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REDOX AND PRECIPITATION REACTION

1.1   Introduction

Oxidation-reduction reactions are some of the most important chemical reactions. Redox reactions, as they are called, are the energy-producing reactions in industry as well as in the body. The core of a redox reaction is the passing of one or more electrons from one species to another. The species that loses electrons is said to be oxidized, and the species gaining electrons is reduced. These are old terms, but they are still used today. Oxidationand reduction occur simultaneously.

Oxidation numbers are assigned to each element in a chemical reaction to help us learn which element is oxidized and which is reduced. If, in a reaction, the oxidation number of an element increases (becomes more positive), the element is being oxidized. On the other hand, if the oxidation number of an element decreases, the element is being reduced. The changes in oxidation numbers are also used to balance redox equations. The goal is to keep the total number of electrons lost in the oxidation equal to the total number gained in the reduction. Clearly, the study of oxidation-reduction reactions should begin by learning about oxidation numbers.

In chemistry, the word precipitation has a different meaning: instead of something that falls out of the sky, a precipitate is something that falls out of a solution. One of the ways a precipitate can be

formed is when two soluble compounds interact. A soluble compound is one that will dissolve in water.insoluble compounds do not dissolve in water.
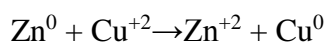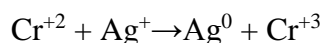
1.2. Qualitative idea about Complementary, Noncomplementary, Disproportionation and ComproportionationRedox Reactios
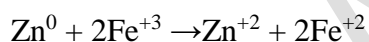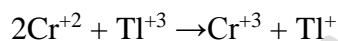
Complementary Reaction

The change in oxidation state of the reducing agent is the same as the change in oxidation state of the oxidizing agent. Some examples are

$Cr^{+2} + Ag^{+} \rightarrow Ag^{0} + Cr^{+3}$

$Zn^{0} + Cu^{+2} \rightarrow Zn^{+2} + Cu^{0}$

Noncomplementary Reaction

The oxidizing agent and reducing agent undergo different net changes in oxidation state. Some examples are

$2Cr^{+2} + Tl^{+3} \rightarrow Cr^{+3} + Tl^{+}$

$Zn^{0} + 2Fe^{+3} \rightarrow Zn^{+2} + 2Fe^{+2}$

The complementary reactions are generally faster than the noncomplementary reactions. The noncomplementary and multiple electron transfer reactions cannot occur in a single step electron transfer and it takes place multistep. If any one step of such reaction is slow then the overall reaction becomes slow, or if any such step is thermodynamically disfavored then it leads to the low concentration of an essential intermediate and consequently the overall reactions become slow.

Disproportionation Reaction

A particular species act as a reducing agent as well as oxidizing agent. Thus a fraction of the species is brought to a higher oxidation state and at the same time, an equivalent fraction is brought down to a lower oxidation state.

$3Au^+ \rightleftharpoons Au^{+3} + 2Au$

$2Cu^+ \rightleftharpoons Cu + Cu^{+2}$

Comproportionation Reaction

The reverse of disproportionation reaction is called a comproportionation reaction in which two species of a particular substance with different oxidation state combine to form a product having an intermediate oxidation state.

$Ag^{+2} + Ag \rightleftharpoons 2Ag^+$

1.3. Standard Redox Potential with Sign Convention

For the process, $Ox + ne \rightleftharpoons Red$, the electrode potential (more correctly, the reduction potential) is given by the Nernst equation as follows:

$E = E^0 + RT/nF \ln{}^a Ox/\,{}^a Red = E^0 + 0.059/n \ln{}^a Ox/\,{}^a Red$, at 25°C

Where n is the number of electrons getting transferred, $F = 96,500$ coulombs per mole of electron, $R = 8.3$ joules/degree/mole, T = temperature in Kelvin scale, E = electrode potential in volt, E^0 = Standard potential in volt. Thus, it is evident that when both the oxidant and reductant are at unit activity, the electrode potential becomes the standard electrode potential.

There are two different sign conventions which are apparently confusing but each one is justified in its own argument. These are European convention and American convention.

According to European convention, sign of the electrode potential is the experimentally observed electrostatic potential with respect to the standard hydrogen electrode (*SHE*). It is obtained from the emf of a cell in which the negative electrode is SHE (for which a potential of 0 V has been arbitrarily assigned) and the positive electrode is made up of the electrode whose potential is to be determined. Thus, in this convention, the sign of the electrode potential is the same as that of the electrostatic charge of the electrode in forming the electrical double layer. On the other hand, the American convention takes care of the thermodynamic property of the electrode reaction.

In the European convention, the $Zn - Zn^{2+}$ electrode has the potential -0.76 volt, because on dipping a Zn-rod in a solution containing Zn^{2+} ions, the Zn-rod becomes negatively charged electrostatically. It happens so due to the higher tendency (compared to the tendency of hydrogen in SHE, i.e. $H_2 \rightarrow 2H^+ + 2e$) of Zn-metal to pass into the solution as Zn^{2+} ions (i.e $Zn \rightarrow Zn^{2+} + 2e$). According to the American convention, the electrode potential for the above process is $+0.76$ volt. The reason is that, if the potential is taken as -ve then the corresponding Gibbs free energy change (i.e. $\Delta G = -nFE'$) becomes positive and the process cannot be spontaneous; but if it is taken as +ve, then ΔG becomes -ve which is in conformity with the thermodynamic criterion of spontaneity of the electrode process, $Zn + 2H^+ \rightleftharpoons Zn^{2+} + H_2$, $\Delta G < 0$.

