$Au + 2CNS^- \rightleftharpoons [Au(CNS)_2]^- + e^-$, $E_0 = -0.69$ volt

$Au + 2CN^- \rightleftharpoons [Au(CN)_2]^- + e^-$, $E_0 = 0.60$ volt

This shows that Au^+ is stabilised with CN^- forming complex ion and will not undergo dispropotionation. Similarly, the potential data in the Table 9.3 indicate that OH^-, CN^-, F^-, PO_4^{3-} can best stabilise Fe^{3+} and organic complexing agents can stabilise Fe^{2+}.

9.04 FACTORS CONTROLLING THE REDOX POTENTIAL

The standard potential of a half-reaction expressed by Nernst Equation includes unit activities of the constituents, but in most cases the activities are other than unity and hence standard potentials change. This can be illustrated with examples:

(a) Effect of concentration

Suppose, in Fe^{3+} / Fe^{2+} system, the potential is

$E = E_0 + \frac{0.0591}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$ when $[Fe^{3+}] = [Fe^{2+}]$, then $E = E_0$. If, say $[Fe^{3+}] = 1$ gm ion per litre and $[Fe^{2+}] = 1\times10^{-4}$ gm ion per litre, then $E = 0.77 + \frac{0.0591}{1}\log\frac{1}{10^{-4}} = 1.002$ volt. Let us explain what difficulties we face during titration of Fe^{2+} with $Cr_2O_7^{2-}$ in 1-2N H_2SO_4 medium. Say, we titrate 10 cc of 0.1M Fe^{2+} solution in 2(N)H_2SO_4 using, say 0.1 M $K_2Cr_2O_7$ solution with barium diphenylamine sulphonate indicator ($E_0 = 0.79$) total volume = 100 cc and gradual addition of $K_2Cr_2O_7$ changes the potential as given below:

$K_2Cr_2O_7$	Excess in ml Fe^{2+}	Excess in ml $Cr_2O_7^{2-}$	$[Fe^{3+}] / [Fe^{2+}]$	$[Cr_2O_7^{2-}] / [Cr^{3+}]$	Potential
50	50	—	50:50	—	0.77
91	9	—	91:9 ≈ 10	—	0.828
99	1	—	99:1 ≈ 100	—	0.886
99.9	0.1	—	99.9:0.1 ≈ 1000	—	0.994
100	—	—	—	—	1.387
100.1	—	0.1	—	0.1:100 = 0.001	1.475
101	—	1	—	100:1 ≈ 0.01	1.487

Thus, with addition of $K_2Cr_2O_7$, more and more Fe^{2+} is oxidised to Fe^{3+}, the cell e.m.f. gradually increases, before equivalence point; the indicator gets oxidised and the colour changes to bluish violet. So to get exact equivalence point H_3PO_4 or NaF is used to form colourless complex $[Fe(HPO_4)]^+$ or $[FeF_6]^{-3}$ such that effective $[Fe^{3+}]$ is not allowed to increase.

(b) Effect of pH of the medium

As stated earlier, the half-reactions where H^+ or OH^- is not used up, their standard potential values remain constant throughout the entire pH range. But if H^+ or OH^- is involved in the half-reaction, their concentrations appear in the Nernst equation and so the potential is influenced by pH of the medium, e.g., in $[MnO_4^-]$/ $[Mn^{2+}]$ system, the reaction is

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

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$$E = E_0 + \frac{0.0591}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

$$= E_0 + \frac{0.0591}{5}\log\frac{[MnO_4^-]}{[Mn^{2+}]} + \frac{0.0591}{5}\log[H^+]^8$$

$$= E_0 + \frac{0.0591}{5}\log\frac{[MnO_4^-]}{[Mn^{2+}]} + \frac{0.0591}{5}\times 8\log[H^+]$$

$$= E_0 + \frac{0.0591}{5}\log\frac{[MnO_4^-]}{[Mn^{2+}]} - \frac{0.0591}{5}\times 8pH$$

So, maximum oxidation power of MnO_4^- is obtained at minimum pH of the solution, i.e., higher acid concentration. In permanganometric or dichromatometric reactions, when $[H^+]$ is raised to higher power, maximum oxidising power is obtained using acids of 1-2N strength with N/10, N/100 and still lower acid concentrations; $E < E_0$ (1.51), e.g., at pH = 6, E = 0.95.

