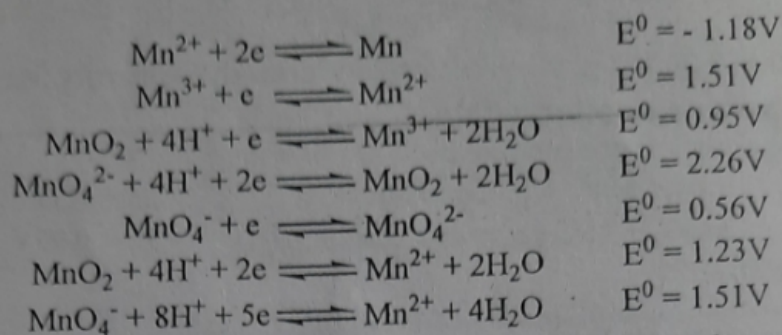


EMF diagrams:

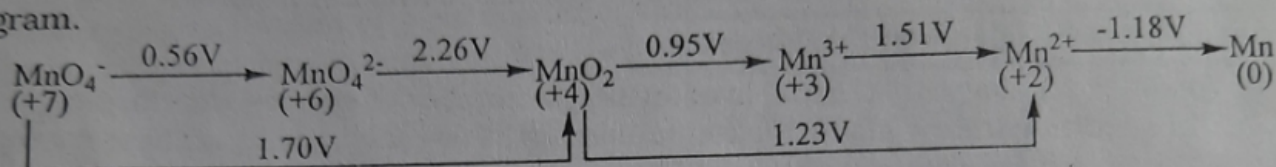
Latimer Diagram:

The redox potentials of different states for a particular element can be summarized in order of gradual decrease in oxidation state from left to right be known as Latimer EMF diagram.

Example:



The whole information can be summarized in the following EMF diagram i.e. Latimer diagram.

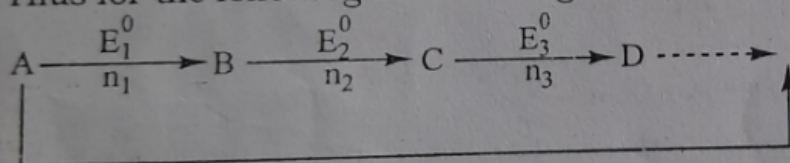


The couple $\text{MnO}_4^-/\text{Mn}^{2+}$, $\text{MnO}_4^-/\text{MnO}_2$, $\text{MnO}_2/\text{Mn}^{2+}$ etc. are referred to as skip-step couple and corresponding potential as skip-step potential.

We know -

$$\Delta G^0 = -nFE^0$$

Again ΔG^0 is a thermodynamic function and total change in the Gibbs free energy does not depend on path and it depends only on initial and final state i.e. ΔG^0 is a state function. Thus for the following Latimer diagram -



$$E^0 = \frac{n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots}{n_1 + n_2 + n_3 + \dots}$$

n = number of electron transfer in that step

Thus from the EMF diagram, we can calculate the potential for any step. The diagram is also helpful in predicting the possibilities of disproportionation and comproportionation reactions.

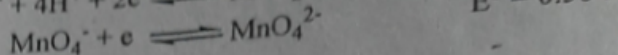
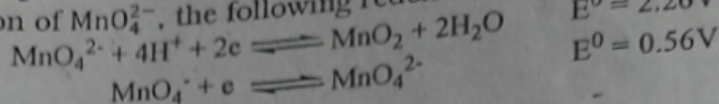
Analysis of Latimer diagram of Mn:

Elements exhibiting wide variety of oxidation state can be represented by a potential diagram, indicating the reduction potential involved in each step of reduction. **The intermediate state which has a higher standard reduction potential for conversion into lower oxidation state than that required for conversion to the higher oxidation state will undergo disproportionation.)**

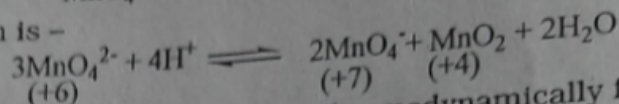
- Both Mn^{3+} & MnO_4^{2-} have higher +ve reduction potential on going forward than backward. Thus they reduce on going forward and oxidize itself on going backward. So self oxidation-reduction reaction i.e. disproportionation reaction occur.
- MnO_2 has higher +ve reduction potential on going backward than forward. So self oxidation-reduction reaction i.e. disproportionation reaction does not occur. Instead MnO_4^{2-} reduce on going forward and Mn^{3+} oxidize itself on going backward. Thus comproportionation reaction occur.

Possibility of disproportionation of MnO_4^{2-} and Mn^{3+} :

In disproportionation of MnO_4^{2-} , the following redox couples are involved -



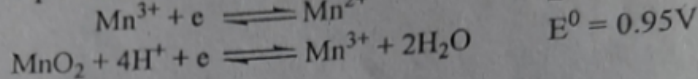
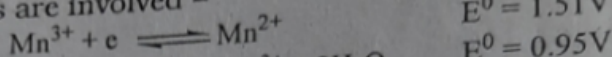
The overall cell reaction is -



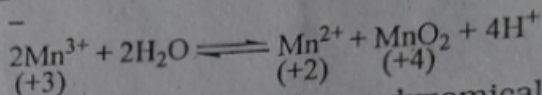
$E_{cell}^0 = (2.26 - 0.56) = 1.70 V$ i.e. the reaction is thermodynamically feasible.

Possibility of disproportionation of Mn^{3+}

the following redox couples are involved -



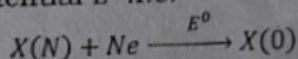
The overall cell reaction is -



$E_{cell}^0 = (1.51 - 0.95) = 0.56 V$ i.e. the reaction is thermodynamically feasible.

Frost Diagram (Ebsworth Diagram):

Let us consider an element 'X' capable of forming a number of species with forming a number of species with varying oxidation number 'N'. For each species we have a couple $X(N)/X(0)$ with a characteristic potential E^0 i.e. -



In Forst diagram of an element NE^0 vs N is plotted. Since, $N = n_1 + n_2 + n_3 + \dots$
Again we know -

$$E^0 = \frac{n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots}{n_1 + n_2 + n_3 + \dots} \quad [n = \text{number of e transfer in that step}]$$

$$\text{Or, } (n_1 + n_2 + n_3 + \dots) E^0 = n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots$$

$$\text{Or, } NE^0 = n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots$$

Again we know -

$$\Delta G^0 = -nFE^0 \Rightarrow nE^0 = -\frac{\Delta G^0}{F}$$

Where, ΔG^0 is the Gibbs free energy change for different half reactions. So this is a plot of Gibbs free energy change against oxidation number.

Diagram: (for Mn - system):

⊕ For O.S.(0): $[Mn(N=0)]$

$$NE^0 = n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots = 0$$

⊕ For O.S.(II): $[Mn^{2+}/Mn(N=2)]$

$$NE^0 = n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots = 2 \times -1.18 = -2.36 V$$

⊕ For O.S.(III): $[Mn^{3+}/Mn(N=3)]$

$$NE^0 = n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots = 2 \times -1.18 + 1 \times 1.51 = -0.85 V$$

⊕ For O.S.(IV): $[MnO_2/Mn(N=4)]$

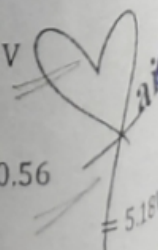
$$NE^0 = n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots = 2 \times -1.18 + 1 \times 1.51 + 1 \times 0.95 = 0.10 V$$

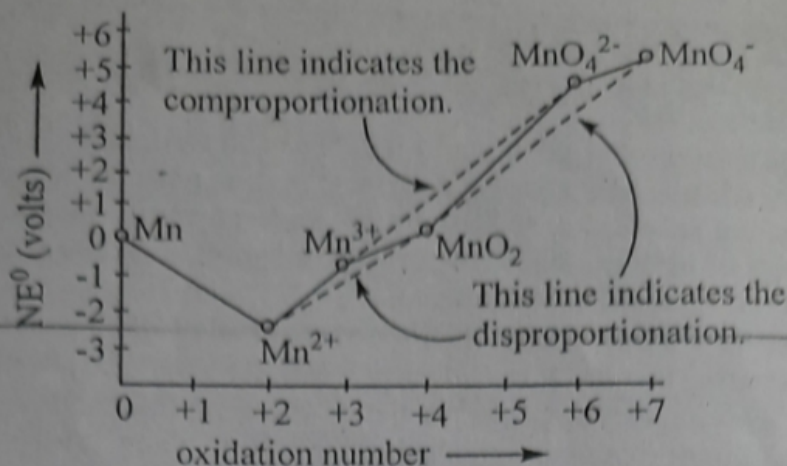
⊕ For O.S.(VI): $[MnO_4^{2-}/Mn(N=6)]$

$$NE^0 = n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots = 2 \times -1.18 + 1 \times 1.51 + 1 \times 0.95 + 2 \times 2.26 = 4.62V$$