To overcome this apparent confusion, IUPAC has recommended the electrostatic potential as the electrode potential designated by V (a sign invariant quantity) and the thermodynamic quantity (i.e. *emf*) designated by E should be related as proper sign in the relation, $\Delta G = -nFE$. Thus, when a standard Zn/Zn^{2+} (*a = 1*) electrode is coupled with a SHE, the experimental potential is -0.76 V and it is actually the standard electrode potential(V) of Zn/Zn^{2+}. When this electrode is used as negative electrode in some cell, the electrode potential will still be taken as -0.76 V (i.e. a sign invariant). But, here we shall follow the thermodynamic convention. Thus -0.76 volt is regarded as standard reduction potential of the couple, $Zn - Zn^{2+}$, while $+0.76$ volt can be taken as the standard oxidation potential. Thus, so-called European convention refers to actually to the reduction potential.

1.4. Electrochemical Series and its Application to Explore the Feasibility of Reactions and Equilibrium Constants

If the standard reduction potentials of the electrode process, $M^{n+}_{(aq)} + ne \rightleftharpoons M_{(s)}$ for different metals are placed in a series in order of increasing value, we get the table1 which gives the electrochemical series.

Here the potential values are given as per the thermodynamic convention. The Gibbs free energy change for the reduction electrode process is given by, $\Delta G^0 = -nFE^0_{red}$. Thus, for the system of higher positive value of E^0_{red}, the reduction process gets more favoured. In fact for the systems having negative E^0_{red}value, the reverse process, i.e. oxidation is favoured. In the table 1, the metals

residing at the top are highly electropositive. With the increase of $E^0_{red,}$ the oxidizing power increases and the reducing power runs in the opposite direction.

Table 1. The electrochemical series (standard reduction potentials, at 25°C)

Element	Electrode couple	$E^0(V)$
Li	Li^+/Li	-3.05
K	K^+/K	-2.93
Ca	Ca^{2+}/Ca	-2.84
Na	Na^+/Na	-2.71
Mg	Mg^{2+}/Mg	-2.36
Al	Al^{3+}/Al	-1.66
Mn	Mn^{2+}/Mn	-1.08
Zn	Zn^{2+}/Zn	-0.76
		Continue
Fe	Fe^{3+}/Fe	-0.44
Cd	Cd^{2+}/Cd	-0.40
Co	Co^{2+}/Co	-0.27
Ni	Ni^{2+}/Ni	-0.23
Sn	Sn^{2+}/Sn	-0.14
Pb	Pb^{2+}/Pb	-0.13
H_2	H^+/H_2	0.00*
Cu	Cu^{2+}/Cu	+0.35
Ag	Ag^+/Ag	+0.80
Au	Au^{3+}/Au	+1.38

*Standard Hydrogen Electrode (SHE)

This difference in the reduction tendencies of the two electrodes in a cell finds many applications in chemistry.

1.5. Applications of electrochemical series

The main applications of the electrochemical series are:

1.5.1. Oxidizing and Reducing Strengths

The electrochemical series helps to pick out substances that are good oxidizing agents and those which are good reducing agents. For example, a very high negative reduction potential of lithium electrode indicates that it is very difficult to reduce Li^+ ions to Li atoms. Therefore, Li^+ cannot accept electrons easily and so loses electrons to behave as a reducing agent. As the reduction potential increases (negative value decreases), the tendency of the electrode to behave as reducing agent decreases. Thus, all the substances appearing on the top of the series behave as good reducing agents. For example Li and K are good reducing agents while F^- and Au are the poorest reducing agents.

Similarly, substances at the bottom of the table have high reduction potential and they can be easily reduced. Therefore, they act as strong oxidizing agents. From the table we can conclude that H^+ is a better oxidizing agent than Zn^{2+} while Cu^{2+} is a better oxidizing agent than H^+; Fe is a better oxidizing agent than Cl_2 and so on. All the substances appearing at the bottom of the table are good oxidizing agents.

1.5.2. Comparison of Reactivities of Metals

The relative ease with which the various species of metals and ions may be oxidized or reduced is indicated by the reduction potential values. The metals with lower reduction potential are not reduced easily but are easily oxidized to their ions losing electrons. These electrons would reduce the other metals having higher reduction potentials. In other words, a metal having smaller reduction potential can displace metals having larger reduction potentials from the solution of their salt.

For example, copper lies above silver in the electrochemical series, therefore, if copper metal is added to $AgNO_3$ solution, silver is displaced from the solution. In general, a metal occupying higher position in the series can displace the metals lying below it from the solutions of their salts and so are more reactive in displacing the other metals. Thus, Li is the most electropositive element in solutions and fluorine is the most electronegative element.

1.5.3. Calculation of the EMF of the Cell

The following steps determine the reduction potential of the cathode and anode:

Step I

The two half-cell reactions are written in such a way that the reaction taking place at the left hand electrode is written as an oxidation reaction and that taking place at the right electrode is written as reduction reaction.

Step II

The number of electrons in the two equations are made equal by multiplying one of the equations if necessary, by a suitable number. However, electrode potential values ($E°$) are not multiplied.

