox]}$$

Q. Write down the simplest form of Nernst equation for the given two half-cell reactions?

1. $AsO_4^{3-} + 2H^+ + 2e = AsO_3^{3-} + H_2O$ at pH=8

2. $MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$

Given that standard reduction potential value E° for AsO_4^{3-}/AsO_3^{3-} & MnO_4^-/Mn^{2+} are +0.56 and 1.51 volt, respectively.

Answer: 1. $E = +0.088 + \frac{0.059}{2}\ln\frac{[AsO_4^{3-}]}{[AsO_3^{3-}]}$

2. $E = +1.51 - 0.094pH + \frac{0.059}{5}\ln\frac{[MnO_4^-]}{[Mn^{2+}]}$

Effect of complexation: The formation of a more thermodynamically stable complex when the metal is in the higher oxidation state of a couple favours oxidation and makes the standard potential more negative; the formation of a more stable complex when the metal is in the lower oxidation state of the couple favours reduction and the standard potential becomes more positive.

The formation of metal complexes affects standard potentials because the ability of a complex (ML) formed by coordination of a ligand (L) to accept or release an electron differs from that of the corresponding aqua ion (M).

$$M^{n+}(aq) + e^- \rightarrow M^{(n-1)+}(aq) \qquad\qquad E^\circ(M)$$

$$ML^{n+}(aq) + e^- \rightarrow ML^{(n-1)+}(aq) \qquad\qquad E^\circ(ML)$$
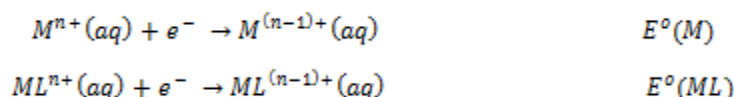
The change in standard potential for the ML redox couple relative to that of M reflects the degree to which the ligand L coordinates more strongly to the oxidized or reduced form of M. The change in standard potential is analysed by considering the thermodynamic cycle shown in Fig. 1. Because the sum of reaction Gibbs energies round the cycle is zero, we can write

$$-FE^\circ(M) - RT\ln K^{ox} + FE^\circ(ML) + RT\ln K^{red} = 0$$

$$E^\circ(M) - E^\circ(ML) = \frac{RT}{F}\ln\frac{K^{ox}}{K^{red}}$$

Where K^{ox} and K^{red} are equilibrium constants for L binding to M^+ and $M^{(n-1)+}$ respectively (of the form $K = [ML] / [M][L]$), and we have used $\Delta rG^\circ = RT \ln K$ in each case.
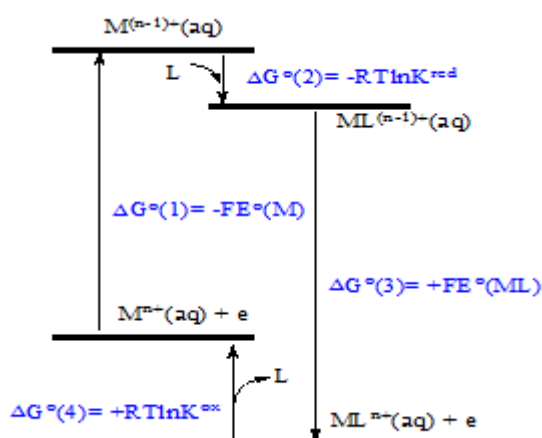
Figure 5.3. Thermodynamic cycle showing how the standard potential of the couple M^+/M is altered by the presence of a ligand L.

We know that at 25°,

$$E^\circ(M) - E^\circ(ML) = (0.059V)\ln\frac{K^{ox}}{K^{red}}$$

Thus, every ten-fold increase in the equilibrium constant for ligand binding to M^+ compared to $M^{(n-1)+}$ decreases the reduction potential by 0.059 V.