⊕ For O.S.(VII): $[MnO_4^-/Mn(N=7)]$

$$NE^0 = n_1 E_1^0 + n_2 E_2^0 + n_3 E_3^0 + \dots = 2 \times -1.18 + 1 \times 1.51 + 1 \times 0.95 + 2 \times 2.26 + 1 \times 0.56$$

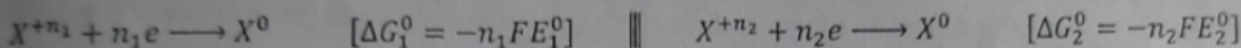




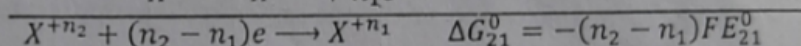
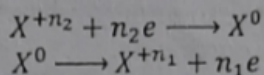
Thermodynamic Significance:

i) Evaluation of E^0 value of a particular couple:

Let us consider the $+n_1$ and $+n_2$ O.S. ($+n_2 > +n_1$) of an element X . Thus -



Thus, for the reduction of X^{+n_2} to X^{+n_1} -



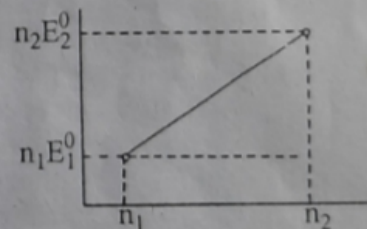
ΔG_{21}^0 = Standard free energy change for the reduction of X^{+n_2} to X^{+n_1} .

ΔE_{21}^0 = is the corresponding standard reduction potential.

$$\Rightarrow \Delta G_{21}^0 = \Delta G_2^0 - \Delta G_1^0 = -n_2FE_2^0 + n_1FE_1^0 = -F(n_2E_2^0 - n_1E_1^0)$$

$$\Rightarrow -(n_2 - n_1)FE_{21}^0 = -F(n_2E_2^0 - n_1E_1^0)$$

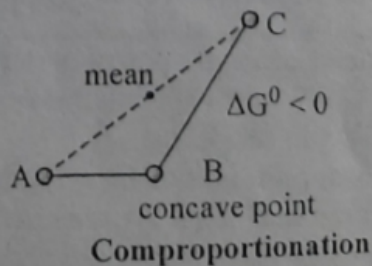
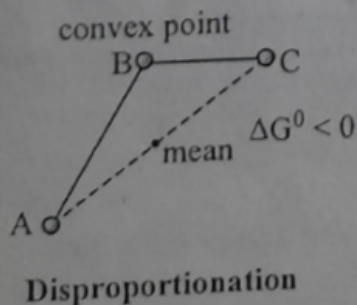
$$\Rightarrow E_{21}^0 = \frac{(n_2E_2^0 - n_1E_1^0)}{(n_2 - n_1)} = \text{slop of the line.}$$



ii) Possibility of disproportionation and comproportionation:

A species is unstable with respect to disproportionation, if it lies above the line connecting two species. It indicates that the average free energy of the terminal species A and C is less than that of intermediate B. Here B lies on a convex point.

On the other hand, a species is unstable with respect to comproportionation, if it lies below the line connecting two species. It indicates that the average free energy of the terminal species A and C is greater than that of intermediate B. Here B lies on a concave point.



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Analysis of Forst diagram of Mn:

- i) Mn^{2+} is located at the bottom of the diagram and it is thermodynamically most stable state of Mn.
- ii) MnO_4^- is located at the top and it is powerful oxidizing agent.
- iii) MnO_2 resides on a concave point and it does not undergo disproportionation. But the terminal species i.e. Mn^{3+} & MnO_4^{2-} undergo comproportionation into MnO_2 .
- iv) MnO_4^{2-} & Mn^{3+} are located at the convex point and they are unstable with respect to disproportionation reaction.
- v) The steeper the line joining the two points, the higher is the potential of the corresponding couple. It indicates that steeper (शार्दा) couple will be better oxidizing agent. Here couple MnO_2/Mn^{2+} is better oxidizing than couple MnO_4^-/MnO_4^{2-} .
- vi) Determination of skip potential of the couple MnO_4^-/MnO_2 :

Slope = $\frac{\text{Change in } nE^0 \text{ value}}{\text{Change in O.N.}} = \frac{+5.18 - (+0.1)}{(+7) - (+4)} = 1.70V$. Latimer diagram also gives same result.

Information obtain From 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 right 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.

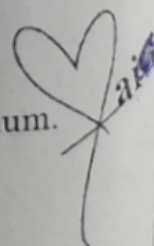
Pourbaix diagram:

The potential of many couples depend on pH. The diagrams are named after Marcel Pourbaix (1904-1998) Russian-born, Belgian chemist.

Features of the diagram:

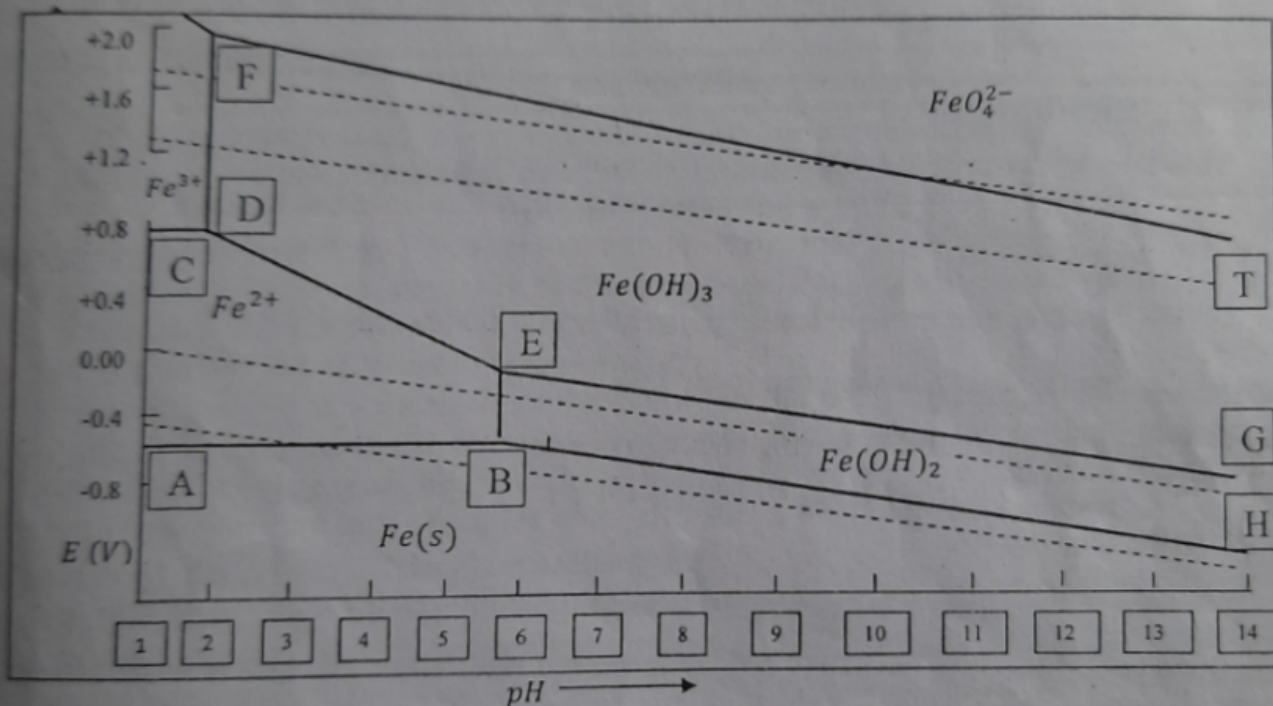
The diagram consists of four types of lines:

- ◆ **Horizontal line:** Representing the pH independent redox equilibrium.
- ◆ **Vertical line:** Representing the potential independent acid base equilibrium.
- ◆ **Slopping line:** Representing the pH dependent redox equilibrium.
- ◆ **Dotted line:** Representing the water stability zone.



