

OXIDATION REDUCTION REACTION :

Oxidation, reduction ^{potential.} reaction can be ^{elucidated} to greater advantage in explaining oxidation-reduction reactions in aq. solution. 0.76
1.11

The reduction potential is related to energy by the eqn.

$$\Delta G = -nFE^\circ$$

where, $\Delta G \rightarrow$ change in gibb's free energy

$n \rightarrow$ valency of the ion.

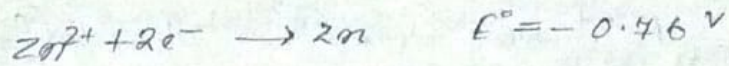
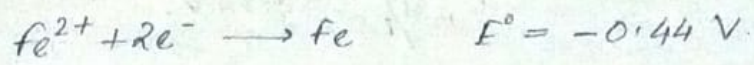
$F \rightarrow$ Faraday.

$E^\circ \rightarrow$ standard electrode potential.

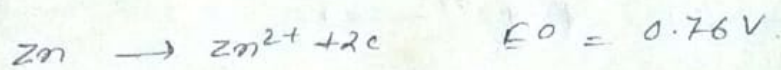
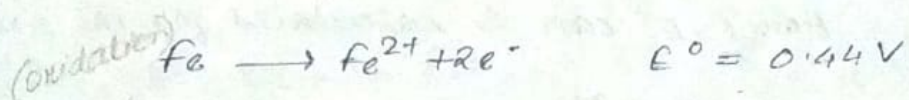
This reaction is really an application of thermodynamics, ultimately whether a reaction occurs or not depends on energy, a reaction will not proceed if the free energy change ΔG is positive and if ΔG is negative then the reaction is thermodynamically possible.

Let us consider the position that may occur when a sheet of galvanised iron is scratched.

The half reactions and the corresponding reduction potentials are



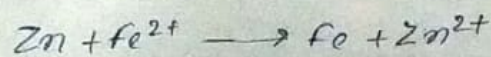
When in contact with water, either metal might be oxidised and lose metal ions, so we require the reverse reaction.



Since $\text{Zn} \rightarrow \text{Zn}^{2+}$ produced the larger E° value.

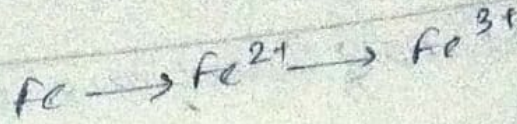
and since $\Delta G = -nFE^\circ$ it will produce the largest negative ΔG value. Thus it is energetically more favourable for Zn to dissolve and hence Zn will corrode away in preference to the ^{Fe} ~~Zn~~.

Thus, when galvanised steel is scratched the air may oxidise some Fe, the Fe^{2+} so produced is immediately reduced to Fe by the Zn and rusting does not occur.

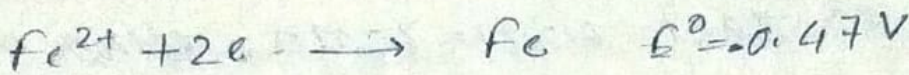
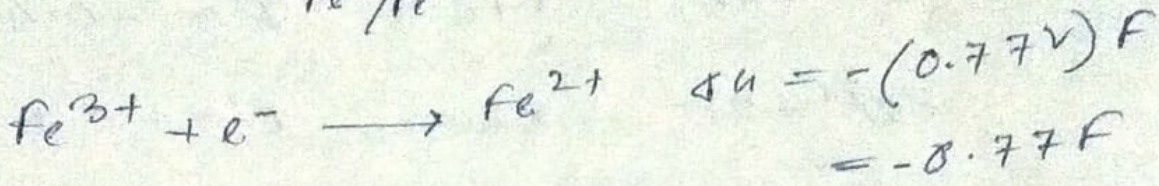


eg: The E° values for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Fe^{2+}/Fe are 0.77V and -0.47V. resp. calculate the reduction potential for Fe^{3+}/Fe .

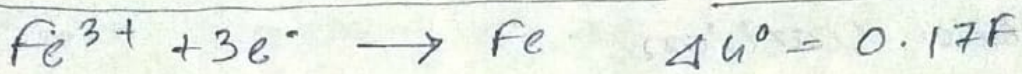
Solⁿ:



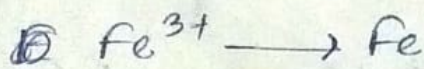
we know, $E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$.



$$\Delta G = -2(0.47)F = +0.94 F$$



Hence, E° can be calculated for the reaction



$$E^{\circ} = - \frac{\Delta G^{\circ}}{nF}$$

$$= (-) \frac{0.17 F}{3 F}$$

$$= -0.057 \text{ V.} //$$

Latimer Diagram:

There are several useful diagrammatic summaries of the relative stabilities of different oxidation states in aq. soln. 'Latimer diagrams' are useful for summarization for quantitative data for individual elements.

In a Latimer diagram of an element the numerical values of the standard potential 'Volt' is written over a horizontal line connecting species with the element in different oxidation states.

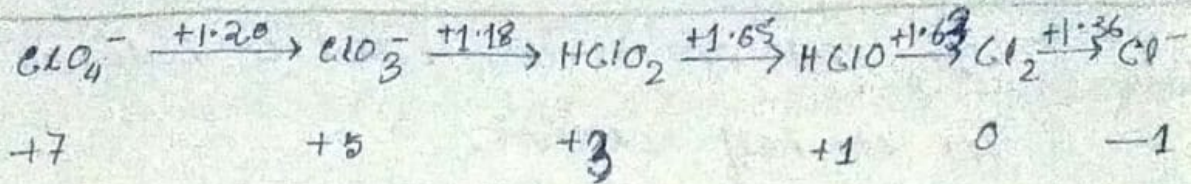
The most highly oxidised form of the element is on the left, and in species to the right the element is in successive lower oxidation states.