Effect of Precipitation:

Precipitation is due to change of concentration of the oxidized and reduced form and precipitation of one product is happened due to low solubility i.e. it depend upon the solubility product of that

compound, $e.g.$ due to low reduction potential of Cu^+/Cu^{2+} (+0.15 volt), it is not expected to oxidize iodide to iodine ($E° = +0.54\ volt$) but in practice due to low solubility of CuI, the concentration of Cu^+ ion reduces in such a way that the reduction potential is substantially increased.

$$Cu^{2+} + e = Cu^+$$
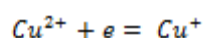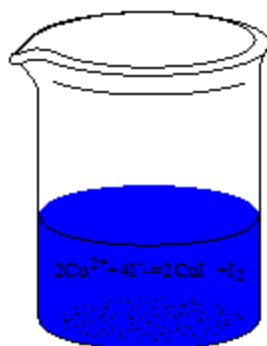
$$E = E^0 - \frac{RT}{nF} \ln \frac{[Cu^+]}{[Cu^{2+}]}$$

The concentration of cuprous ion (Cu^+) is determined by the solubility product (k) of CuI,

$$k = [Cu^+][I^-] = 10^{-12}$$

$$\text{So, } E = E^0 - \frac{RT}{nF} \ln \frac{10^{-12}}{[Cu^{2+}][I^-]}$$

$$E = 0.15 + 12 X 0.059 + 0.059 \log[Cu^{2+}][I^-]$$

$$= +0.86 + 0.059 \log[Cu^{2+}][I^-]$$

The effective potential thus rises above the reduction potential of the iodide-iodine system and iodide ion is oxidized by cupric ion in solution. In fact, the reaction proceeds almost toward the right.

$$2Cu^{2+} + 4I^- = 2CuI \downarrow + I_2$$
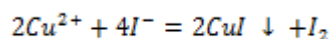
Cupper may be estimated by treating the liberated iodine with a solution of sodium thiosulfate.

Acid and Base Chemistry

The Arrhenius Theory (1880-1890):

An acid is any hydrogen-containing compound that provides hydrogen ion in aqueous medium. Similarly, according to the theory, a base is any compound that gives hydroxyl ion in aqueous medium.

Example:

$$\text{Acid} \quad H_2SO_4 \xrightarrow{\text{Water}} 2\,H^+ + SO_4^{2-}$$

$$\text{Base} \quad NaOH \xrightarrow{\text{Water}} Na^+ + HO^-$$
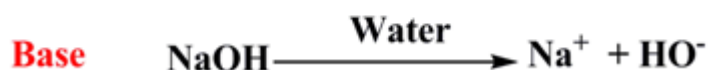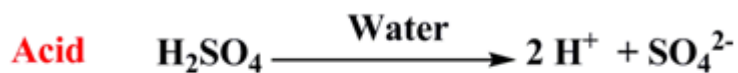
Merit:

A. With the help of this theory, the strength of acids and bases could be explained in terms of ionization equilibrium:
B. The existence of bare H^+ in aqueous medium was questioned. The size of proton is extremely small and therefore, it was proposed that it combined with water molecule and exists as H_3O^+ (hydronium) ion.
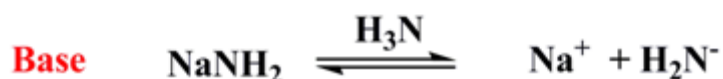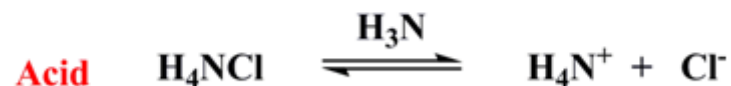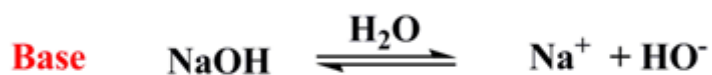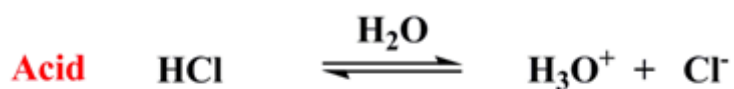
Franklin Theory (1905):

This theory concerns the acidic and basic properties of a substance in non-aqueous medium, mainly, in ammonium.

