**Pourbaix diagram**

❑ Usage of thermodynamic theory or in other words the Nernst equation to create potential (E) – pH diagram

❑ This is typically comparable to the composition – temperature diagrams (phase diagrams) which is generally for alloy systems

❑ Both diagrams are guide <u>maps</u>

❑ Pourbaix diagrams are plotted in the axes Electrode potential of the metal vs. pH of the electrolyte

❑ Oxidizing conditions are described by the top part of the diagram (high positive electrode potential)

❑ Reducing conditions are described by the bottom part of the diagram (high negative electrode potential)

❑ Acidic solutions are presented in the left side of the diagram (pH lower than 6)

❑ Alkaline solutions are presented in the right side of the diagram (pH higher than 6)

❑ Pourbaix diagrams are used to determine the corrosion behavior of a metal in water solutions

❑ In other words, the direction of electro-chemical processes and the equilibrium state of the metal at a certain electrode potential in a water solution at a certain value of pH

❑ Normally the Poubaix diagrams are built for the water solutions with the concentrations of metal ions $10^{-6}$M and at the temperature 298K (77ºF/25ºC).

❑ The lines of the diagrams dividing different zones of the equilibrium states are calculated by the Nernst equation

$$E = E^0 - (0.059/n)*lnC_{ion}$$

Where:
$E^0$ - Standard electrode potential, V;
$n$ - number of electrons transferred;
$C_{ion}$ - molar activity (concentration) of ions.

<u>Diagrams have three domains:</u>

❑ **Immunity** – region of <u>thermodynamic</u> stability of the <u>pure</u> metal. Corrosion is <u>thermodynamically</u> impossible

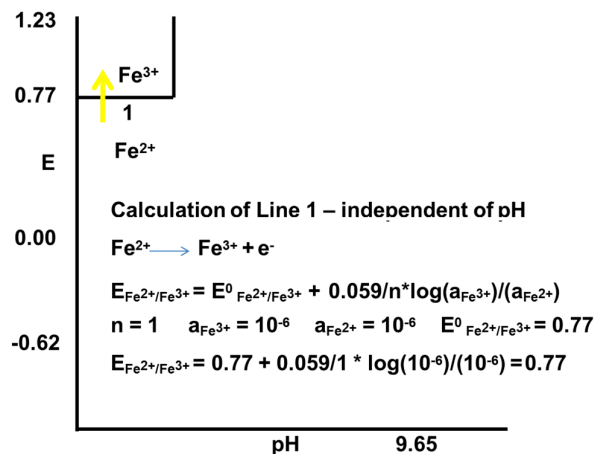❑ **Corrosion** - region of <u>thermodynamic</u> stability of the metal ion and dissolution will occur

❑ **Passivity** - region of <u>thermodynamic</u> stability of the metal oxide. Corrosion is mitigated by the formation of a "passive" protective oxide

**Fe system**
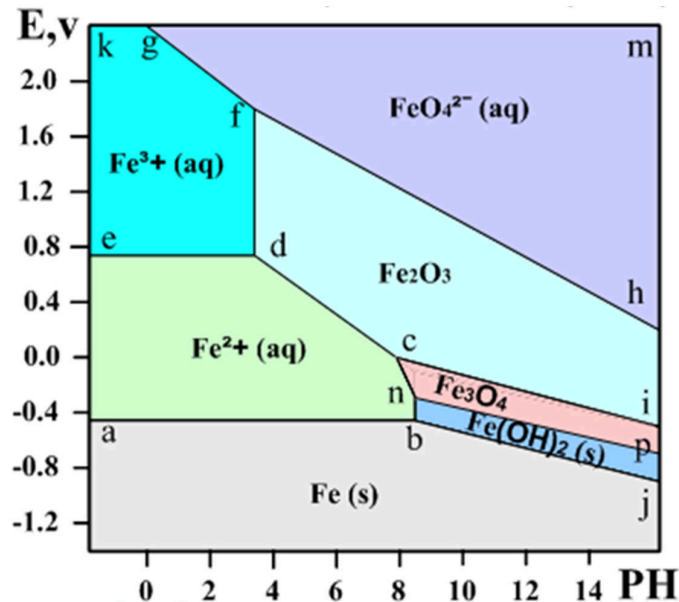


❑ **Areas** in the Pourbaix diagram mark regions where a single species ($Fe^{2+}$(aq), $Fe_3O_4$(s), etc.) is stable. More stable species tend to occupy larger areas.

❑ **Lines** mark places where two species exist in equilibrium.

