

1.4.1. Latimer Diagrams (Reduction Potential Diagram)

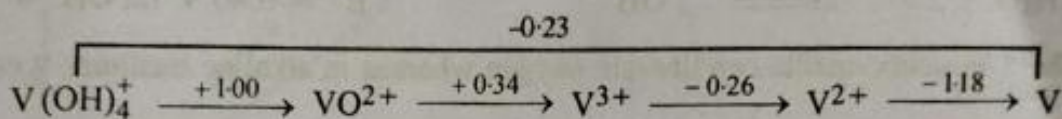
A Latimer diagram of an element presents redox potential data for a series of compounds of that element in different oxidation states. The most highly oxidised form of an element is placed on the left, in species placed on the right, the element has successively lower oxidation states. The transfer of electrons from one metal oxidation state to another in solution is conventionally written as reduction equation. The electrode potential diagrams for aqueous solutions of some first-row transition metals are given below.

Titanium has +3 and +2 oxidation states in addition to the most common +4 oxidation state in its compounds.



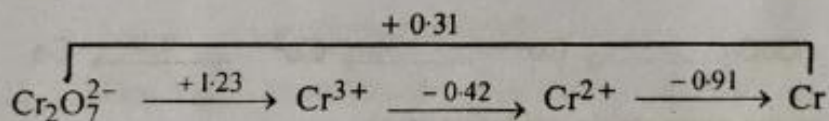
Ti^{3+} is a good reducing agent and it has existence as $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ under acidic conditions. Ti^{4+} ions are conveniently hydrolysed into TiO^{2+} and $[\text{Ti}(\text{OH})_2]^{2+}$.

Vanadium has an extensive redox chemistry. Oxidation state of vanadium is found as high as +5. The +4 oxidation state is the most stable one.



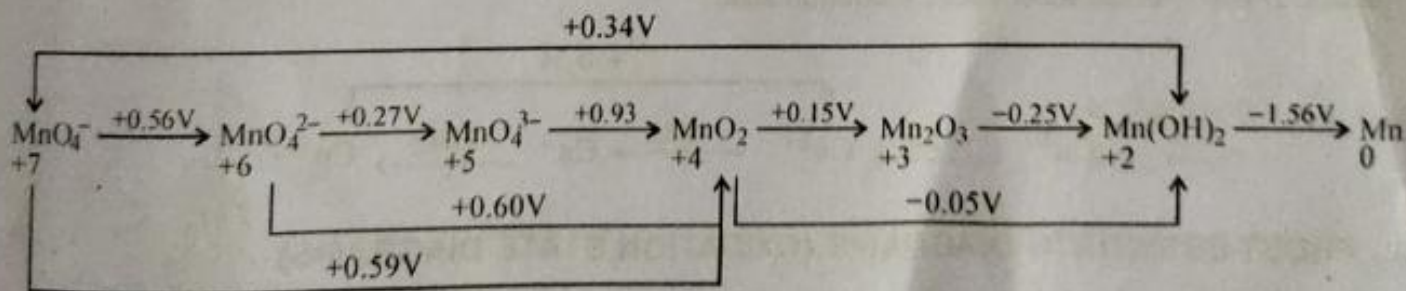
V^{2+} and V^{3+} are strong reducing agents but only V^{3+} is stable in water. V^{5+} shows good oxidising properties in concentrated acids only as with decreasing H^+ ion concentration, the reduction of V^{5+} becomes difficult.

Chromium has strongly oxidising highest oxidation state of +6. The most stable oxidation state is +3, mostly found in its compounds.

