POURBAIX DIAGRAM

- In 1938, Marcel Pourbaix introduced a diagram to account the chemical properties of species present in corrosion system which is useful in corrosion science and environmental science.
- It is a potential (E) - pH diagram or predominance-area diagram.
- It Basically defines the thermal stability of species presence during corrosion under the condition of pH and potential (E).
- Potential is plotted on Y-axis while pH is plotted on x-axis.
- Negative value of potential indicate strong reducing nature while the Possitive value of potential indicate strong oxidising nature.

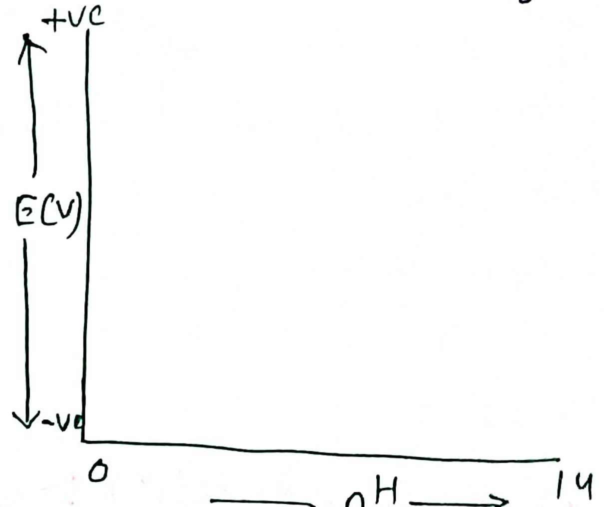

Fig:- A typical Pourbaix diagram

- However, low pH corresponds to strong acid while the high pH corresponds to the strong base.

POURBAIX DIAGRAM OF IRON :- (Most common)

- When iron comes in water the following species exist in the water system i.e., Fe^{3+}, Fe^{2+}, $(Fe(OH)_2$, $Fe(OH)_3$, H_2 & O_2.
- The stability of these species in pH range and potential range is explained using the pourbaix diagram taking the examples of following reactions.

(I) Reduction of $Fe^{3+}(aq)$ to $Fe^{2+}(aq)$:→ (line AB)

- The conversion occurs as —

$$\underbrace{Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}}_{\text{Reduction}} \quad E° = +0.77\ V$$

(Redox reaction)

- It is a Reduction reaction and no H^+ ion is produced or consumed, hence this reaction does not depends on pH (So remains parallel to x-axis).
- It means on increasing pH no reaction.
- It also serve as boundary, above which Fe^{3+} dominates (more stable), below which Fe^{2+} dominate (more stable).