General features of Pourbaix Diagram:

1. The species corresponding to any point of the diagram represents the thermodynamically most stable & most abundant form of the element at the pH and potential of the point.
When the species extends over a wide range of the diagram at a given pH, it is expected to show no redox properties or acid-base properties.
2. Strongly oxidizing form appears at the upper region while reducing appear lowe region.
3. The horizontal lines separate species whose redox equilibrium does not involve H^+/OH^- ions in the redox equilibrium.
4. Species separated vertically without overlap are expected to undergo redox reactions. If the gap between two species is greater than 1V, highly exothermic reactions are predicted. If the predominance area of a species is in an intermedlate OS totally disappears above or below a particular pH, undergo disproportionation to adjacent OS.
5. Vertical lines separate species having same OS which enter acid-base equilibria. Strong acids are confined to the left & strong bases are at right.
6. Dotted lines represent the stability zone of water. Any species above or below the lines should oxidize or reduce water. Over voltage & kinetic barrier may influence.
7. Limitation: It does not tell about concentration & temperature dependence. Thus, normally $25^\circ C$ & 1(M) concentration is employed.



Construction:

Step-1: (Horizontal line)

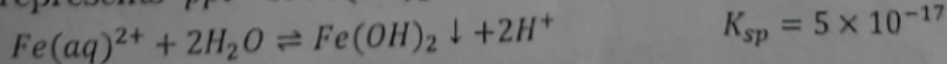
AB: $Fe(aq)^{2+} + 2e \rightleftharpoons Fe(s)$, $E = -0.44 + \frac{0.059}{2} \log [Fe^{2+}] = -0.44 V$ (at $1 \text{ mol dm}^{-3} \text{ sol}^n$)

CD: $Fe(aq)^{3+} + e \rightleftharpoons Fe(aq)^{2+}$, $E = 0.77 + \frac{0.059}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]} = 0.77 V$ (at $1 \text{ mol dm}^{-3} \text{ sol}^n$)

These horizontal lines AB & CD will extend until the pH become sufficiently high to allow pptⁿ reaction.

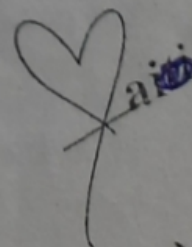
Step-II: (Vertical line)

BE: This line represents pptⁿ of $Fe(OH)_2$.



Again,

$K_{sp(Fe(OH)_2)} = [Fe^{2+}][OH]^2 \Rightarrow [Fe^{2+}] \left(\frac{K_w}{[H^+]} \right)^2$



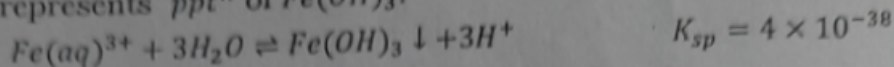
$$\Rightarrow \log K_{sp(Fe(OH)_2)} = \log[Fe^{2+}] + 2\log K_w - 2\log[H^+]$$

$$\Rightarrow 2 pH = \log(5 \times 10^{-17}) - \log(1) - 2\log(10^{-14}) = 11.7$$

$$pH = \frac{11.7}{2} = 5.58$$

Thus, for 1M solution pptⁿ of Fe²⁺ starts at pH = 5.58. The AB line extend up to pH = 5.58.

DF: This line represents pptⁿ of Fe(OH)₃.



Again,

$$K_{sp(Fe(OH)_3)} = [Fe^{3+}][OH^-]^3 \Rightarrow [Fe^{3+}] \left(\frac{K_w}{[H^+]}\right)^3$$

$$\Rightarrow \log K_{sp(Fe(OH)_3)} = \log[Fe^{3+}] + 3\log K_w - 3\log[H^+]$$

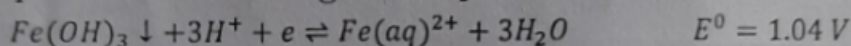
$$\Rightarrow 3 pH = \log(4 \times 10^{-38}) - \log(1) - 3\log(10^{-14}) = 4.6$$

$$pH = \frac{4.6}{3} = 1.53$$

Thus, for 1M solution pptⁿ of Fe³⁺ starts at pH = 1.53. The CD line extend up to pH = 1.53.

Step-III: (Sloping line)

DE: This line represents the following redox equilibrium

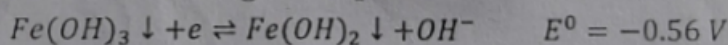


The potential is given by,

$$E = 1.04 + \frac{0.059}{1} \log \frac{[H^+]^3}{[Fe^{2+}]} = 1.04 - 0.177pH \quad (\text{at } 1M \text{ sol}^n)$$

Slope of the line is -0.177 having intercept 1.04.

EG: This line represents the following redox process,

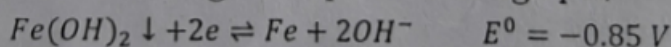


The potential is given by,

$$E = -0.56 + \frac{0.059}{1} \log \frac{1}{[OH^-]} = -0.56 + 0.059(14 - pH) = 0.26 - 0.059pH$$

Thus, the slope of the line is -0.059 having intercept 0.26. since DE line is more steeper than EG line.

BH: This line represents the following redox process at high pH,

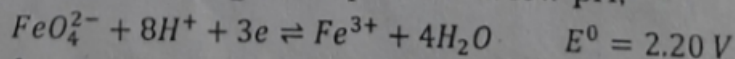


The potential is given by,

$$E = -0.85 + \frac{0.059}{2} \log \frac{1}{[OH^-]^2} = -0.85 + 0.059(14 - pH) = -0.024 - 0.059pH$$

Thus, the slope of the line is -0.059 having intercept -0.024. since BH line is parallel with EG line.

FP: This line represents the following redox process at low pH,

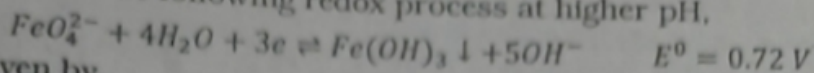


The potential is given by,

$$E = 2.20 + \frac{0.059}{3} \log \frac{[FeO_4^{2-}][H^+]^8}{[Fe^{3+}]} = 2.20 - \frac{0.059 \times 8}{3} pH = 2.20 - 0.157 pH \quad (\text{at } 1M \text{ sol}^n)$$

Thus, the slope of the line is -0.157 having intercept 2.20. At lower pH it can oxidise water to O₂.

TF: This line represents the following redox process at higher pH,



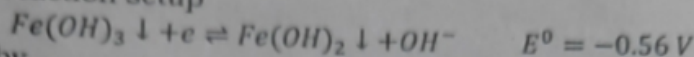
The potential is given by,

$$E = 0.72 + \frac{0.059}{3} \log \frac{[FeO_4^{2-}]}{[OH^+]^5} = 0.72 + \frac{0.059 \times 5}{3} (14 - pH) = 2.1 - 0.098 pH \quad (\text{at } 1M \text{ sol}^n)$$

Thus, the slope of the line is -0.098 having intercept 2.1 . since FP line is more steeper than TF line. Stability of FeO_4^{2-} in alkaline sol^n arises mainly due to over potential of O_2 .

Note: Standard reduction potential of the couples $Fe^{3+}/Fe^{2+} = 0.77V$ & $O_2/2H_2O = 1.23$ indicates that aerial oxidation of Fe^{2+} is possible. But due to overpotential for the O_2 -evolution, Fe^{2+} -solution survives from the aerial oxidation.

At high pH new redox reaction setup



The potential is given by,

$$E = -0.56 + \frac{0.059}{1} \log \frac{1}{[OH^-]} = -0.56 + 0.059(14 - pH) = 0.26 - 0.059pH$$

Since, formal potential decreases significantly. Thus, aerial oxidation of Fe^{2+} is possible both thermodynamically & kinetically.

Ellingham Diagram:

The Gibbs free energy (ΔG) of a reaction is a measure of the thermodynamic driving force that makes a reaction spontaneous or non-spontaneous. This is given by:

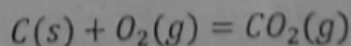
$$\Delta G = \Delta H - T\Delta S$$

where ΔH is the enthalpy, T is absolute temperature, and ΔS is entropy.

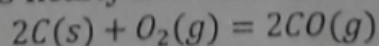
- The enthalpy (ΔH) is a measure of the actual energy that is liberated when the reaction occurs (the "heat of reaction"). If it is negative, then the reaction gives off energy, while if it is positive the reaction requires energy.
- The entropy (ΔS) is a measure of the change in the possibilities for disorder in the products compared to the reactants. For example, if a solid (an ordered state) reacts with a liquid (a somewhat less ordered state) to form a gas (a highly disordered state), there is normally a large positive change in the entropy for the reaction.