According to this theory,

An acid is a solute that gives the cationic character of the solvent, and a base is a solute that provides anionic character of the solvent.

Similar to aqueous medium,

$$H_2O + H_2O \rightleftharpoons H_3O^+ + HO^-$$

$$\text{Acid} \quad HCl \xrightleftharpoons{H_2O} H_3O^+ + Cl^-$$

$$\text{Base} \quad NaOH \xrightleftharpoons{H_2O} Na^+ + HO^-$$

$$H_3N + H_3N \rightleftharpoons H_4N^+ + H_2N^-$$

$$\text{Acid} \quad H_4NCl \xrightleftharpoons{H_3N} H_4N^+ + Cl^-$$

$$\text{Base} \quad NaNH_2 \xrightleftharpoons{H_3N} Na^+ + H_2N^-$$

Merit and demerits:

Arrhenius theory was limited to aqueous medium, while, with the help of this theory acidic and basic properties of some substances in non-aqueous medium can be explained.

This definition also failed to define inherent acid-base character of a substance. Isotope labeling experiments showed that there was no dissociation and association of substance and solvent, hence, autoionization of solvents was questioned.

The Protonic Theory (Brønsted-Lowry concept, 1923):

Any species that tends to give up a proton is an acid, and any species that tends to accept a proton is a base.
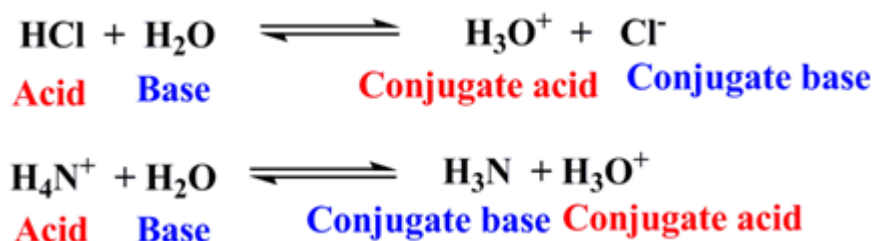
Examples:

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
Acid   Base

$$H_4N^+ + H_2O \rightleftharpoons H_3N + H_3O^+$$
Acid   Base
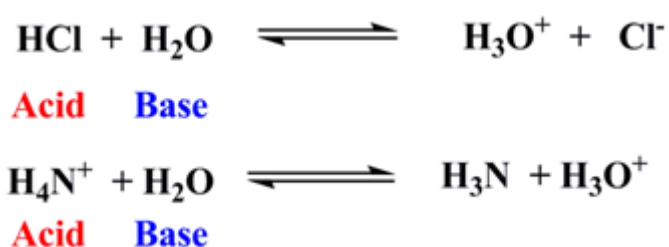
Conjugate acid-base pair:

Two chemical species, which are inter-convertible to each other by means of a proton, are known as conjugate acid-base pairs.

Example:

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
Acid   Base   Conjugate acid   Conjugate base

$$H_4N^+ + H_2O \rightleftharpoons H_3N + H_3O^+$$
Acid   Base   Conjugate base   Conjugate acid

A species, which has high tendency to give up proton(s) in a medium, will behave as a strong acid. The corresponding conjugate base, then, must be weak in nature, $i.e.$ its tendency for accepting proton(s) will be very low. The strength of an acid-species is also dependent to the stability of the corresponding conjugate base. The higher stability of the conjugate base favors the deprotonation process by the easy release of proton.

Example:

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
Acid   Base   Conjugate acid   Conjugate base
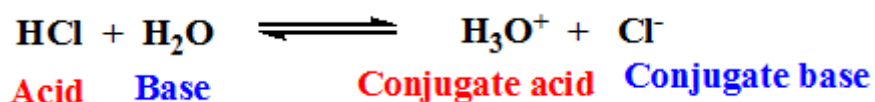
Similarly, a conjugate acid of a strong base should be weak in nature.