MnO_4^- (E=1.51volts) can easily oxidise $Cl^- \rightarrow Cl_2$, $Br^- \rightarrow Br_2$ and $I^- \rightarrow I_2$ at low pH. At pH 6, MnO_4^- cannot oxidise Br^-or Cl^- whose potential is higher than that of MnO_4^- / Mn^{2+} system at this pH.

Another example is the reaction between AsO_4^{3-}/ AsO_3^{3-} and I_2/I^- system. The half-reactions are

$AsO_4^{3-} + 2H^+ + 2e^- = AsO_3^{3-} + H_2O$, $E_0 = 0.56$ volt

$I_2 + 2e^- = 2I^-$, $E_0 = 0.54$ volt

At 25°C, $$E_{AsO_4^{3-}/AsO_3^{3-}} = 0.56 + \frac{0.0591}{2}\log\frac{[AsO_4^{3-}][H^+]^2}{[AsO_3^{3-}]}$$

$$= 0.56 - 0.0591\,pH + \frac{0.0591}{2}\log\frac{[AsO_4^{3-}]}{[AsO_3^{3-}]}$$

At higher acid concentration, say in 1-2 M acid strength [pH ≈ 0] and then only AsO_4^{3-} can oxidize $I^- \rightarrow I_2$. (This technique is followed in the identification of AsO_4^{3-} in presence of PO_4^{3-} or AsO_3^{3-}.) But at high pH, say at pH = 8,

$$E = 0.56 - 0.0591\times 8 + \frac{0.0591}{2}\log\frac{[AsO_4^{3-}]}{[AsO_3^{3-}]}$$

$$= 0.088 + \frac{0.0591}{2}\log\frac{[AsO_4^{3-}]}{[AsO_3^{3-}]}$$

This value is much lower than that of I_2/I^- system. Hence, I_2 will then oxidize AsO_3^{3-} to AsO_4^{3-}, i.e., the reverse reaction occurs. In practice, $NaHCO_3$ is used that maintains the pH to 8. If stronger alkalis like NaOH, Na_2CO_3 are used, then pH > 9 and I_2 will react with strong alkali giving IO^-. This can be generalised as, when H^+ is used up in the half-reaction, the reaction is to be carried out in strong acid medium, and when H^+ is produced in the half-reaction, then H^+ produced must

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Another example is the identification of NO_2^-.

In neutral or alkaline medium, $E_{NO_2^-/NO}$ is $NO_2^- + H_2O + e^- = NO + OH^-$, $E = 0.46$ volt.

This value is lower than that of E_{I_2/I^-} system. So, if KI is added to KNO_2 solution (pH = 7), no noticeable change takes place. If few drops of HCl or H_2SO_4 are added, vigorous reaction takes place with evolution of NO and precipitation of dark grey iodine.

$$2NO_2^- + 2I^- + 4H^+ \rightleftharpoons I_2\downarrow + 2NO\uparrow + 2H_2O$$

In acid medium, the standard potential for NO_2^-/NO

$HNO_2 + H^+ + e^- = NO + H_2O$, $E_0 = 0.99$ volt; it is higher than that of I_2/I^- system.

(c) Change of standard potential with precipitation

This effect is also due to change of concentration of the oxidised or reduced form from the reaction medium, e.g., iodometric estimation of copper $E_{Cu^{2+}/Cu^+} = 0.15$ volt and for $E_{I_2/I^-} = 0.54$, $S_{CuI} = 10^{-12}$.