Construction of an Ellingham Diagram

- An Ellingham diagram is a plot of ΔG versus temperature. Since ΔH and ΔS are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines, where ΔS is the slope and ΔH is the y-intercept. The slope of the line changes when any of the materials involved melt or vaporize.
- Free energy of formation is negative for most metal oxides, and so the diagram is drawn with $\Delta G=0$ at the top of the diagram, and the values of ΔG shown are all negative numbers.
- The Ellingham diagram shown is for metals reacting to form oxides. The oxygen partial pressure is taken as 1 atmosphere, and all of the reactions are normalized to consume one mole of O_2 .
- The majority of the lines slope upwards, because both the metal and the oxide are present as condensed phases (solid or liquid). The reactions are therefore reacting a gas with a condensed phase to make another condensed phase, which reduces the entropy. A notable exception to this is the oxidation of solid carbon. The line for the reaction

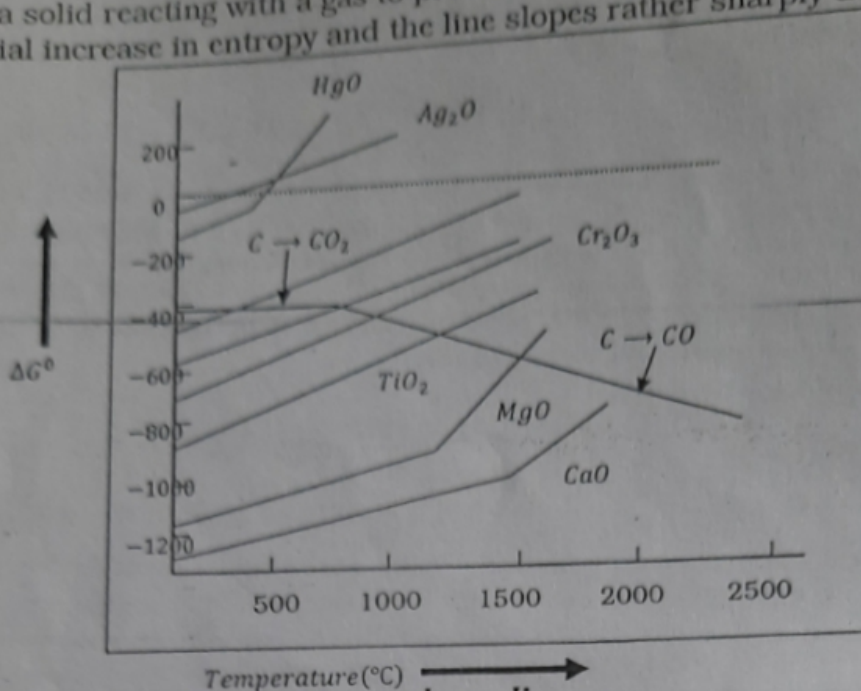


is a solid reacting with a mole of gas to produce a mole of gas, and so there is little change in entropy and the line is nearly horizontal. For the reaction



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we have a solid reacting with a gas to produce two moles of gas, and so there is a substantial increase in entropy and the line slopes rather sharply downward.



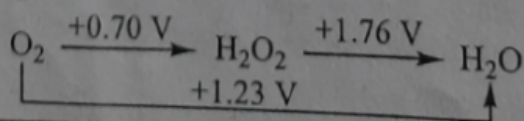
There are three main uses of the Ellingham diagram:

- ◆ A) Determine the relative ease of reducing a given metallic oxide to metal;
- ◆ B) Determine the partial pressure of oxygen that is in equilibrium with a metal oxide at a given temperature;
- ◆ C) Determine the ratio of carbon monoxide to carbon dioxide that will be able to reduce the oxide to metal at a given temperature.

Ease of Reduction

- The position of the line for a given reaction on the Ellingham diagram shows the stability of the oxide as a function of temperature. Reactions closer to the top of the diagram are the most "noble" metals (for example, mercury, gold and platinum), and their oxides are unstable and easily reduced. As we move down toward the bottom of the diagram, the metals become progressively more reactive and their oxides become harder to reduce.
- A given metal can reduce the oxides of all other metals whose lines lie above theirs on the diagram. For example, the $2Mg + O_2 \rightleftharpoons 2MgO$ line lies below the $Ti + O_2 \rightleftharpoons TiO_2$ line, and so magnesium can reduce titanium oxide to metallic titanium.
- Since the $2C(s) + O_2(g) = 2CO(g)$ line is downward-sloping, it cuts across the lines for many of the other metals. This makes carbon unusually useful as a reducing agent, because as soon as the carbon oxidation line goes below a metal oxidation line, the carbon can then reduce the metal oxide to metal. So, for example, solid carbon can reduce chromium oxide once the temperature exceeds approximately $1225^\circ C$, and can even reduce highly-stable compounds like silicon dioxide and titanium dioxide at temperatures above about $1620^\circ C$ and $1650^\circ C$, respectively. For less stable oxides, carbon monoxide is often an adequate reducing agent.

Problem: Construct Frost diagram from the following Latimer diagram and comment on the disproportionation of H_2O_2 :



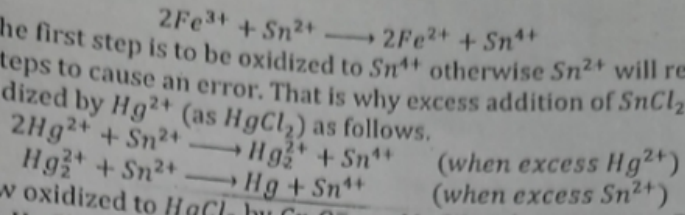
Hint: Do it yourself. Since disproportionation reaction is thermodynamically feasible but due to evolution of O_2 gas overpotential factor introduces kinetic stability.

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Why drop wise SnCl₂ is added? Why excess solution to be avoided during reduction of Fe(III)? Oxidation of Sn(II) by Hg(II), excess HgCl₂ is added at a time why?

Reduction of Fe(III) by SnCl₂ in aqueous HCl medium is carried out by the drop wise addition of SnCl₂ to avoid excess addition.

Un consumed Sn²⁺ at the first step is to be oxidized to Sn⁴⁺ otherwise Sn²⁺ will react with Cr₂O₇²⁻ or MnO₄⁻ in subsequent steps to cause an error. That is why excess addition of SnCl₂ is to be avoid. Some what excess Sn²⁺ is oxidized by Hg²⁺ (as HgCl₂) as follows.



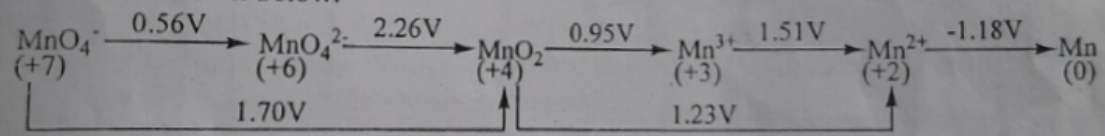
Now formed Hg can now oxidized to HgCl₂ by Cr₂O₇²⁻ or MnO₄⁻ and cause error. Thus formation of Hg₂²⁺ is attained when excess HgCl₂ is added. If HgCl₂ is added drop wise, local excess concentration of Sn²⁺ may reduce Hg²⁺ up to Hg which reacts with titrant cause significant error. That is why excess HgCl₂ is added at a time.

Why HCl medium is required?

During the reduction of Hg(II) by Sn(II), it should be stopped at mercurous step. E⁰ values indicates Hg²⁺(aq) & Hg₂²⁺(aq) are almost equally oxidizing and thermodynamically it is difficult to stop at mercurous stage. However, formation of insoluble mercurous salt makes Hg(II) more oxidizing but Hg(I) less oxidizing. Thus increased E⁰ value for Hg²⁺/Hg₂Cl₂ couple makes Hg₂Cl₂ less oxidisable. Consequently possibility of oxidation of Hg₂Cl₂ by Cr₂O₇²⁻ or MnO₄⁻ becomes less favored. Moreover, disproportionation of Hg₂²⁺(aq) may be stopped at lower pH in presence of HCl. Thus, important role of HCl are: reduction of Hg(II) stopped at the mercurous step i.e. Hg₂Cl₂; prevention of disproportionation of mercurous ion; inner sphere electron transfer reaction through the chloro-bridge formation.

Write short notes on: i) Latimer diagram, ii) Frost diagram & iii) Pourbiac diagram

Latimer Diagrams: 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.