Example:

$$H_4N^+ + H_2O \rightleftharpoons H_3N + H_3O^+$$

Acid   Base   Conjugate base   Conjugate acid
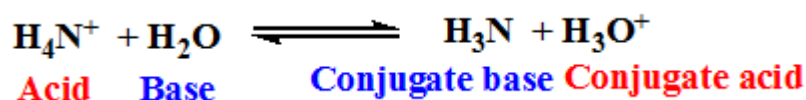
Merits and demerits:

Merits:

Acidic-basic properties of substances can be explained in any protonic solvent such as liquid ammonia, sulphuric acid, etc.

With the help of this theory the strength of acids and bases can be calculated. Further more, the reason that tunes the strength of acidic and basic properties (conjugate acid-base theory) can be understood.

Demerit:

In this theory, the acid-base properties are determined solely by proton exchange parameter. Therefore, some other substances that do not contain any proton but have inherent acidic or basic properties, $e.g.$ BF_3, I_2, $AlCl_3$, etc cannot be explained with the help of the theory.

Lux-Flood Definition (1939):

According to this theory, acid and base is define as, acid is an oxide acceptor and base is an oxide donor.

Example:

Here, CaO donates oxygen, therefore, it is a basic oxide. SiO_2 is an oxide acceptor, hence, it is a acidic oxide.

Merits and demerits:

Merit:

This approach emphasizes the acid and basic-anhydride aspects. Acidic oxides are acid anhydride and in the aqueous medium generate protonic acids, while, basic oxides are basic anhydride and generate hydroxyl ion in the aqueous medium.
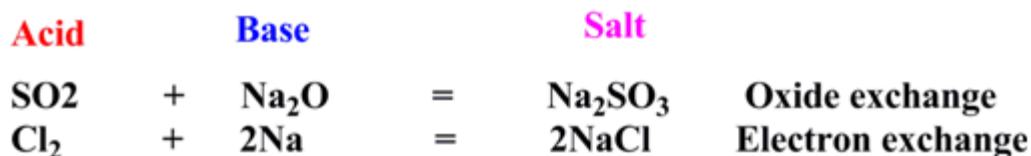
Demerit:

The usefulness of this concept is limited to inorganic metal oxide and their reactions in molten state.

The Usanovich Definition (1939):

The Usanovich definition includes all reactions of Lewis acids and bases and extended the latter concept by removing the restriction that the donation or acceptance of electrons be as shared pairs. According to him,

an acid is any chemical species which (i) reacts with a base, or (ii) accept anions or electrons, or (iii) furnish cations; and a base is any chemical species which (i) reacts with acids, or (ii) gives up anions or electrons, or (iii) combines with cations.

Examples:

	Acid		Base		Salt	
	SO_2	+	Na_2O	=	Na_2SO_3	Oxide exchange
	Cl_2	+	$2Na$	=	$2NaCl$	Electron exchange

Merits and demerits:

Merits:

Lewis concept and protonic concepts have been covered under the Usanovis definition for acid-base. Besides that it states that the donation or acceptance of electrons need not take place as shared pairs. Accordingly, oxidation-reduction reactions may be classified as acid-base reaction.

Demerits:

This concept is extremely general and therefore, almost all reactions can be considered as acid-base reaction. Because of this, the convenience of treating a particular type of compounds as acids or bases has been lost.

The Lewis acid-base definition:

Lewis proposed a definition of acid-base behavior of a substance in terms of electron-pair donation and acceptance. According to him, an acid is any species that accepts an electron pair forming a covalent bond, while; a base is any species that can donate a pair of electrons to build a covalent bond. In short, Lewis acid is electron pair acceptor and Lewis base is electron pair donor.

Lewis acid should, therefore, empty vacant orbital that can accept lone pair of electon from filled orbital of Lewis base.