The reaction that takes place in this case, $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

From the solubility product value of CuI,

$$S_{CuI} = [Cu^+][I^-] = 10^{-12}, \quad \therefore [Cu^+] = \frac{10^{-12}}{[I^-]}$$

$$\text{So, } E_{Cu^{2+}/Cu^+} = E_0 + \frac{0.0591}{1}\log\frac{[Cu^{2+}]}{[Cu^+]}$$

$$= 0.15 + \frac{0.0591}{1}\log\frac{[Cu^{2+}]}{\frac{10^{-12}}{[I^-]}} = 0.15 + \frac{0.0591}{1}\log\frac{[Cu^{2+}][I^-]}{10^{-12}}$$

$$= 0.15 + \frac{0.0591}{1}\times 12 + \frac{0.0591}{1}\log[Cu^{2+}][I^-].$$

$$= 0.86 + \frac{0.0591}{1}\log[Cu^{2+}][I^-]$$

The formal potential of Cu^{2+}/Cu^+ is now high enough than that of I_2/I^- system, and Cu^{2+} will quantitatively liberate, I_2 that can be titrated by $S_2O_3^{2-}$ and hence Cu^{2+} can be estimated.

Let us see now whether Cu^{2+} is estimated quantitatively. Say, 25 ml of 0.2 M Cu^{2+} is mixed with 25 ml of 1M I^-. Now, the volume is doubled, so strength is halved. $[Cu^{2+}]$=0.1M and $[I^-]$ = 0.5M. After reaction, say, x M Cu^{2+} is left at the equilibrium.

$$\log K = \frac{1(0.86-0.54)}{0.0591} = \frac{0.32}{0.0591} = 5.3 \quad \therefore K = 1.6\times 10^5$$

At equilibrium, $[I^-]$ is the difference of its concentration initially less I^- consumed by Cu^{2+}.

$$[I^-] = \{0.5 - 2(.1-x)\}M = (0.5-0.2+2x)M = (0.3+2x)M \approx 0.3M$$

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$$K=\frac{[I_2][CuI]}{[Cu^{2+}][I^-]}$$ or, $$1.6\times10^5=\frac{1}{[Cu^{2+}][I^-]}$$

or, $$[Cu^{2+}]=x=\frac{1}{(0.3)^3\times1.6\times10^5}=6.9\times10^{-5}\text{ gm ion/lit.}$$

So, the reaction is complete and estimation is quantitative.

Another example can be discussed. The E_0 for $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system is 0.36 volt which is much below I_2/I^-. So ordinarily, $Fe(CN)_6]^{3-}$ will not oxidize I^- to I_2.

We have, $$E_{0[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}}=0.36+\frac{0.0591}{1}\log\frac{[Fe(CN)_6]^{3-}}{[Fe(CN)_6]^{4-}}$$

In neutral or slightly acid medium, if $ZnSO_4$ solution is added, the ferrocyanide ion reacts with Zn^{2+} as follows:

$$2[Fe(CN)_6]^{4-}+2K^++3Zn^{2+}=K_2Zn_3[Fe(CN)_6]_2$$

So, as long as Zn^{2+} is present in solution, $K_2Zn_3[Fe(CN)_6]_2$ is precipitated, thus, removing ferrocyanide ion from solution, potential of ferricyanide will increase and will oxidise I^- ion. The liberated iodine is estimated by $Na_2S_2O_3$ solution and hence Zn^{2+} can be estimated.

1ml N $Na_2S_2O_3$ = 0.3293 gm $K_3[Fe(CN)_6]$ = 0.0982 gm Zn

In practice, $ZnSO_4$ is taken in a conical flask, starch solution is added as indicator, KI solution is added, then 2 cc of $K_3[Fe(CN)_6]$ is added at a time and the liberated iodine is estimated by standard $Na_2S_2O_3$ solution when no more I_2 is liberated, all Zn^{2+} has been precipitated and that will be the end point of the titration.

(d) Change of potential due to complex formation

Sometimes, addition of some complexing agent may form complex ion of any of the oxidised or reduced form decreasing the effective concentration or activity of any one species and hence may change the standard potential of the system. The titration of $Fe^{2+}$with $Cr_2O_7^{2-}$ in 1N H_2SO_4 using barium diphenylamine sulphonate indicator may be discussed here. As stated before (in the Section 9.04 change of E_0 with concentration), addition of NaF removes Fe^{3+} as $[FeF_6]^{3-}$ or $[FeF]^{2+}$, $[FeF_2]^+$, etc., For the simple reaction

$$Fe^{3+}+F^-\rightleftharpoons[FeF]^{2+},\quad K_{instablity}=10^5=\frac{[FeF]^{2+}}{[Fe^{3+}][F^-]}$$

or, $$[Fe^{3+}]=\frac{[FeF]^{2+}}{10^5\times[F^-]}$$

$[FeF_6]^{3-}$ is less stable and paramagnetic due to half-filled high spin d-shell but ionisable as it is outer orbital complex.