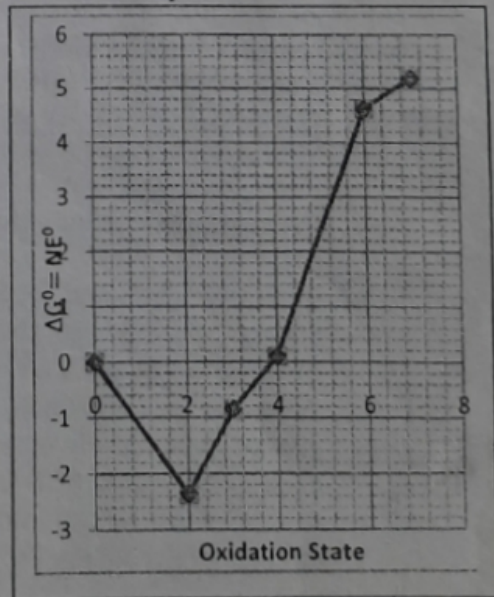
The standard reduction potential for the reduction half-reaction involving the two species joined by the arrow is shown above the arrow. Latimer diagrams show the redox information about a series of species in a very condensed form. From these diagrams you can predict the redox behavior of a given species. 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. Half-reactions can be written from these diagrams.

Frost Diagrams:

In Forst diagram of an element NE⁰ vs N is plotted. Since, N = n₁ + n₂ + n₃ + ...
Again we know -

$$\Delta G^0 = -nFE^0 \Rightarrow nE^0 = -\frac{\Delta G^0}{F}$$

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.

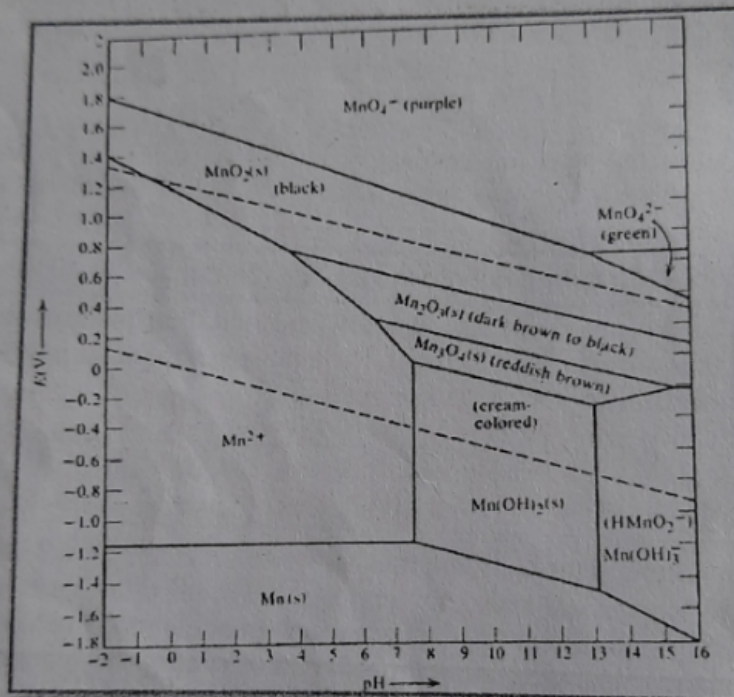


Pourbaix Diagrams

Pourbaix or Eh-pH diagrams depict the thermodynamically form of an element as a function of potential and pH. The Pourbaix diagram is a type of predominance diagram -- it shows the predominate form in an element will exist under a given set of environmental conditions. These diagrams give a visual representation of the oxidizing and reducing abilities of the major stable compounds of an element and are used frequently in geochemical, environmental and corrosion applications. Like Frost diagrams, Pourbaix diagrams display thermodynamically preferred species. Kinetics is not incorporated.

How to Read a Pourbaix Diagram

- Vertical lines separate species that are in acid-base equilibrium.
- Non vertical lines separate species related by redox equilibria.
 - Horizontal lines separate species in redox equilibria not involving hydrogen or hydroxide ions.
 - Diagonal boundaries separate species in redox equilibria in which hydroxide or hydrogen ions are involved.
- Dashed lines enclose the practical region of stability of the water solvent to oxidation or reduction.



What You Can Learn From a Pourbaix Diagram

- Any point on the diagram will give the thermodynamically most stable (and theoretically most abundant) form of that element at a given potential and pH condition.
- Strong oxidizing agents and oxidizing conditions are found only at the top of Pourbaix diagrams. Strong oxidizing agents have lower boundaries that are also high on the diagram. **Permanganate is an oxidizing agent over all pH ranges. It is very strongly oxidizing at low pH.**
- Reducing agents and reducing conditions are found at the bottom of a diagram and not elsewhere. Strong reducing agents have low upper boundaries on the diagram. **Manganese metal is a reducing agent over all pH ranges and is strongest in basic conditions.**
- When the predominance area for a given oxidation state disappears completely above or below a given pH and the element is in an intermediate oxidation state, the element will undergo disproportionation **MnO4 2- tends to disproportionate.**
- A species that ranges from the top to the bottom of the diagram at a given pH will have no oxidizing or reducing properties at that pH.

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Why aqua regia dissolve noble metals like Pt, Au and covalent sulphides?

Conventionally, it is stated that in aqua regia, conc. HNO_3 oxidises conc. HCl to produce the nascent chlorine which is responsible to oxidize the noble metals. But nascent chlorine never be thermodynamically more powerful than HNO_3 as an oxidizing agent. If nascent chlorine would oxidize noble metals, then HNO_3 should alone oxidize them. But it is not occur so.

Again for covalent sulphides due to good soft-soft interaction and very low solubility product they are insoluble in water. The solubilisation is attained only when S^{2-} is oxidized. Though HNO_3 is powerful oxidizing acid, it cannot perform the work alone.

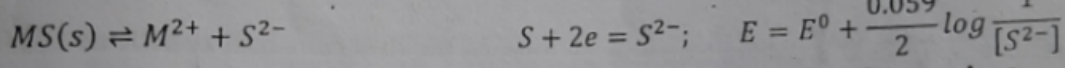
But in presence of excess Cl^- (coming from three part HCl of aqua regia) the oxidant of the redox couples of the noble metals and metal ions of covalent sulphides form stable chloro complexes.

- For dissolution of metals:

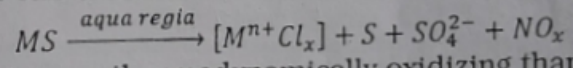
$$M^{n+} + ne = M; \quad E = E^0 + \frac{0.059}{n} \log[M^{n+}]$$

As a result reduction potential of the metals get significantly decreased, so that now NO_3^- can oxidize the metals. In the experimental condition, the formal potential of NO_3^-/NO system exceeds that of $[M^{n+}Cl_x]/M$ couple. Thus, in aqua regia noble metals get dissolve. Au & Pt forms

- For dissolution of covalent sulphides:



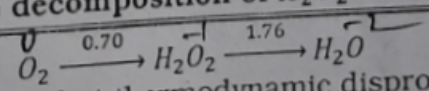
Due to formation of stable complex the above ionization process favor. As a consequence more S^{2-} produced which lower the formal potential of S/S^{2-} couple. Since NO_3^-/NO system can oxidize S^{2-} .



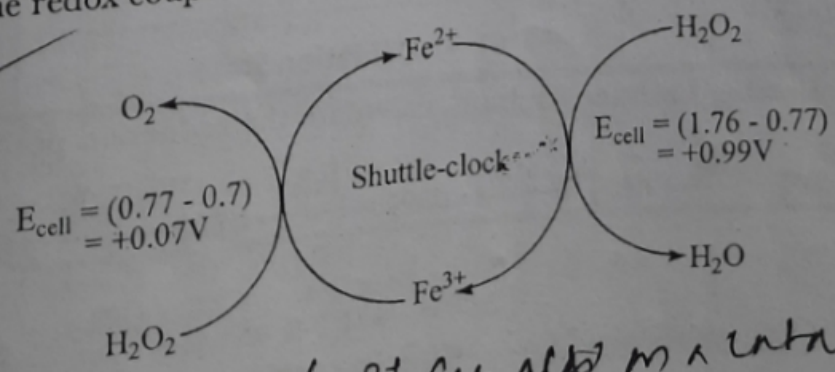
Since aqua regia is not more thermodynamically oxidizing than conc. HNO_3 but formation of said stable chloro-complex makes S^{2-} more readily oxidisable by HNO_3 . This makes covalent sulphides soluble.

Hg	Pt	Au	Pd	Co	Ni
$HgCl_4^{2-}$	$PtCl_4^{2-}$	$AuCl_4^-$	$PdCl_4^{2-}$	$CoCl_4^{2-}$	$NiCl_4^{2-}$

Explain how Fe^{3+} catalyses the decomposition of H_2O_2 ? ans.



From the above diagram it is clear that thermodynamic disproportionation is possible. But this requires to evolution O_2 which cause overpotential. This reaction is catalysed by any redox couple having reduction potential between the values 0.70 - 1.76. Since oxidant of the redox couple will oxidize H_2O_2 to O_2 , while the reductant of the couple will oxidized by H_2O_2 . Thus the redox couple of the catalyst plays a **shuttle-cock** role.