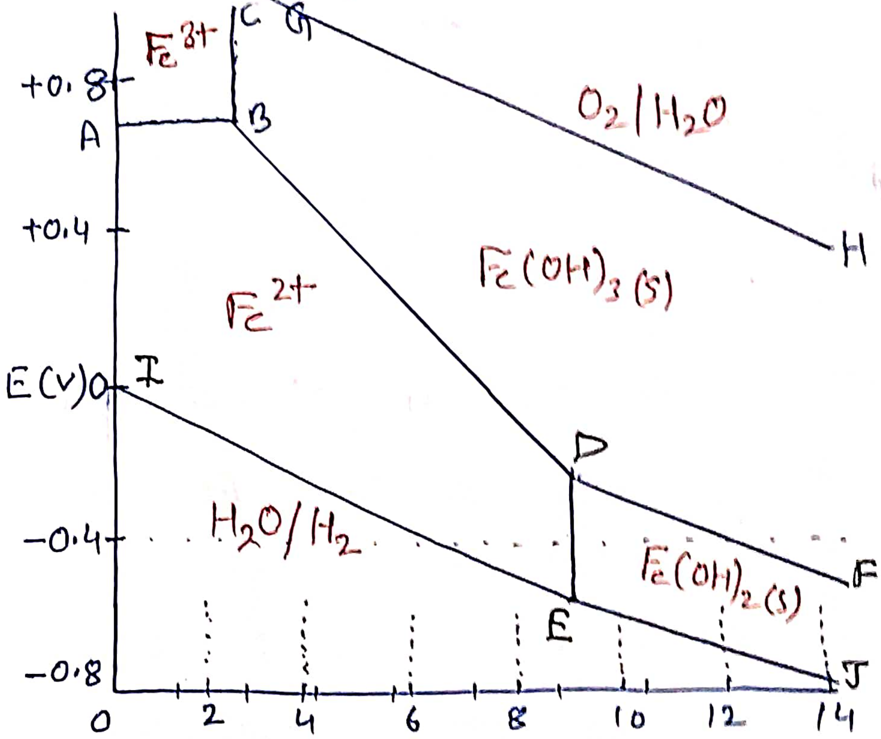

Fig:- Pourbaix diagram for iron species

(II) Acid-base reaction:-

- Reaction between $Fe^{3+}(aq)$ and H_2O is acid-base reaction, and account as H^+ change hence depends on pH, but remains indipendent of potential, hence parallel to y-axis.

$$\underbrace{Fe^{3+}(aq) + 3H_2O(l) \longrightarrow \overset{+3}{Fe}(OH)_3(s)}_{\text{No change}} + 3H^+(aq)$$

(Not a redox reaction)

- Hence in diagram represented by BC line.
- It depends on pH, hence a low pH, $Fe^{3+}(aq)$ favours while at high pH $Fe(OH)_3(s)$ favours.

(iii) Reduction of $Fe(OH)_3(s)$ to $Fe^{2+}(aq)$:-

- The net reaction is given as -

$$Fe(OH)_3(s) + 3H^+ + e^- \longrightarrow Fe^{2+}_{(aq)} + 3H_2O_{(l)}$$

- Since this reaction involves H^+ and e^-, hence combination of redox as well as acid-base reaction.
- The line BD corresponds to the pH and potential dependance of species.
- Left to the BD $Fe^{2+}(aq)$ is major species (stable) while right to the line $Fe(OH)_3(s)$ is major species.

(iv) Reaction; $Fe^{2+}(aq)$ to $Fe(OH)_2(s)$:-

$$Fe^{2+}_{(aq)} + 2H_2O_{(l)} \longrightarrow \overset{+2}{Fe}(OH)_2(s) + 2H^+(aq)$$

- Here in this reaction no involvement of e^-, only H^+ participate hence a typical acid-base reaction so it will be independent of potential or remains parallel to Y-axis.
- Line DE corresponds to the change of $Fe^{2+}(aq)$ to $Fe(OH)_2(s)$.
- Left to the line $Fe^{2+}_{(aq)}$ is major species while right to the line $Fe(OH)_2(s)$ is major species.

(v) Conversion of $Fe(OH)_3(s)$ to $Fe(OH)_2(s)$:-

$$Fe(OH)_3(s) + H^+(aq) + e^- \longrightarrow Fe(OH)_2(s) + H_2O_{(l)}$$

- In this involvement of both $H^+_{(aq)}$ and e^- occurs hence a combination of redox and acid-base both reaction.
- The slaint line DF corresponds to this reaction.
- Above the line $Fe(OH)_3(s)$ is major species while below this line $Fe(OH)_2(s)$ is major species.

NOTE :-

- There are two slaint line GH (upper line) and IJ (lower line).
- These lines indicates the stability of water
- For upper line GH, if E (potential) is more positive favour oxidation, hence water oxidises to the O_2

$$H_2O \longrightarrow O_2$$

- For lower line IJ, if potential value is more negative favours reduction, hence water reduces to the H_2.

$$H_2O \longrightarrow H_2$$

- From Pourbain-diagram it's also clear that all reaction fall within the stability belt of water, hence no any species can oxidise or reduce water.