The potential for Fe^{3+}/Fe^{2+} system now becomes

$$E=E_0+\frac{0.0591}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

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$$= 0.77 + \frac{0.0591}{1}\log\frac{\{[FeF]^{2+}\}}{10^5 \times [F^-][Fe^{2+}]}$$

$$= 0.77 + \frac{0.0591}{1}\log 10^{-5} + \frac{0.0591}{1}\log\frac{\{[FeF]^{2+}\}}{[F^-][Fe^{2+}]}$$

$$= 0.472 + \frac{0.0591}{1}\log\frac{\{[FeF_2]^{2+}\}}{[F^-][Fe^{2+}]}$$

This potential goes below that of I_2/I^- system and hence from a mixture of Cu^{2+} and Fe^{2+}/Fe^{3+} direct estimation of Cu^{2+} can be done using NaF or NH_4HF_2 in excess. This also masks the colour of Fe^{3+} and so clear end point can be obtained.

Another example is the displacement of zinc from zinc salt solution by copper. Their reduction potentials are $Zn^{2+}/Zn = 0.76$ and $Cu^+/Cu = 0.52$. Ordinarily, Zn displaces Cu from copper salt solution. When excess KCN is added to this solution, both Cu^{2+} and Zn^{2+} form complexes with CN^-, but $[Cu(CN)_4]^{3-}$ is most stable, where Cu is in +1 state, and decreasing the concentration of Cu^+ and E_{Cu^+/Cu^0} then falls below that of Zn^{2+}/Zn system and the reaction occurs.

$Zn + 4CN^- \rightleftharpoons [Zn(CN)_4]^{2-} + 2e^-$, $E_0 = 1.26$ $K_{instability}$ of $[Cu(CN)_4]^{3-} = 5\times10^{-28}$

$Cu + 4CN^- \rightleftharpoons [Cu(CN)_4]^{3-} + e^-$, $E_0 = 0.43$ $K_{instability}$ of $[Zn(CN)_4]^{2-} = 2\times10^{-17}$

Another example can be cited with Co^{3+}/Co^{2+} system.

$Co^{3+}(aq) + e \rightleftharpoons Co^{2+}(aq)$, $E_0 = 1.842$ volt

So, oxidation of $Co^{2+} \rightarrow Co^{3+}$ is very difficult. When complexing agent like NH_3 or CN^- is added to Co^{2+} salt solution, the process takes place immediately even in presence of atmospheric oxygen and potential falls to 0.1.volt.

$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}$, $E_0 = 0.1$ volt

NH_3 is a strong ligand in the spectrochemical series. In its presence, quenching of *d* orbital of cobalt takes place, t_{2g} is more established than the e_g state, and the Co^{2+} has $t_{2g}{}^6 e_g{}^1$.

Now, NH_3 being a strong ligand, forces the $e_g{}^1$ electron to remove to higher energy 4*d* state and is removed. So, instability constant for $Co(NH_3)_6^{3+}$ complex is very low compared to that of $[Co(NH_3)_6]^{2+}$ and $[Co^{3+}] << [Co^{2+}]$. Hence, $E_{0\,Co^{3+}/Co^{2+}}$ decreases.

The oxidation potential data of some complex ions are given in the table.

$K_{instability}$ of $[Co(NH_3)_6]^{2+} = 1.25 \times 10^{-5}$

$K_{instability}$ of $[Co(NH_3)_6]^{3+} = 6 \times 10^{-36}$

Table 9.3 : Standard reduction potentials of some metal ions showing the effect of complex formation (aqueous medium, 25 °C)

Couple	E_0 volt
$Fe(H_2O)_6^{3+}/Fe(H_2O)_6^{2+}$	0·77
Fe (phen)$_3^{+3}$/Fe (phen)$_3^{2+}$	1·14
Fe (bipy)$_3^{+3}$/Fe (bipy)$_3^{2+}$	~ 1·1

Contd.

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