Step III

The electrode potentials of both the electrodes are taken to be reduction potentials and so the EMF of the cell is equal to the difference between the standard potential of the right- hand side and the lef- hand side electrode.
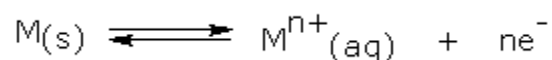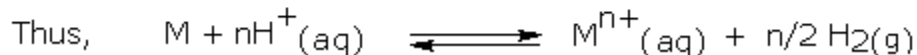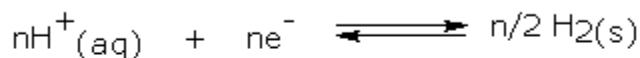
$E_{cell} = E_R - E_L$

Step IV

If the EMF of the cell is +ve, the reaction is feasible in the given direction and the cell is correctly represented, i.e., oxidation occurs at left electrode (anode) and reduction occurs at the right electrode (cathode). If it is -ve, the cell reaction is not feasible in the given direction and the cell is wrongly represented. Thus, to get positive value for the EMF the electrodes must be reversed.

1.5.4. Predicting the Liberation of Hydrogen Gas from Acids by Metals

All metals having negative electrode potentials (negative $E°$ values) show greater tendency of losing electrons as compared to hydrogen. So, when such a metal is placed in an acid solution, the metal gets oxidized, and H^+ (hydrogen) ions get reduced to form hydrogen gas. Thus, the metals having negative $E°$ values liberate hydrogen from acids.

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

metal having negative E° value

$$nH^+(aq) + ne^- \rightleftharpoons n/2\ H_2(s)$$

$$\text{Thus,}\quad M + nH^+(aq) \rightleftharpoons M^{n+}(aq) + n/2\ H_2(g)$$

For example, metals such as Mg (E (Mg^2+ →Mg) = - 2.37 V),

Zn (E (Zn^{2+} Zn) = - 0.76 V), Iron (E (Fe^{2+} Fe) = - 0.44 V) etc., can displace hydrogen from acids such as HCl and H_2SO_4. But metals such as Copper, (E (Cu^{2+} Cu) = + 0.34V), silver (E (Ag^+ Ag) = + 0.80V) and gold (E (Au^{3+} Au) = +1.42 V) cannot displace hydrogen from acids because of their positive reduction potential value.

1.5.5. Predicting Feasibility of a Redox Reaction

From the E° values of the two electrodes one can find out whether a given redox reaction is feasible or not. A redox reaction is feasible only if the species which has higher potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidized i.e., loses electrons.

The electrochemical series gives the increasing order of electrode potentials (reduction) of different electrodes on moving down the table. This means that the species, which accept the electrons (reduced) must be lower in the electrochemical series as compared to the other which is to lose electrons. (oxidized). For example,
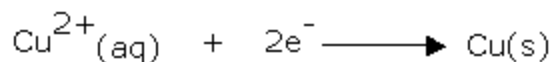
$$2Ag(s) + Cu^{2+}(aq) \longrightarrow 2Ag^+(aq) + Cu(s)$$
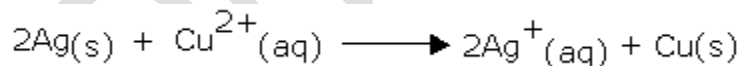
From the electrochemical series E° value of Cu = +0.34 V and that of Ag = +0.80 V since the reduction potential of Ag is more than that of Cu, this means that silver has greater tendency to get reduced in comparison to copper. Thus, the reaction
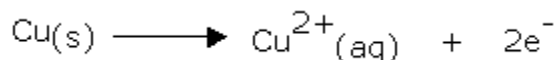
$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$
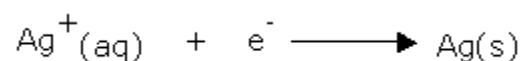
occurs more readily than the reaction

$$Cu^{2+}{}_{(aq)} + 2e^- \longrightarrow Cu(s)$$

The reduction potential of copper is less than that of Ag, this means that copper will be oxidized or will go into solution as ions in comparison to Ag. Thus, the reaction,

$$Cu(s) \longrightarrow Cu^{2+}{}_{(aq)} + 2e^-$$

occurs more readily than

$$Ag(s) \longrightarrow Ag^+{}_{(aq)} + e^-$$

Therefore, silver will be reduced and copper will be oxidized and the above reaction is not feasible. Rather the reverse reaction,

$$2Ag^+{}_{(aq)} + Cu(s) \longrightarrow 2Ag(s) + Cu^{2+}{}_{(aq)}$$
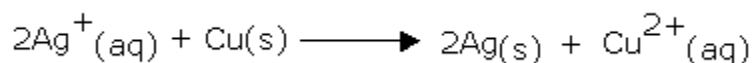
can occur. Thus a metal will displace, any other metal, which occurs below it in the electrochemical series from its salt solution. When a metal having lower $E°$ value is placed in a solution, containing ions of another metal having higher $E°$ value, then the metal having lower $E°$ value gets dissolved and the ions of the metal having higher $E°$ value get precipitated.

1.5.6. The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG^0 and the equilibrium constant K, to obtain a relationship between $E°_{cell}$ and K. Recall that for a general reaction of the type $aA+bB \rightarrow cC+dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$\Delta G° = -RT\ln K$

Given the relationship between the standard free-energy change and the standard cell potential

$-nFE°_{cell} = -RT\ln K$

Rearranging this equation,

$E°_{cell} = (RT/nF)\ln K$

For T = 298 K,

$E°_{cell} = [[8.314J/(mol \cdot K)(298K)]/n[96,486J/(V \cdot mol)]]2.303\log K = (0.0591 \ V/n)\log K$

$\log K = nE°_{cell} /0.0591 \ V$

Thus $E°_{cell}$ is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of $E°_{cell}$ and vice versa.