Handwritten note: Fe^{3+}/Fe^{2+} can act as a catalyst catalyse the rxn.

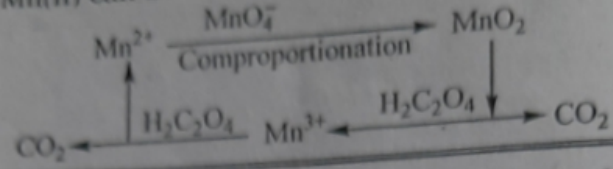
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During standardization of $KMnO_4$ by oxalic acid initial heating is required but after reaction starts it is not required. Why?

During titration of $H_2C_2O_4$ by $KMnO_4$, at the initial stage the rate of the reaction is very slow. Thus it requires heating to start the reaction. But after the initial stage, the rate becomes quite fast. As reaction starts produced Mn^{2+} plays as autocatalyst.

- First produced Mn^{2+} and added MnO_4^- undergo disproportionation & produce MnO_2 .
- Produced MnO_2 oxidises $H_2C_2O_4$ & itself reduces to Mn^{3+} .
- Produced Mn^{3+} again oxidizes $H_2C_2O_4$ & itself reduces to Mn^{2+} .

The catalytic action of Mn(II) can be outlined as follows:



$ClO_3^- \xrightarrow{1.18V} ClO_2^- \xrightarrow{1.70V} HClO \xrightarrow{1.63V} Cl_2$. Construct a Frost diagram using the above diagram chlorine and hence explain the feasibilities of disproportionation.

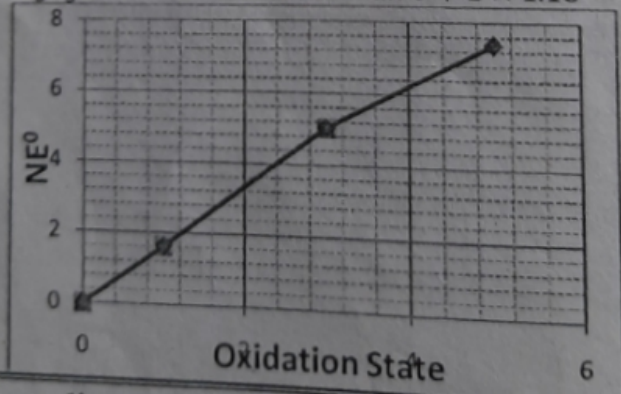
We know -

$$\Delta G^0 = -nFE^0 \Rightarrow nE^0 = -\frac{\Delta G^0}{F}$$

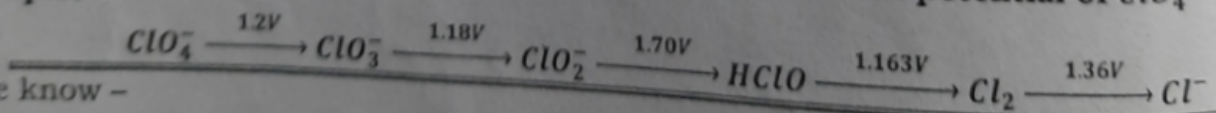
Where, ΔG^0 is the Gibbs free energy change for different half reactions. This is a plot of Gibbs free energy change per faraday of electricity ($-\frac{\Delta G^0}{F}$) against oxidation number.

Diagram: (for Chlorine - system):

- ⊕ For O.S.(0): [$Cl(N = 0)$]
 $NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 0$
- ⊕ For O.S.(I): [$HClO/Cl_2 (N = 1)$]
 $NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 1 \times 1.63 = 1.63 \text{ V}$
- ⊕ For O.S.(III): [$ClO_2^-/Cl_2 (N = 3)$]
 $NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 1 \times 1.63 + 2 \times 1.70 = 5.03 \text{ V}$
- ⊕ For O.S.(V): [$ClO_3^-/Cl_2 (N = 5)$]
 $NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 1 \times 1.63 + 2 \times 1.70 + 2 \times 1.18 = 7.39 \text{ V}$



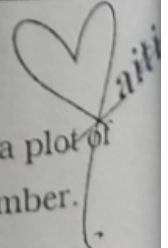
From the following Latimer diagram, calculate the reduction potential of $ClO_4^- - Cl^-$ couple:

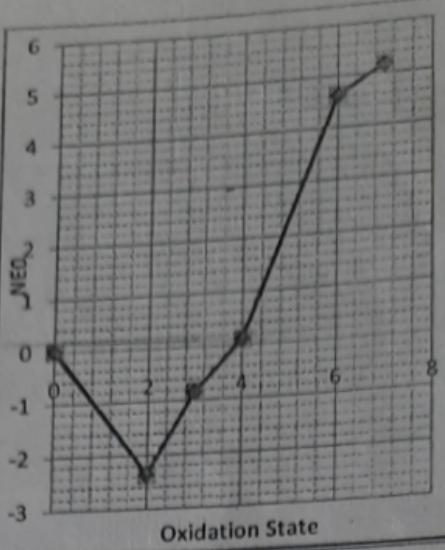


We know -

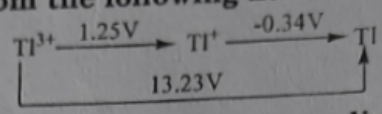
$$\Delta G^0 = -nFE^0 \Rightarrow nE^0 = -\frac{\Delta G^0}{F}$$

Where, ΔG^0 is the Gibbs free energy change for different half reactions. This is a plot of Gibbs free energy change per faraday of electricity ($-\frac{\Delta G^0}{F}$) against oxidation number.





Construct the Frost Diagram from the following Latimer Diagram.



Show the conditions necessary for the evaluation of coordinate of each point of the plot.

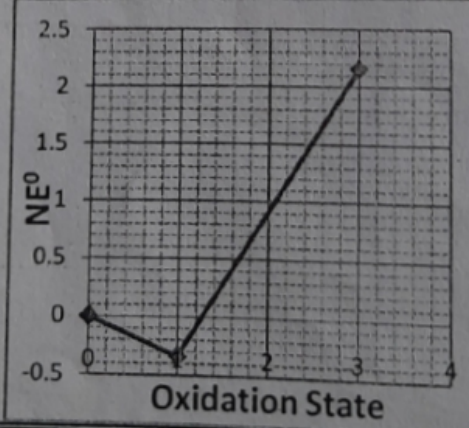
We know -

$$\Delta G^0 = -nFE^0 \Rightarrow nE^0 = -\frac{\Delta G^0}{F}$$

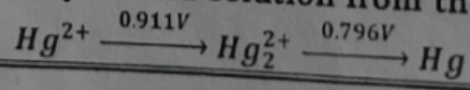
Where, ΔG^0 is the Gibbs free energy change for different half reactions. This is a plot of Gibbs free energy change per faraday of electricity ($-\frac{\Delta G^0}{F}$) against oxidation number.

Diagram: (for Tl - system):

- ⊕ For O.S.(0): [Tl(N = 0)]
 $NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 0$
- ⊕ For O.S.(I): [Tl⁺/Tl(N = 1)]
 $NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 1 \times -0.34 = -0.34 \text{ V}$
- ⊕ For O.S.(III): [Tl³⁺/Tl(N = 3)]
 $NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 1 \times -0.34 + 2 \times 1.25 = 2.16 \text{ V}$



Draw the Frost diagram for mercury in acid solution from the given Latimer diagram:



We know -

$$\Delta G^0 = -nFE^0 \Rightarrow nE^0 = -\frac{\Delta G^0}{F}$$

Where, ΔG^0 is the Gibbs free energy change for different half reactions. This is a plot of Gibbs free energy change per faraday of electricity ($-\frac{\Delta G^0}{F}$) against oxidation number.