Examples (Lewis acid):

i.   Molecules containing an atom processing incomplete valence shell.

Example:

BF_3 , $AlCl_3$, PCl_3 , SO_3 , etc.

ii. Cations with a stable, low-lying empty or partially filled orbitals.

Transition metal ions are good examples for this category. Coordination of these ions with electron donating ligands are then must be consider as Lewis acid-base reactions.
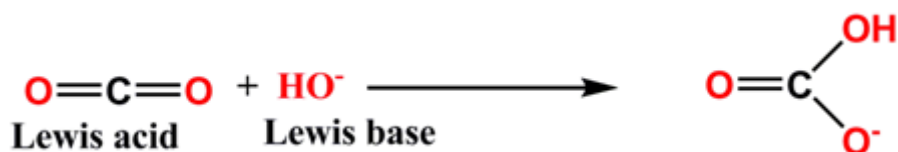
Example:

$$Cu^+ + NH_3 \longrightarrow [Cu(NH_3)]^+$$

Here, Cu^+ accepts electron pair from NH_3 . Hence, Cu^+ is Lewis acid and NH_3 is Lewis base.

iii. Compounds with hetero atomic double bonds.

Example:

$$O=C=O + HO^- \longrightarrow O=C\begin{smallmatrix}OH\\O^-\end{smallmatrix}$$

Lewis acid   Lewis base

Examples (Lewis base):

i. Molecules having one or more unshared pair of electrons.

The basic character decreases as the number of unshared electrons holds by the donor atom increases, *e . g* . decreasing basicity order, NH_3 (1 lone pair of electron), H_2O (2 lone pair of electron), HF (3 lone pair of electron).

ii. Negatively charged ions.

Example:

F^- , Cl^- , I^- , etc

iii. Compounds containing homo atomic double bonds.

Example:

Ethylene, benzene, etc forms bonds with metals, like, Pt, Rh, Ag, etc, and forms stable acid-base complexes.

Merits and demerits:

Merits:

With the help of this concept acid-base property of both Brønsted-type and nonprotonic substances can be explained. Besides that, with the help of this theory acid-base character and oxidation-reduction power of a substance can be postulated. For example, Lewis base donates electron pair, which is equivalent to reduction. Therefore, with increase of Lewis base character reducing power should increase. Lewis acid accepts lone pair of electrons, therefore, it is an oxidizing agent.

Demerits:

i. The conventional protonic acids, like H_2SO_4, HCl, HNO_3, etc are not covered directly by this theory, because no covalent bond is formed by between accepting a pair of electrons.
ii. The strength of acid-base cannot be generalized by the theory. For example, fluoride complex of beryllium(II) is more stable than that of fluoride complex of copper(II). Therefore, beryllium(II) should be more Lewis acidic that copper(II). On the other hand, the ammonium complex of copper(II) is more stable that beryllium(II). This indicates copper(II) is more acidic that beryllium(II).
iii. The reaction catalyzed by Lewis acid is not catalyzed by protonic acid.
   iv. **Strength of Lewis acids and bases [Hard (H) and Soft (S) Acid (A) Base (B) Concept = HSAB Concept), 1963]:**
   v. Lewis defines acids are electrons acceptor and bases are electron donor. Therefore, the strength of acids and bases is determined by the nature of electron transfer in a particular reaction. Hence, the strength is dependent on a particular reaction. Accordingly, assignment of any single consistent criterion for acid-base strength becomes very difficult in the Lewis definition. However, a qualitative correlation between the various Lewis acids and Bases has been obtained by classifying the acids and bases in to two different groups, known as hard and soft.
   vi. In 1963, R. G. Pearson proposed that hard acids prefer to combine with hard bases and soft acids prefer to combine with soft bases. This is known as HSAB concept or theory.

vii. **The features distinguish Hard and Soft acids:**

viii.

Hard acids	Soft acids
(I) Small in size.	(I) Large in size.
(II) High positive oxidation state.	(II) Zero or low positive oxidation state.
(III) Absence of any outer electrons that are easily excited to higher states.	(III) Several easily excitable valence electrons.

ix. **The features distinguish Hard and Soft bases:**

x.