1.6. Nernst equation, Effect of pH, Complexation and Precipitation on Redox Potential, Formal Potential

1.6.1. Formal Potential

In the process, $Ox + ne \rightleftharpoons Red$, the potential is given by:

$E = E^0 + RT/nF \ln {}^aOx/ {}^aRed = E^0 + 0.059/n \ln {}^aOx/ {}^aRed$, at 25°C

Where n is the number of moles of electrons getting transferred, $F = 96,500$ coulombs per mole of electron, $R = 8.3$ joules/degree/mole, T = temperature in Kelvin scale, E = electrode potential in volt, E^0 = Standard potential in volt.

$E = E^0 + 0.059/n \ln [Ox]/ [Red]$ (in dilute solution)

Here it is believed that all the involved species will remain in their simple forms and the activity equals the concentration. Such a situation may only exist in a very dilute condition. In practice, the solution is sufficiently concentrated to disallow the condition, activity = concentration. But in reality, we deal with the concentration terms instead of the activity term. Beside this, the ions may not exist as in simple forms in presence of other electrolytes. In such cases, the concept of standard potential is of no practical use and it requires another parameter called formal potential or conditional potentialwhich takes care of the actual situation existing in solution.

The formal potential of a system is the experimentally observed potential of the system in solution where the formal concentration of the oxidized and reduced forms is same. The formal potentials cover the effect of the concentration of the species, pH of the solution, the possibility of complexation and other factors.

1.6.2. Formal Potential Depending on the pH of the Medium

Nernst equation describes potential of electrochemical cell as a function of concentrations of ions taking part in the reaction:

$$E = E_0 - \frac{RT}{nF} \ln (Q)$$

Where Q is a reaction quotient and n is number of electrons exchanged. For constant temperature expression RT/F has constant value. To simplify the calculation, it is often combined with conversion factor between natural logarithm (denoted here by ln) and decimal logarithm (denoted here by log) to form value of 0.0591 (for 25°C). Thus, for example for half reaction of MnO_4^- in acidic media:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^0_{MnO4^-/Mn^{2+}} = + 1.51$ volt
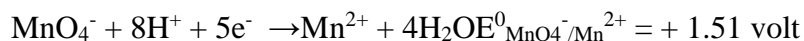
potential is given by

$$E = 1.51 - \frac{0.0591}{5} \log\left(\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right)$$

To be precise we should use not concentrations, but thermodynamic activities of the ions present in the solution.

$E = 1.51 - 8/5(0.059)\, pH + 0.059/5 \log[MnO_4^-]/[Mn^{2+}]$

$E = E^0_f + 0.059/5 \log[MnO_4^-]/[Mn^{2+}]$ [where $E^0_f = 1.51 - 8/5(0.059)\, pH$]

To express E^0_f, the pH term is to be included with in the E^0 term. Thus, we can write:

$E = E^0_f = E^0 - 8/5(0.059)\, pH = E^0 - 0.0944\, pH$ when $[MnO_4^-] = [Mn^{2+}] = 1M$; activity coefficients are taken to be unity.

Thus the Nernst equation in terms of E^0_f (formal potential) of the couple is given by:

$E = E^0_f + 0.0118 \log[MnO_4^-]/[Mn^{2+}]$

1.6.3. Formal Potential Depending on the Complexation of the Medium

Potential(in aqueous solution) of the involved couples are: $E^0_{Cu^{2+}/Cu} = 0.34$ V $> E^0_{Zn^{2+}/Zn} = -0.76$ V. Hence, on the electrolysis of a solution containing both Cu^{2+} and Zn^{2+}, copper deposition should start earlier. But in presence of excess CN^-, Zn^{2+} forms $Zn(CN)_4^{2-}$ complex while Cu^{2+} oxidises CN^- to CN_2 gas and itself reduced to $Cu(CN)_4^{2-}$ which is must stabler than zinc complex. In fact the stability constants are so widely different that the deposition potentials of the couples becomes

comparable, i.e. $E^0_{Cu(CN)_4^{2-}/Cu} \approx E^0_{Zn(CN)_4^{2-}/Zn}$. Thus the simultaneous deposition of both Cu and Zn can be achieved by the complexation with excess cyanide in the medium.

$Cu^+ + e \rightleftharpoons Cu$ $\qquad\qquad$ $E^0 = 0.52$ V

$Cu^+ + 4CN^- \rightleftharpoons Cu(CN)_4^{2-}$, log K $\approx$ 30.0

$K = [Cu(CN)_4^{3-}]/[Cu^{2+}][CN^-]^4$

$E = E^0 + 0.059 \log [Cu^+] = E^0 + 0.059 \log[Cu(CN)_4^{3-}]/K[CN^-]^4$

$= (0.52 - 0.059 \times 30) + 0.059 [Cu(CN)_4^{3-}]/[CN^-]^4 = -1.25 + [Cu(CN)_4^{3-}]/[CN^-]^4$

$E = -1.25 - 0.059 \times 4 \log [CN^-] + 0.059 \log [Cu(CN)_4^{3-}]$

$E = -1.25 + 0.236 \log [CN^-]$ when $[Cu(CN)_4^{3-}] = 1$ M

Thus the standard potential of the following couple is -1.25 V ($= E^0_f$ for$[CN^-] = 1$ M)

$[Cu(CN)_4^{3-}] + e \rightleftharpoons Cu + 4CN^-$,
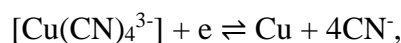
We can calculate the change of potential of the system Zn^{2+}/Zn couple in the presence of CN^- in the same way.