  ➤ **Pure redox** reactions are **horizontal** lines - these reactions are not pH-dependent

  ➤ **Pure acid-base** reactions are **vertical** lines - these do not depend on potential

  ➤ Reactions that are **both** acid-base and redox have a slope of -0.0592 V/pH x #$H^+$/#$e^-$

**Pourbaix diagram for Fe-$H_2O$ at 25 °C  Line 1**



Calculation of Line 1 – independent of pH

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$E_{Fe2+/Fe3+} = E^0_{Fe2+/Fe3+} + 0.059/n*log(a_{Fe3+})/(a_{Fe2+})$

$n = 1$    $a_{Fe3+} = 10^{-6}$    $a_{Fe2+} = 10^{-6}$    $E^0_{Fe2+/Fe3+} = 0.77$

$E_{Fe2+/Fe3+} = 0.77 + 0.059/1 * log(10^{-6})/(10^{-6}) = 0.77$

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**Four types of reactions:**

❑ **Independent of $H^+$ ions (pH) and E (electrons):**

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

❑ **pH dependent and E independent:**

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$$
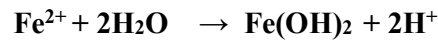
❑ **E dependent and pH independent:**

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

❑ **E and pH dependent**

$$2Fe^{2+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 2e^-$$
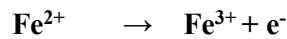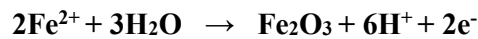
The diagram defines the following zones of the equilibrium states:

❑ **below the line a-b-j**: Solid iron (**immunity zone**). The electrochemical reactions in this zone proceed in the direction of reduction of iron ions. No corrosion occurs in this zone.

❑ **a-b-n-c-d-e**: Aqueous solution of ion $Fe^{2+}$ (**corrosion zone**). Metallic iron oxidizes in this zone.

❑ **e-d-f-g-k**: Aqueous solution of ion $Fe^{3+}$ (**corrosion zone**). Metallic iron oxidizes (corrodes) in this zone.

❑ **h-f-g-m**: Aqueous solution of ion $FeO_4^{2-}$ (**corrosion zone**).

❑ **c-d-f-h-i**: Solid ferrous oxide $Fe_2O_3$ (**passivation zone**). Iron oxidizes (corrodes) in this zone however the resulted oxide film depresses the oxidation process causing **passivation** (corrosion protection of the metal due to formation of a film of a solid product of the oxidation reaction

❑ **n-c-i-p**: Solid oxide $Fe_3O_4$ ($Fe_2O_3*FeO$) (**passivation zone**). The oxide film causes passivation.

❑ **b-n-p-j**: Solid hydroxide (II) $Fe(OH)_2$ / $FeO*nH2O$ / green rust (**passivation zone**).

❑ **Horizontal lines** of the Pourbaix diagrams correspond to the redox reactions which are independent of pH

❑ **Vertical lines** of the Pourbaix diagrams correspond to the non-redox reactions (electrons are not involved), which are dependent on pH

❑ **Diagonal lines** of the Pourbaix diagrams correspond to the redox reactions, which are dependent on PH.

- ❏ Some of the reactions and the corresponding lines of the Fe-$H_2O$ Pourbaix diagram are as follows -

- ❏ **a-b: Fe(s) = Fe$^{2+}$(aq) + 2e$^-$** Redox reaction independent of PH. The equilibrium occurs at the electrode potential value -0.44V, which is equal to the standard electrode potential of iron (see the Electrochemical series

- ❏ **e-d: Fe$^{2+}$(aq) = Fe$^{3+}$(aq) + e$^-$** Redox reaction independent of PH.

- ❏ **d-f: 2Fe$^{3+}$(aq) + 3O$^{2-}$ = Fe$_2$O$_3$(s)** Non-redox reaction dependent on pH

- ❏ **b-n: Fe$^{2+}$(aq) + 2OH$^-$(aq) = Fe(OH)$_2$(s)** Non-redox reaction dependent on pH

- ❏ **c-d: 2Fe$^{2+}$(aq) + 3H$_2$O = Fe$_2$O$_3$(s) + 6H$^+$(aq) +2e$^-$** Redox reaction dependent on pH

- ❏ **b-j: Fe(s) + 2OH$^-$(aq) = Fe(OH)$_2$(s) + 2e$^-$** Redox reaction dependent on pH

**Pourbaix diagram limitations**

- ❏ M-$H_2O$ diagrams present equilibria among metal, metal ions and solid oxides in systems where only metal, water, H$^+$ and OH$^-$ exist. This is not the real world scenario. Missing out on many things…..

- ❏ The diagrams consider pure metals and aqueous solutions at standard conditions ONLY (temperature 298K, pressure 1 bar, ion concentration 10$^{-6}$M).

- ❏ Diagram is based on <u>pure</u> metals, not alloys

- ❏ These equilibrium thermodynamic diagrams reveal nothing concerning corrosion kinetics

- ❏ Criteria for passivity is a concern (e.g., Fe$_2$O$_3$ [rust] is considered passive!)

- ❏ Bulk chemistries are different than chemistries inside a crevice, pit or crack, i.e., the local environment must be considered

**Summary**

<u>Thermodynamic aspects</u>

- ❏ Equilibrium between metals and their environments

- ❏ Corrosion tendency of metals

- ❏ <u>Qualitative</u> picture of what can happen at a given pH and potential (Pourbaix Diagram)

But,

- ❏ Considerations of equilibrium are irrelevant to the study of corrosion rates (that is kinetic aspects is missing)