Hard bases	Soft bases
(I) High electronegativity.	(I) Low electronegativity.
(II) Low polarisability.	(II) High polarisability.
(III) Presence of filled orbitals; empty orbitals may exist at high energy level.	(III) Presence of partially filled orbitals; empty orbitals are low-lying.

xi. **Table showing strength of HSAB, and border line case:**

xii.

Bases (Nucleophiles)	Acids (Electrophiles)
Hard	*Hard*
H_2O, OH^-, F^-	H^+, Li^+, Na^+, K^+
$CH_2CO_2^-$, PO_4^{3-}, SO_4^{2-}	Be^{2+}, Mg^{2+}, Ca^{2+}
Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	Al^{3+}, Ga^{3+}
ROH, RO^-, R_2O	Cr^{3+}, Co^{3+}, Fe^{3+}
NH_3, RNH_2, N_2H_4	CH_3Sn^{3+}
	Si^{4+}, Ti^{4+}
	Ce^{3+}, Sn^{4+}
	$(CH_3)_2Sn^{2+}$
	$BeMe_2$, BF_3, $B(OR)_3$
	$Al(CH_3)_3$, $AlCl_3$, AlH_3
	RPO_2^+, $ROPO_2^+$
	RSO_2^+, $ROSO_2^+$, SO_3
	I^{7+}, I^{5+}, Cl^{7+}, Cr^{6+}
	RCO^+, CO_2, NC^+
	HX (hydrogen bonding molecules)
Soft	*Soft*
R_2S, RSH, RS^-	Cu^+, Ag^+, Au^+, Tl^+, Hg^+
I^-, SCN^-, $S_2O_3^{2-}$	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+,
R_3P, R_3As, $(RO)_3P$	$Co(CN)_5^{2-}$
CN^-, RNC, CO	Tl^{3+}, $Tl(CH_3)_3$, BH_3
C_2H_4, C_6H_6	RS^+, RSe^+, RTe^+
H^-, R^-	I^+, Br^+, HO^+, RO^+
	I_2, Br_2, ICN, etc.
	trinitrobenzene, etc.
	chloranil, quinones, etc.
	tetracyanoethylene, etc.
	O, Cl, Br, I, N, RO, RO_2
	M^0 (metal atoms)
	bulk metals
	CH_2, carbenes
Borderline	*Borderline*
$C_6H_5NH_2$, C_5H_5N, N_3^-, Br^-, NO_2^-,	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+},
SO_3^{2-}, N_2	Sn^{2+}, $B(CH_3)_3$, SO_2, NO^+, R_3C^+,
	$C_6H_5^+$

xiii.

xiv. **General trends in acid strength:**

xv. Protonic acids can be classified in two groups, (A) hydro-acids, and (B) oxo-acids.

xvi. **(A) Hydro-acids:** In hydro-acids proton(s) is(are) directly attached to some second element. In the periodic table the acidity of hydro-acids increases from left to right along a period and top to bottom along a group.

xvii. **Example:** $HF > H_2O > NH_3$

xviii.   Here, on going from left to right in a period, electronegativity of the elements attached to proton increases, therefore, the proton-element bond become more polar. As the polarity of the bond increases, release of proton becomes easier. Hence, acidity increases.

xix. **Example:** HI > HBr > HCl > HF

xx. In this case, the size of the elements increases and electronegativity decreases on moving from top to bottom in a group. Here, size is the dominating factor over electronegativity. As size increases, the extent of overlap between small proton and big elements becomes low and proton-element bond becomes weak. Therefore, the release of proton becomes easier as the size of element increases, consequently, acidity increases.

xxi. **(B) Strength of oxy-acids:** In case of oxo acid of type $X - O - H$, the acidity of the acid decreases with lower the position of X in the periodical table. As we go down along a column in a periodical table, the electronegativity decreases. Hence, the electron pulling effect by the X through s - induction decreases. Therefore, the polarity of the H-O bond decreases along a column on going from top to bottom.