$Zn^{2+} + 2e \rightleftharpoons Zn$ $\qquad\qquad$ $E^0 = -0.76$ V

$Zn^{2+} + 4CN^- \leftrightarrow Zn(CN)_4^{2-}$, log K $\approx$ 20.0
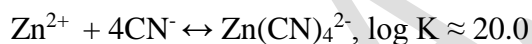
$K = [Zn(CN)_4^{2-}]/[Zn^{2+}][CN^-]^4$

$E = E^0 + 0.059 \log [Zn^{2+}] = E^0 + 0.059 \log [Zn(CN)_4^{2-}]/K[CN^-]^4$

$E = E^0 + (0.059/2) \log (1/K) + (0.059/2) \log [Zn(CN)_4^{2-}]/[CN^-]^4$

$= -1.35 + (0.059/2) \log [Zn(CN)_4^{2-}]/[CN^-]^4$

i.e. for the couple, $Zn(CN)_4^{2-} + 2e \rightleftharpoons Zn + 4CN^-$ the standard potential is -1.35 V.

1.6.4. Effects of Precipitation on Electrode Potentials

Iodometric determination of copper is based on the oxidation of iodides to iodine by copper (II) ions, which get reduced to Cu^+.

Comparison of standard potentials for both half reactions (Cu^{2+}/Cu^+ E^0=0.15 V, I_2/I^- E^0=0.54 V) suggests that it is iodine that should be acting as oxidizer. However, that's not the case, as copper (I) iodide CuI is very weakly soluble ($K_{sp} = 10^{-12}$). That means concentration of Cu^+ in the solution is very low and the standard potential of the half reaction Cu^{2+}/Cu^+ in the presence of iodides is much higher (around 0.85 V).

Cu^{2+} e $\rightleftharpoons$ Cu^+ E^0=0.15 V; E = E^0+ 0.059 log $[Cu^{2+}]/[Cu^+]$, (in dilute solution)

In presence of I^-, Cu^+ is precipitated as CuI, having the solubility product 10^{-12}, i.e.

Cu^++ I^- $\rightleftharpoons$CuI($\downarrow$), $K_{sp} = 10^{-12.}$

Now we get;

E = E^0+0.059 log $([Cu^{2+}][I^-]/ K_{sp})$

E = E^0- 0.059 logK_{sp} + 0.059 log $([Cu^{2+}][I^-]$

E = 0.85 + 0.059 log $([Cu^{2+}][I^-]$

E = 0.85 + 0.059 log $[I^-]$ when $[Cu^{2+}]$ = 1 M

We can express E^0_f as follows:

E^0_f = E = E^0 - 0.059 log K_{sp} + 0.059 log $[I^-]$ = 0.85 + 0.059 log $[I^-]$

Thus formal potential of the system depends on the concentration of the iodide. Under the condition, $[I^-]>>[Cu^{2+}]$, the formal potential becomes: E^0_f= 0.85 + 0.059 log $[I^-]$

It explains the oxidation of iodide by Cu(II) in presence of excess iodide. The reaction is

2C

u^{2+} + 4I^- → 2CuI(s) + I_2
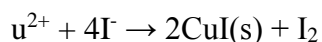
1.7 Basis of Redox Titration and Redox Indicators

All of us know that wine is made from the fermentation of grape juice using specific yeast cells. However, do you know wine requires a particular amount of fruit acid? So how is this acid content measured in industries? The determination of acid content is done by titration. Yes, the lab technique we all have done as well as read about.

Moreover, a specialized titration technique known as redox titration is used for analysis of wines for sulfur dioxide. This is just one example. Similarly, many other industrial processes require titration with respect to redox reactions. So let us know more about redox reactions as the basis of titration.

1.7.1 Titration

It is a very common laboratory technique. Titration helps in the quantitative chemical analysis. It helps in the determination of an unknown concentration of an already known analyte. Moreover, titration also helps in volumetric analysis or measurement of volume. There are different types of titration techniques which is applicable according to the goals and methods.

Types of Methods

- Acid-base Titrations

- Redox Titrations

- Precipitation Titrations

- Complexometric Titrations

The most common titration methods that are commonly in use for "quantitative chemical analysis" are Redox and Acid-Base Titration. In the acid-base system, a titration method helps in finding out the strength of one solution against another solution by the use of the pH-sensitive indicator.

Similarly, in redox system, a titration method helps in determination of the strength of a particular oxidant or a reductant with the help redox-sensitive indicator. We will now discuss the definition of redox titration and how to use indicators in this technique.

Redox Titrations

When the oxidation-reduction reactions happen in a titration method, it is known as a redox titration. In this technique, transfer of electrons occurs in the reacting ions present in the aqueous solutions during the chemical reaction. This is further classified on the basis of reagent used in the redox titration.

Sub-Divisions of Redox Titrations

- Permanganate Titrations

- Dichromate Titrations

- Iodometric Titrations

Permanganate Titrations

Potassium Permanganate is the oxidizing agent in this type of redox titration method. Maintenance of the solution is done with the help of dilute sulphuric acid. Moreover, the addition of Sulphuric acid also helps to increase the hydrogen ions present in the solution.