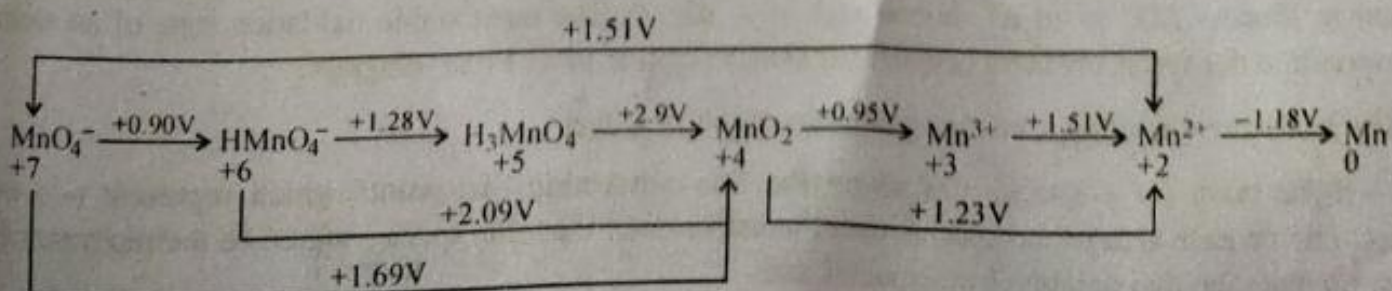


The Cr^{6+} ions in basic solution (Chromate ions, CrO_4^{2-}) are not as powerful oxidising agents as of Cr^{6+} ions in acidic solution (dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$) due to decreased H^+ ion concentration.

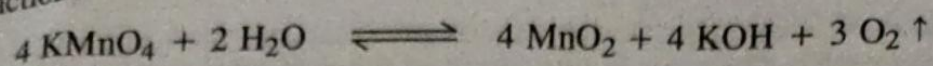
The Latimer diagram for various oxidation states of manganese ions in basic solution is represented as :



The values of standard reduction potentials, E° in acidic solution are given according to the following Latimer diagram :



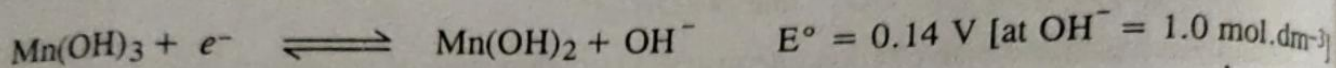
Therefore, the reaction



$$E^\circ_{\text{cell}} = 1.33 - 0.81 = 0.52 \text{ V}$$

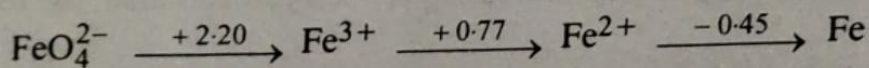
occurs at a reasonable speed. This process gets catalysed by light. That is the reason, KMnO_4 is always stored in dark glass bottles.

The couples $\text{MnO}_4^{2-}/\text{MnO}_2$ ($E^\circ = 2.26 \text{ V}$) and $\text{Mn}^{3+}/\text{Mn}^{2+}$ ($E^\circ = 1.151 \text{ V}$) are capable of oxidising water in acidic medium as their reduction potential are greater than 1.23 V . It is also important to mention that in strongly acidic media, the potential of $\text{Mn}^{2+}/\text{Mn}^{3+}$ system is independent of pH . However, in alkaline media, because of the formation of insoluble hydroxide, the potential becomes pH dependent. As a result, in alkaline media, the following redox couples are to be considered

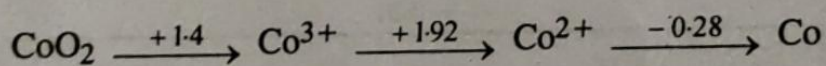


It means Mn^{3+} in acidic media can liberate oxygen whereas in alkaline medium, it can not liberate oxygen.

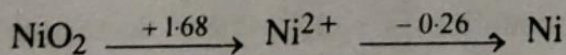
Iron Almost all the aqueous chemistry of iron is confined to the +2 and +3 oxidation states.



Cobalt tends to be stable only in the +2 oxidation state.



Nickel also has +2 as the most stable oxidation state.



Copper is unstable in its +1 oxidation state in aqueous solution. It undergoes disproportionation into Cu^{2+} and Cu . Cu^{2+} is the most stable oxidation state.