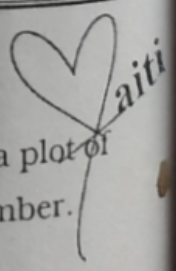


Diagram: (for Hg- system):

⊕ For O.S.(0): [Hg(N = 0)]

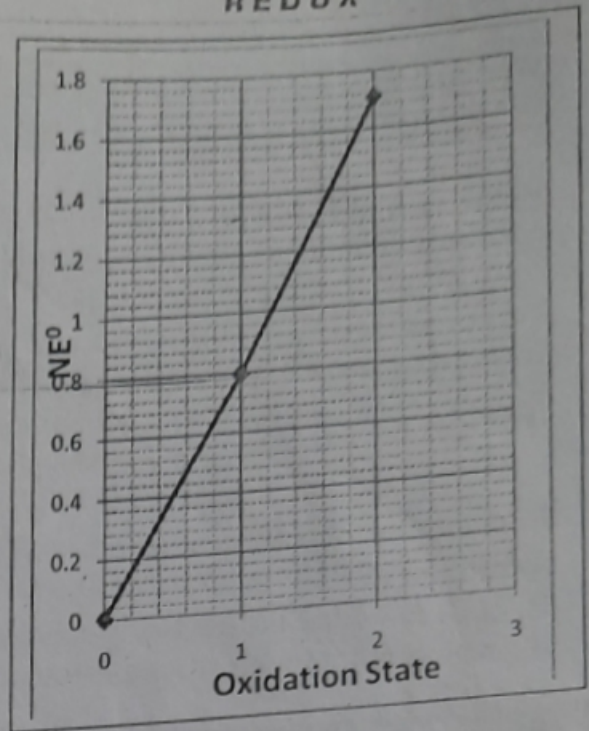
$$NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 0$$

⊕ For O.S.(I): [Hg²⁺/Hg(N = 1)]

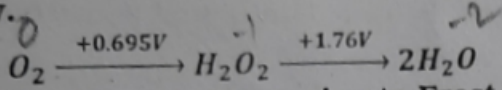
$$NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 1 \times 0.796 = 0.796V$$

⊕ For O.S.(II): [Hg²⁺/Hg(N = 2)]

$$NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 1 \times 0.796 + 1 \times 0.911 = 1.707V$$



Find E⁰ value for the reduction of O₂ to H₂O with the help of the Latimer diagram of oxygen given below.



And hence construct an approximate Frost diagram of oxygen in acid medium using these informations.

We know -

$$\Delta G^0 = -nFE^0 \Rightarrow nE^0 = -\frac{\Delta G^0}{F}$$

Where, ΔG⁰ is the Gibbs free energy change for different half reactions. This is a plot of Gibbs free energy change per faraday of electricity (-ΔG⁰/F) against oxidation number.

Diagram: (for O₂- system):

⊕ For O.S.(0): [O₂(N = 0)]

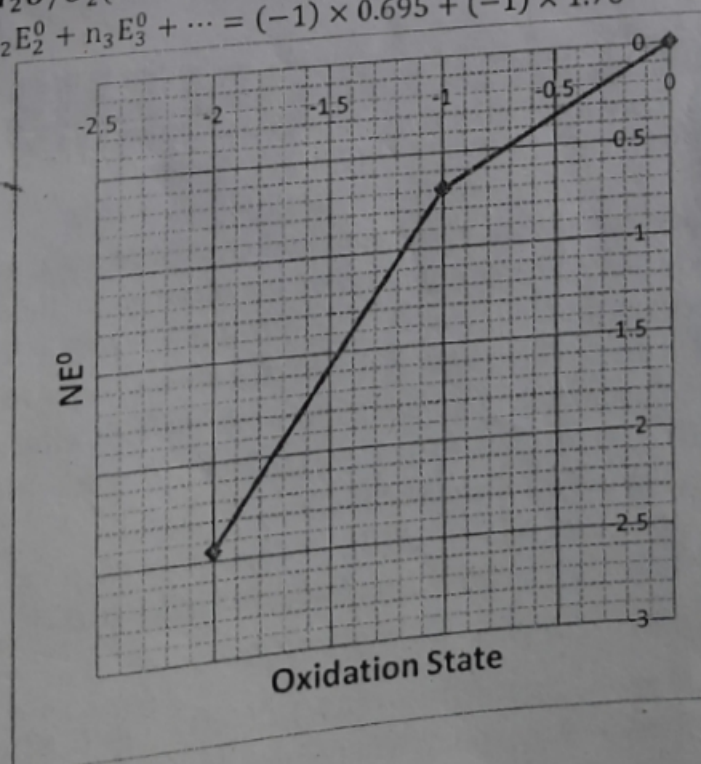
$$NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = 0$$

⊕ For O.S.(-I): [H₂O₂/O₂(N = -1)]

$$NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = (-1) \times 0.695 = -0.695V$$

⊕ For O.S.(-II): [H₂O/O₂(N = -2)]

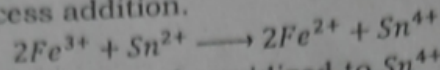
$$NE^0 = n_1E_1^0 + n_2E_2^0 + n_3E_3^0 + \dots = (-1) \times 0.695 + (-1) \times 1.76 = -2.4557V$$



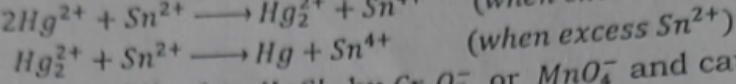
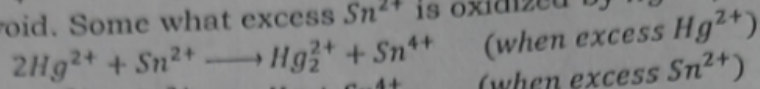
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Why drop wise SnCl_2 is added? Why excess solution to be avoided during reduction of Fe(III) ?
 Oxidation of Sn(II) by Hg(II) , excess HgCl_2 is added at a time why?

Reduction of Fe(III) by SnCl_2 in aqueous HCl medium is carried out by the drop wise addition of SnCl_2 to avoid excess addition.



Un consumed Sn^{2+} at the first step is to be oxidized to Sn^{4+} otherwise Sn^{2+} will react with Cr_2O_7^- or MnO_4^- in subsequent steps to cause an error. That is why excess addition of SnCl_2 is to be avoid. Some what excess Sn^{2+} is oxidized by Hg^{2+} (as HgCl_2) as follows.



Now formed Hg can now oxidized to HgCl_2 by Cr_2O_7^- or MnO_4^- and cause error. Thus formation of Hg_2^{2+} is attained when excess HgCl_2 is added.

If HgCl_2 is added drop wise, local excess concentration of Sn^{2+} may reduce Hg^{2+} up to Hg which reacts with titrant cause significant error. That is why excess HgCl_2 is added at a time.

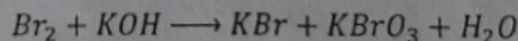
Why HCl medium is required?

During the reduction of Hg(II) by Sn(II) , it should be stopped at mercurous step. E^0 values indicates $\text{Hg}^{2+}(\text{aq})$ & $\text{Hg}_2^{2+}(\text{aq})$ are almost equally oxidizing and thermodynamically it is difficult to stop at mercurous stage. However, formation of insoluble mercurous salt makes Hg(II) more oxidizing but Hg(I) less oxidizing. Thus increased E^0 value for $\text{Hg}^{2+}/\text{Hg}_2\text{Cl}_2$ couple makes Hg_2Cl_2 less oxidisable. Consequently possibility of oxidation of Hg_2Cl_2 by Cr_2O_7^- or MnO_4^- becomes less favored.

Moreover, disproportionation of $\text{Hg}_2^{2+}(\text{aq})$ may be stopped at lower pH in presence of HCl . Thus, important role of HCl are: reduction of Hg(II) stopped at the mercurous step i.e. Hg_2Cl_2 ; prevention of disproportionation of mercurous ion; inner sphere electron transfer reaction through the chloro-bridge formation.

REDOX PROBLEMS

1. Balance the following equation by ion electron method.

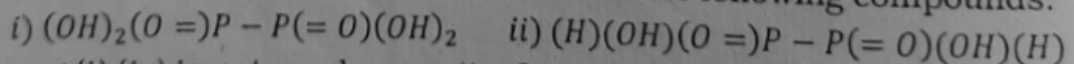


2. Sodium nitrite when boiled with aluminum and caustic potash, ammonia gas is evolved. Form the balanced ionic equation by ion electron method.

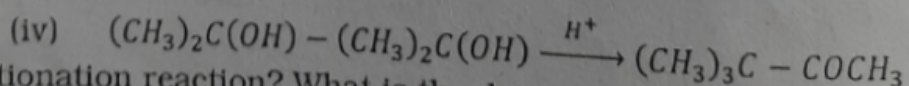
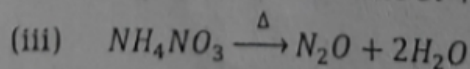
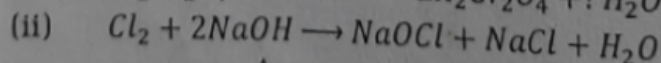
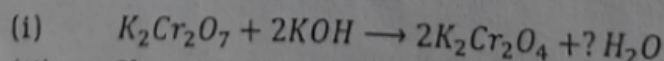
3. Balance by ion-electron method: $\text{NaNO}_3 + \text{Zn} + \text{NaOH} \longrightarrow \text{NH}_3 + \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O}$.