In this technique, the reagent has intense colour due to the permanganate ion $MnO4^-$. In the case, the permanganate ion acts as a self-indicator in this method. The solution remains colourless prior to the endpoint. The equation of redox reaction

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 3H_2 + 5[O]$

$MnO_4^- + 8H+ +5e \rightarrow Mn^{2+} + 4H_2O$
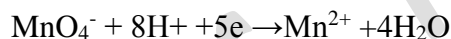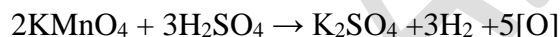
The result of the endpoint is noticeable when oxidation of the last of the reductant such as Fe^{2+} or $C_2O_4^{2-}$ occurs. At this point, the solution retains the first lasting tinge of the MnO_4 (pink colour) appears. The concentration can be minimum of 10^{-6} mol L^{-1}. This assures the minimal "overshoot" of the pink colour after the equivalence point.

The equivalence point is where reductant and oxidant are equal with respect to the mole stoichiometry or the total number of electrons lost and electron gained in oxidation and reduction reaction will be equal. The potassium permanganate titration helps in the estimation of oxalic acid, hydrogen peroxide, ferrous salts, oxalates and more. However, it is very important to always standardize the solution prior to use.

Dichromate Titrations

In this method, potassium dichromate acts as the oxidant in the acidic medium. It is necessary to maintain the acidity of the medium by addition of dilute sulphuric acid. The equation of the reaction is

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2Cr_2(SO_4) + 4H_2O + 3[O]$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$$
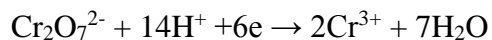
In this situation, there is no substantial auto colour change as seen in the MnO_4^- titration. $Cr_2O_7^{2-}$ is not a self-indicator. However, $Cr_2O_7^{2-}$ oxidizes the indicator substance diphenylamine soon after achieving the equivalence point thereby producing an intense blue colour. The change in signals the end point of the titration. We can use the potassium dichromate solution in titrations directly. This method helps in the estimation of ferrous salts and iodides.

Iodometric Titrations

This is an interesting but common method. In this case, free iodine reduction to iodide ions occurs as well as iodine ion oxidation to free iodine occurs. The oxidation and reduction reactions are

$$I_2 + 2e \rightarrow 2I^- \qquad \text{Reduction}$$

$$2I^- \rightarrow I_2 + 2e \qquad \text{Oxidation}$$

The solution acts as an indicator. The use of this method is limited to the reagents capable of oxidizing I^- ions. One of the examples of such reaction is of Cu(II)

$$2Cu^{2+} (aq) + 4I^- (aq) \rightarrow Cu_2I_2 (s) + I_2(aq)$$
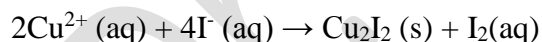
The ability of iodine to produce intense blue colour with starch as the substance and its capacity to react with thiosulphate ions ($S_2O_3^{2-}$) forms the basis of this method. The specific reaction with ($S_2O_3^{2-}$) is also a redox reaction.

$$I_2 (aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^- (aq) + S_4O_6^{2-}(aq)$$
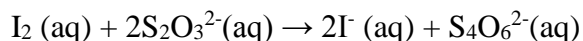
In this case, I_2 is insoluble in nature with water but it remains in the solution in the form of KI_3 that contains KI. After the addition of starch, the iodine in the reaction liberates as iodide ions producing intense blue colour. However, the colour disappears on the consumption of iodine by

the thiosulphate ions. The endpoint of the reaction is easily noticeable. Thus, it is easy to determine the concentration of the unknown solution by stoichiometric calculation.

1.7.2. Redox Indicator

Redox indicators are the chemicals used during the redox titration in order to detect the endpoint. In acid-base titrations, the indicators used were weak acids or bases which had two forms: dissociated (ionized) or non-ionized and both of these forms have a different color. Some common redox indicators with characteristic properties are listed in table 2.

Similarly, the redox indicators have two forms: oxidized form and reduced form. In both the forms, the color is different. Both the form has got a specific standard reduction potential.

$In_{ox} + ne \rightarrow In_{red}$
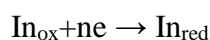
Here we apply the same concept.

Let us suppose an indicator (In), and represent its oxidized form as (In_{ox}) and reduced form as (In_{red}).

Applying Nernst equation,

Thus, the electrode potential of the indicator when the ratio of (In_{ox}) to (In_{red}) is 10:1 would be:

$E = E°_{In} - 0.059 \log[In_{red}]/[In_{ox}]$

n = transfer of electrons = 1.

$E = E°_{In} - 0.059 \log (1/10)$

$E = E°_{In} + 0.059$

Thus, the electrode potential of the indicator when the ratio of (In_{ox}) to (In_{red}) is 1:10 would be:

$E = E°_{In} - 0.059 \log 10$

$E = E°_{In} - 0.059$

$E_{tp} = E^0_{In} \pm 0.059/n$

The change in the potential of the indicator which is required during the redox titration for the indicator to impart a color change is called transition potential.

The transition potential should coincide with the potential of the solution at the equivalence point (E_{ep}) for getting a better end point. $E_{ep} = E_{tp}$

Table 2: Some common redox indicators with characteristic properties

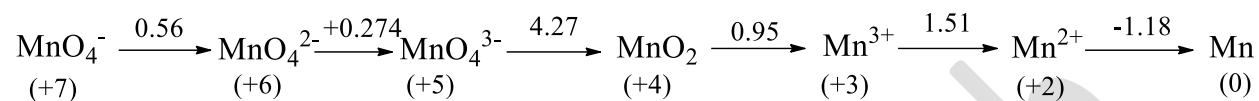| Indicators	colour		$E^0_{Ind}[H+] = 1.0$ mol dm^{-3}
	Ind_{Ox}	Ind_{Red}	
Methylene blue	Blue	Colourless	0.53
Diphenylamine	Blue-violet	Colourless	0.76
Diphenylamine-sulphonic acid	Red-violet	Colourless	0.85
N-Phenylanthranilic acid	Red-violet	Colourless	1.08
Ferroin, (Fe(II)-phenanthroline complex)	Paleblue	Red	1.14

1.8   Potential diagrams

In addition to Pourbaix diagrams, there are two other kinds of redox stability diagrams known as Latimer and Frost diagrams. Each of these diagrams contains similar information, but one representation may be more useful in a given situation than the others. Latimer and Frost diagrams help predict stability relative to higher and lower oxidation states, usually at one fixed pH.