A Latimer diagram summarises a great deal of information in a compact form and shows the relationship between ^{various} species in a particularly clear manner.

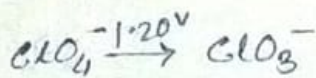
① CONSTRUCTION:

In a Latimer diagram oxidation no. decreases from left to right and the numerical values of E° are written over the line joining the species involved in the $\frac{0}{0}$ in the couple. For eg:

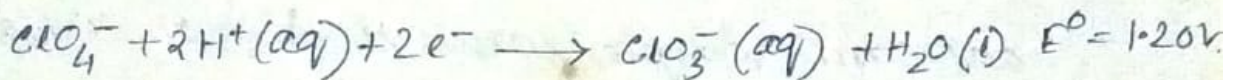
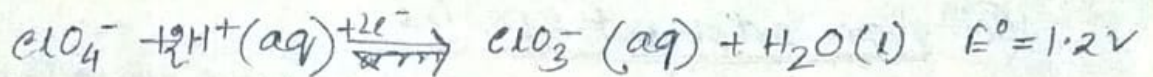
Latimer diagram for Cl in acidic soln.



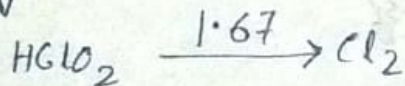
As in this example oxidation no's are sometimes written over and under or (over) the species. The notation



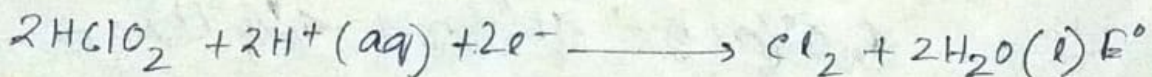
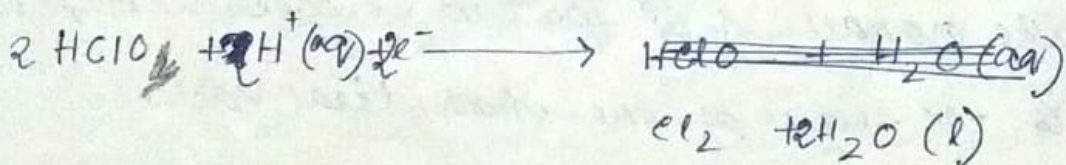
denotes



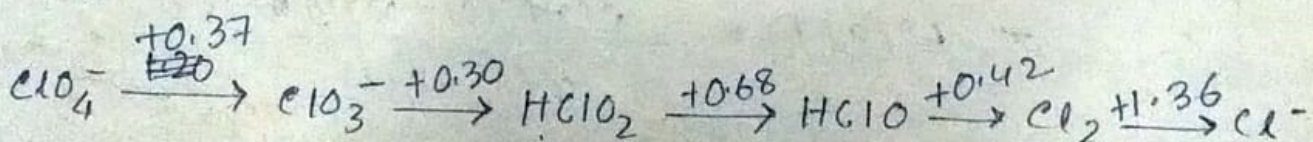
Similarly,



denotes



In basic aq. solⁿ the Latimer diagram for Cl is



② Non adjacent species:

To derive the standard potential of a non adjacent couple what it is not listed explicitly we cannot in general just add the E° values but must make use of

$$\Delta G^\circ = -nFE^\circ$$

The overall ΔG° for two successive steps 'a' and 'b' is the sum of the individual values.

$$\Delta G^\circ(a+b) = \Delta G^\circ(a) + \Delta G^\circ(b)$$

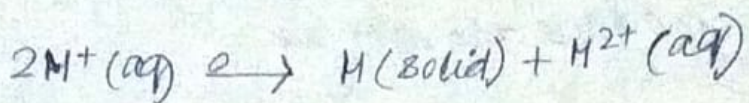
$$\Rightarrow -nFE^\circ(a+b) = -n(a)FE^\circ(a) - n(b)FE^\circ(b)$$

$$\Rightarrow -n(a+b)FE^\circ(a+b) = -n(a)FE^\circ(a) - n(b)FE^\circ(b)$$

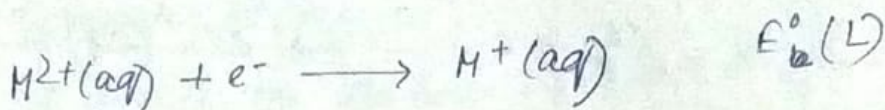
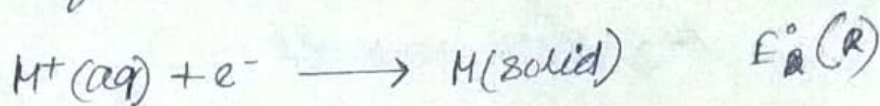
$$\therefore E^\circ(a+b) = \frac{n(a)E^\circ(a) + n(b)E^\circ(b)}{n(a) + n(b)}$$

③ Disproportionation

Let us consider the disproportionation



This reaction has $K > 1$ if $E^\circ > 0$. To analyse the criteria involved in a Latimer diagram, we express the overall reaction as the difference of two half reactions.



The ^{designation} ~~designation~~ L and R refer to the relative positions left and right resp, of that couple in a Latimer diagram, ~~this~~ because more highly oxidised species rest to the left in the periodic table. The ~~over~~ standard potential for the overall reaction is —

$$E^\circ = E^\circ_R(R) - E^\circ(L)$$

$$= \text{may be positive if } E^\circ(R) > E^\circ(L)$$

We can conclude that a species has a tendency to disproportionate into its ^{two} neighbors if the potential on the right of the species ~~higher~~ than the potential on the left.