4. Balance by ion electron method: $\text{NaNO}_3 + \text{Al} + \text{NaOH} \longrightarrow \text{NH}_3 + \text{NaAlO}_2 + \text{H}_2\text{O}$

5. Indicate the oxidation number of all the P atoms in the following compounds:



6. Which among (i)-(iv) is not a redox reaction?



7. What is disproportionation reaction? What is the driving force behind a disproportionation reaction? Explain it with example.

8. What is a disproportionation and comproportionation reactions? Give two examples of each case.
 9. "Disproportionation and comproportionation reactions are actually redox reaction". Justify the statement with suitable examples.

10. Establish the Nernst equations for the following couples

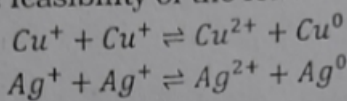
- i) MnO_4^- / Mn^{2+} in acid medium.
 ii) BrO_3^- / Br^- in alkaline medium.

11. E^0 value of Fe^{3+} / Fe^{2+} is 0.77 Volt at 25°C. Calculate the equilibrium constant for the reaction between Fe^{2+} and MnO_4^- ions in 1M H_2SO_4 at this temperature.

12. What do you mean by standard electrode potential (E^0 of a redox couple)? E^0 values of MnO_4^- / Mn^{2+} and $Cr_2O_7^{2-} / Cr^{3+}$ couples are 1.51 and 1.33 volts respectively at 25°C. At what acidity the two couples will have the same redox potential?

13. Calculate the equilibrium constant of the reaction between Fe^{2+} and MnO_4^- in 1(M) acid medium. [Given: $E_{Fe^{3+}/Fe^{2+}}^0 = 0.77V$ and $E_{MnO_4^-/Mn^{2+}}^0 = 1.51V$].

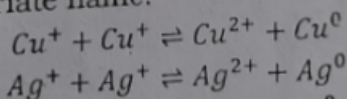
14. Estimate the thermodynamic feasibility of the following reaction:



Indicate the directions in which the reactions would precede spontaneously. Give standard reduction potential E^0 values.

Couple	$E^0(V)$ at 25°C
Cu^{2+} / Cu^+	+0.16
Cu^+ / Cu^0	+0.52
Ag^{2+} / Ag^+	+1.98
Ag^+ / Ag^0	+0.80

15. Indicate the directions in which the following reactions would precede spontaneously and assign them with appropriate name.



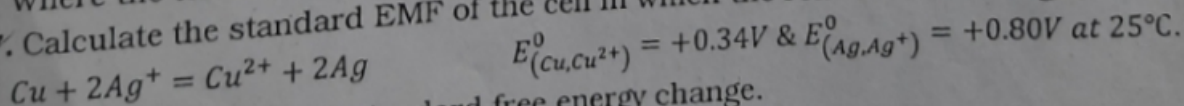
Couple	$E^0(V)$ at 25°C
Cu^{2+} / Cu^+	+0.16
Cu^+ / Cu^0	+0.52
Ag^{2+} / Ag^+	+1.98
Ag^+ / Ag^0	+0.80

16. Show that equilibrium constant k of a redox process is given by the equation:

$$\log k = \frac{n}{0.059} (E_1^0 - E_2^0)$$

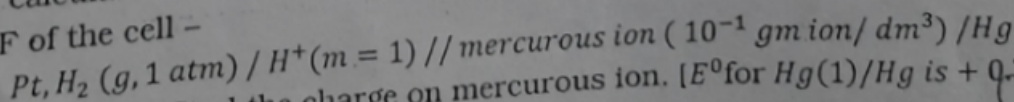
Where the term has usual meaning and n is the number of transferable electrons.

17. Calculate the standard EMF of the cell in which the reaction occurring is:



And also calculate the standard free energy change.

18. The EMF of the cell -

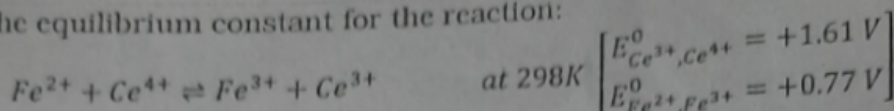


Is 0.770 volt at 25°C Find the charge on mercurous ion. [E^0 for $Hg(1)/Hg$ is +0.799 volt at 25°C

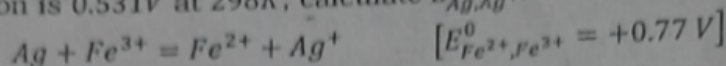
19. Construct the cell for the reaction - $Co + Ni^{2+}(1M) = Co^{2+}(0.1M) + Ni$
 And calculate its EMF at 298K [Given, $E_{Co,Co^{2+}}^0 = -0.288V$, $E_{Ni,Ni^{2+}}^0 = -0.250V$].

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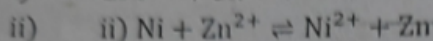
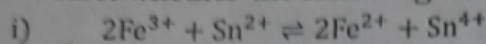
20. Calculate the equilibrium constant for the reaction:



21. K_{eq} for the reaction is 0.531V at 298K, calculate E_{Ag, Ag^+}^0 :



22. Predict whether the following reactions are spontaneous or not -

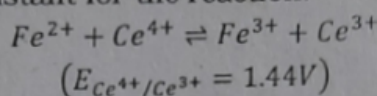


[Given: $E_{Fe^{3+}/Fe^{2+}}^0 = 0.77V$; $E_{Sn^{4+}/Sn^{2+}}^0 = 0.15V$]

[Given: $E_{Ni^{2+}/Ni}^0 = -0.25V$; $E_{Zn^{2+}/Zn}^0 = -0.76 V$]

23. Is Ag will be oxidized, when it is immersed into a solution of $CuSO_4$? [Given: $E_{Cu^{2+}/Cu}^0 = 0.34V$ and $E_{Ag^+/Ag}^0 = 0.80V$]

24. Calculate the equilibrium constant for the reaction:



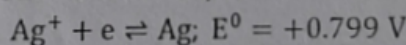
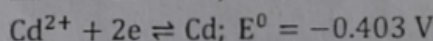
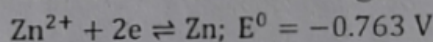
25. Construct different cells from given redox potential data and answer the following -

i) The e.m.f. of this cell.

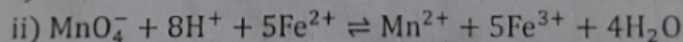
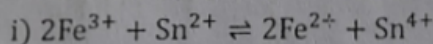
ii) Which electrode will function as anode and which as cathode?

iii) In which way electrons will flow in the outer circuit?

iv) Which one of these three metals is the most reducing in nature?

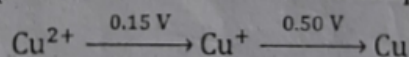


26. Calculate equilibrium constant (K) of the reactions given below -

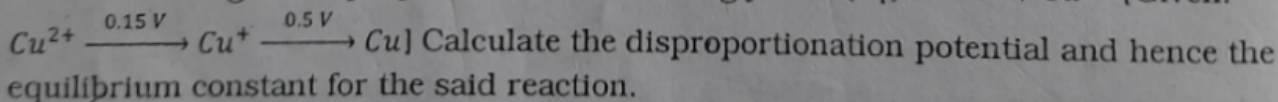


[Given: $E_{Fe^{3+}/Fe^{2+}}^0 = 0.77V$; $E_{Sn^{4+}/Sn^{2+}}^0 = 0.15V$; $E_{MnO_4^-/Mn^{2+}}^0 = 1.51V$]

27. From the following diagram predict whether Cu^+ will disproportionate or not?



28. Define disproportionation and comproportionation reactions. Cu^+ ion in aqueous solution undergoes disproportionation accordingly $2Cu^+(aq) \rightleftharpoons Cu^0 + Cu^{2+}$ [Given:



29. The equilibrium constant for the reaction $Fe^{3+} + Ag \rightleftharpoons Fe^{2+} + Ag^+$ is 0.531 at 298K. Calculate $E_{Ag^+/Ag}^0$. Given: $E_{Fe^{3+}/Fe^{2+}}^0 = 0.77V$.

30. Only positive e.m.f. corresponds to a spontaneous cell reaction. Explain.

31. In aqueous solution containing Fe^{3+} and Fe^{2+} ions, the redox potential is 0.70V at 25°C. Taking the E^0 value of Fe^{3+}/Fe^{2+} couple +0.77volt, calculate the Fe^{3+}/Fe^{2+} ratio in the solution.

32. What happens when I_2 is added to excess aqueous acidic $HClO_3$? Write the half reactions. Predict which net reaction will occur. Given E^0 values for I_2/I^- and ClO_3^-/ClO_2 couples are 0.54 V and -1.20 V respectively. $+1.20 V$

33. What is formal potential? Why is it more important than standard potential?

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