1.8.1 Latimer Diagram

Latimer diagrams are the oldest and most compact way to represent electrochemical equilibria for substances that have multiple oxidation states. Electrochemical potential values are written for successive redox reactions (from highest to lowest oxidation state), typically under standard conditions in either strong acid ([H$^+$] = 1 M, pH 0) or strong base ([OH$^-$] = 1 M, pH 14). The oxidation states of successive substances in a Latimer diagram can differ by one or more electrons.

Oxidation states for the element undergoing redox are typically determined by difference; we assign the oxygen atoms an oxidation state of -2 and the hydrogen atoms an oxidation state of +1.
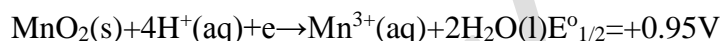
The Latimer diagram for Mn illustrates its standard reduction potentials (in 1 M acid) in oxidation states from +7 to 0.

$$\underset{(+7)}{MnO_4^-} \xrightarrow{0.56} \underset{(+6)}{MnO_4^{2-}} \xrightarrow{+0.274} \underset{(+5)}{MnO_4^{3-}} \xrightarrow{4.27} \underset{(+4)}{MnO_2} \xrightarrow{0.95} \underset{(+3)}{Mn^{3+}} \xrightarrow{1.51} \underset{(+2)}{Mn^{2+}} \xrightarrow{-1.18} \underset{(0)}{Mn}$$

The Latimer diagram compresses into shorthand notation all the standard potentials for redox reactions of the element Mn. For example, the entry that connects Mn^{2+} and Mn gives the potential for the half-cell reaction:

$Mn^{2+}(aq)+2e \rightarrow Mn(s) E^o_{1/2}=-1.18V$

and the entry connecting Mn^{4+} and Mn^{3+} represents the reaction:

$MnO_2(s)+4H^+(aq)+e \rightarrow Mn^{3+}(aq)+2H_2O(l) E^o_{1/2}=+0.95V$

We can also calculate values for multi-electron reactions by first adding $\Delta G^\circ(=-nFE^\circ)$ values and then dividing by the total number of electrons

For example, for the 5-electron reduction of MnO_4^- to Mn^{2+}, we write

$E^o=[1(0.564)+1(0.274)+1(4.27)+1(0.95)+1(1.51)]/5=+1.51V$

and for the three-electron reduction

$E^o= [1(0.564)+1(0.274)+1(4.27)]/3=+1.70V$

Remember to divide by the number of electrons involved in the oxidation number change (5 and 3 for the above equations).

In general we can write:

$E^0 = (n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + ...)/(n_1 + n_2 + n_3 +......)$

1.8.2 Frost Diagrams

Frost diagram or Frost-Ebsworth diagram is a type of graph to illustrate the relative stability of a number of different oxidation states of a particular substance. The graph illustrates the oxidation state vs free energy of a chemical species. This effect is dependent on pH, so this parameter also must be included. The free energy is determined by the oxidation–reduction half-reactions. The Frost diagram allows easier comprehension of these reduction potentials than the Latimer diagram, because the "lack of additivity of potentials" was confusing.In a Frost diagram, we plot $\Delta G°/F$ (= $nE°$) vs. oxidation number. The zero oxidation state is assigned a $nE°$ value of zero.
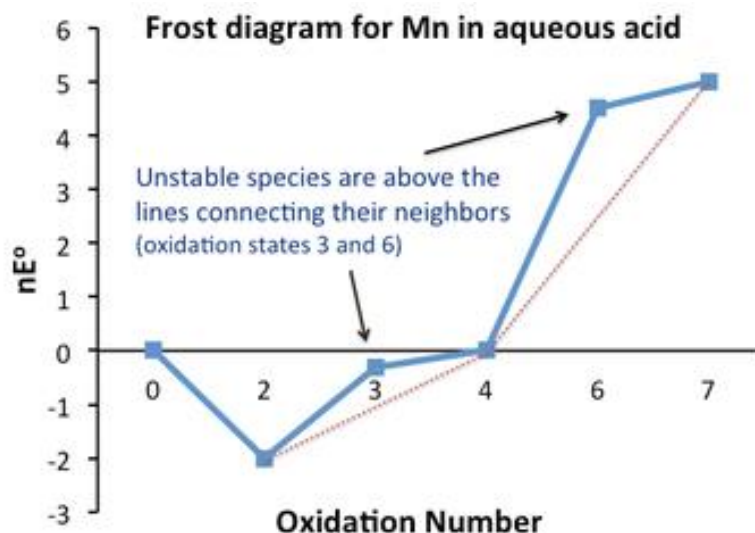
Stable and unstable oxidation states can be easily identified in the plot. Unstable compounds are higher on the plot than the line connecting their neighbors. Note that this is simply a graphical representation of what we did with the Latimer diagram to determine which oxidation states were stable and unstable.