xxii. **Example:**

xxiii.   HOCl > HOBr > HOI (as decreasing order of electronegativity is Cl > Br > I)

xxiv.   When the element X acquire additional oxygen, the electron pulling power by the group X further increases due to increase of –I inductive effect exerted by the additional oxygen atom.
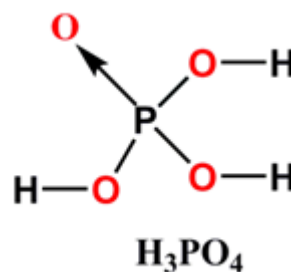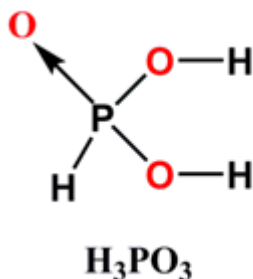
xxv. **Example:**

xxvi. $HOCl < HOClO_2 < HOClO_3$

xxvii.   It is also to note the number of oxo group operation of the number of O - H bonds

xxviii.   **Example:**

xxix. H_3PO_3 is more acidic than that of H_3PO_4

        xxx.

xxxi.   In case of H_3PO_3 one oxo group affect on two O - H bonds, while in H_3PO_4 one oxo group affect on three O - H bonds. Therefore, because of more –I inductive effect experienced by the O - H bonds present in H_3PO_3 , H_3PO_4 behaves as less acidic.

xxxii.   **Acid base behavior of metal compounds:**

xxxiii.   Metal oxides are generally basic in nature. Few of them are amphoteric. In the periodic table oxides becomes more basic on moving from top to bottom of the table, and more acidic on going from left to right.

xxxiv.   **Example:**

xxxv.   BeO is amphoteric, MgO, CaO, SrO, BaO are basic and basicity increases from BaO to MgO

xxxvi. Na_2O, MgO are basic, Al_2O_3 is amphoteric, SiO_2, P_4O_{10} , SO_3 , Cl_2O_7 are acidic and the acidity increases from SiO_2 to Cl_2O_7

xxxvii.   With an increase in charge/radious ratio the acidity of metal oxides increases.

xxxviii.   **Non aqueous solvents and ionic liquids:**

xxxix.   Studies on non-aqueous system, particularly on liquid ammonia revealed that auto-ionization of liquid NH_3 similar to water occurs.

$$NH_3 + NH_3 \leftrightarrow NH_4^+ + NH_2^-$$
xl.
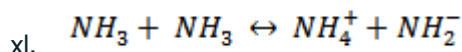
xli. Akin to substances producing H_3O^+ ions in water acts as acids in aqueous medium, substances that produce NH_4^+ ions in liquid ammonia medium acts as acids and it may also be expected to behave as an acid in that medium. Similarly, NH_2^- producing substance behaves as a base in liquid ammonia medium.

xlii. Acids in liquid ammonia medium: NH_4Cl, NH_4NO_3 , $(NH_4)_2SO_4$, etc.

xliii. Bases in liquid ammonia medium: KNH_2 , $NaNH_2$, etc.

xliv. Similarly, $SOCl_2$ behaves as an acid and $CaSO_3$ behaves as a base in liquid SO_2 solvent and their neutralization reaction can be expressed as

$$SOCl_2 + CaSO_3 = CaCl_2 + 2SO_2$$

xlv.
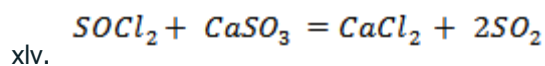
xlvi. Acid–base behavior is also known to show by some other ionic pair (salts). e.g. In BrF_3, $BrF_2 AsF_6$ increases the concentration of the cation and hence the salt is defined as an acid in the solvent system.

For further details please read Ak das Vol III and Miessler and Tarr 5 th edition