The standard potential for any electrochemical reaction is given by the slope of the line connecting the two species on a Frost diagram. For example, the line connecting Mn^{3+} and MnO_2 on the Frost diagram has a slope of +0.95, the standard potential of MnO_2 reduction to Mn^{3+}. This is the number

that is written above the arrow in the Latimer diagram for Mn. Multielectron potentials can be calculated easily by connecting the dots in a 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 favorable 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.

1.9   Solubility and Solubility Product Principle

1.9.1 Solubility

When a sparingly soluble ionic substance is dissolved in any solvent, it dissociates into positively charged cations and negatively charged anions. The extent of solubility of the ionic substance depends on different factors like temperature, pressure, presence of common ions etc. The ability of a ionic substance to dissolve in any solvent is called solubility.

1.9.2 Solubility Product Principle

Solubility product of a sparingly soluble electrolyte is defined as the product of its ions in its saturated condition at 25 ºC. The value of solubility product of a sparingly soluble salt is always constant at given temperature. For example the solubility product of AgCl at 25ºC is 1.6×10^{-10}. It represents the level at which a solute dissolve in solution.

Let us consider a sparingly soluble electrolyte AB that dissolves very slightly in water. It dissociates into cations and anions.

$AB \rightleftharpoons A^+ + B^-$
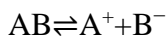
At first, AB dissociates to give A^+ and B^-. As the concentration of A^+ and B^- is increased, the backward reaction initiates and the reaction comes under equilibrium. When the solution is saturated at 25ºC, the concentration of AB, A^+ and B^- remains constant. Now,we can apply the law of mass action to this equilibrium system.

$K=[A^+][B^-]/[AB]$ or, $K\times[AB]=[A+][B-]$, At saturated condition in 25ºC,

$K\times[AB]=Ksp \therefore Ksp=[A+][B-]$

The above expression defines the solubility product principle.

1.9.3 Application of Solubility Product Principle

1. It is used for the precipitation of:

- Group I cations[Pb, Hg(I), Ag] form precipitates as metal chloride with dilute hydrochloric acid.
- Group II cations [Hg(II), Cu, Bi, Cd, As(III), Sb(V), Sn(II)] form precipitate as metal sulfide with hydrogen sulphide.
- Group III cations [Co(II), Ni(II), Fe(II), Fe(III), Cr(III), Al, Zn, Mg(II)] form precipitate as metal hydroxide with treatment of ammonium chloride in neutral or ammoniacal media.
- Group IV cations [Ba, Sr, Ca) forms precipitate as carbonates with treatment of ammonium chloride and in ammonium carbonate.
- Group V cations [Mg, Na, K, NH_4^+] form precipitate as hydrogen phosphate salt by the treatment with NH_4OH, NH_4Cl and HPO_4^{2-} salt.

2. It has wide range of application in qualitative analysis.

3. This principle is used for the purification of common salt.

When the solubility product of given salt is less than its ionic product value, then precipitation occurs. This is called solubility product principle.

1.9.4 Ionic Product

When the temperature of solubility is greater or less than 25 ºC, then the product of its ion is called ionic product.

$[A^+][B^-]$ = Ionic product

We know that if the product of concentration of ions present in any solution at a given temperature is less than K_{sp}, the solution is called unsaturated and more solute can be dissolved in the solution. Thus,

- When solubility product is greater than ionic product, the solution is unsaturated.
- When solubility product is equal to ionic product, the solution is saturated.

- When ionic product is greater than solubility product, the solution is unsaturated.

1.10 Common Ion Effect

Let us consider the dissociation of equilibrium $HA \rightleftharpoons H^+ + A^-$. Dissociation constant $K_a = C_{H+}.C_{A-}/C_{HA}$[assuming very dilute solution where $f\pm = 1$]. To this solution if we add common ion say H^+ or A^-, then in order to keep K_a constant some of the added ions will combine with opposite ion to produce HA. The net result is an increase in amount of undissociated part i.e. decrease in degree of dissociation. So, effect of common-ion is to depress degree of dissociation.

1.11 Questions

(1) What are the complementary, noncomplementary, disproportionation and comproportionation redox reactions?

(2) What is standard oxidation and reduction potential?

(3) What is electrochemical series? How you can explain the feasibility of the any reaction and reactivity of certain metal from electrochemical series?

(4) How can you calculate the equilibrium constant in terms of standard electrode potential?

(5) What is called formal potential? Why it is more important than standard potential?

(6) How formal potential varies with the change of pH of the reaction medium?

(7) Why excess cyanide is used in the electrolysis of Cu and Zn for the simultaneous and equal deposition of both Cu and Zn for the preparation of brass.

(8) How copper is estimated in the iodometric titration of iodine?

(9) What is called redox titration? State the basic principles of permanganate and dichromate titrations.

(10) What is called redox indicator? Derive the Nernst equation for the redox indicator at equivalence point?

(11) What is Latimer diagram? How standard electrode potential of Mn for different oxidation states can be calculated?

(12) What is Frost diagram? How can you explain the thermodynamic stability of certain oxidation state of any complex.

(13) What is called solubility product and ionic product? How basic radicals are separated with the help of solubility product principle in the qualitative group separation?

1.12 Answers

(1) See the section 1.2

(2) See the section 1.3

(3) See the section 1.5 and 1.5.5

(4) See the section 1.5.6

(5) See the section 1.6.1

(6) See the section 1.6.2

(7) See the section 1.6.3

(8) See the section 1.6.4

(9) See the section 1.7.1

(10) See the section 1.7.2

(11) See the section 1.8.1

(12) See the section 1.8.2

(13) See the section from 1.9.1 to 1.9.4

1.13   References

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