Pourbaix diagram (stability diagram)

Potential-pH diagrams are also called Pourbaix diagrams after the name of their originator, Pourbaix (1963), a Belgium electrochemist and corrosion scientist. These diagrams represent the stability of a metal as a function of potential and pH. at a particular combination of pH and potential, a stable phase can be determined from the Pourbaix diagram. In such diagrams, the redox potential of the corroding system is plotted on a vertical axis and the pH on a horizontal axis. These diagrams are constructed from calculations based on Nernst equations and solubility data for metal and its species, such as Fe, Fe_2O_3, $Fe(OH)_2$, Fe_3O_4, etc in equilibrium. And we can identify the stability region (immunity, corrosion, and passivity), however these are only indications ;actual rates cannot be derived from the diagrams.
The information in the diagrams can be beneficially used to control corrosion of pure metals in the aqueous environment. By altering the pH and potential to the regions of immunity and passivation, corrosion can be controlled.

Thus, Pourbaix diagrams introduce the concept of the following three states of metals, depending on the potential in the given aggressive medium and the determination of its corrosion behavior: corrosion (active state), passivity (forming passive layers inhibiting the corrosion process on the surface of the metal, including thermodynamically active metals) and immunity (thermodynamic stability) of the metals. Further, it will be shown that these three metal states in aggressive media have a special value when corrosion action by an external current on the metal is considered and when methods and means of protection from electrocorrosion are developed.

Characteristics of a Pourbaix Diagram
1-pH is plotted on the horizontal axis and redox potential E *vs*. SHE on the horizontal axis.
2-The horizontal lines represent electron transfer reactions. They are pH -independent, but potential-dependent.
3-The vertical lines are potential-independent but pH-dependent and not accompanied by any electron transfer.
4-The sloping, straight lines give the redox potentials of a solution in equilibrium with hydrogen and oxygen, respectively. This equilibrium indicates electron transfer as well as pH.
5-The concentration of all metal ions is assumed to be 10- 6 mol per liter of solution. At lower concentration, corrosion should not occur.
6-The diagram is computed for the equilibrium conditions at 25°C.
7-The upper end of the redox potential axis is the noble end and the lower end, the active end, meaning that the oxidizing power increase with increasing potential.
8-The hydrogen and oxygen lines are indicated in Pourbaix diagrams by dotted line.
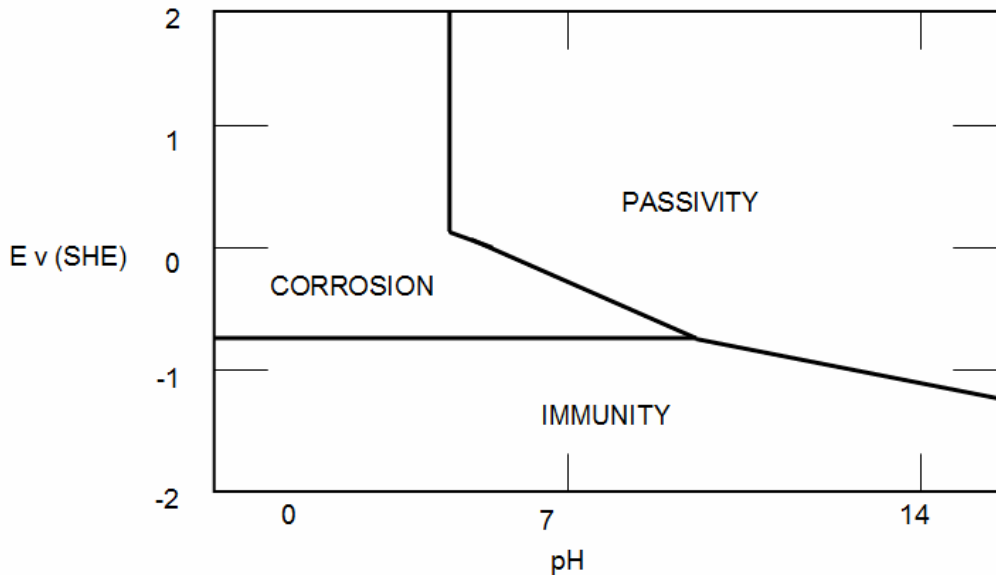
The main objectives of the Pourbaix diagrams are:
1. To show the directions of the various reactions at given pH and potential.
2. To make a basis for estimation of the corrosion product compositions at various pH and potential combinations.
3. To show which environmental pH and potential changes will reduce or prevent corrosion.

Pourbaix for water
Each line of a Pourbaix diagram represents conditions of thermodynamic equilibrium for some reaction. The Pourbaix diagram for water is presented in below figure, above line b, oxygen is evolved in accord with the reaction

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$
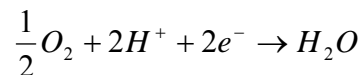
By use the Nernst equation we can write relationship between potential and pH as below

$$E = E^\circ - 2.303\frac{RT}{zF}\log\frac{1}{\left[H^+\right]^2}$$

With E°=1.299 volt, T=298 °K, R=8.134 J/ °K. mol and F=96500 C/ mol we have
$$E = 1.299 - 0.0592\,pH$$

Above line b, defined by this equation, oxygen is evolved at the surface of an immersed electrode. Below this line, water is stable. Below line a, hydrogen is evolved in accord with the reaction : $2H^+ + 2e^- \rightarrow H_2$
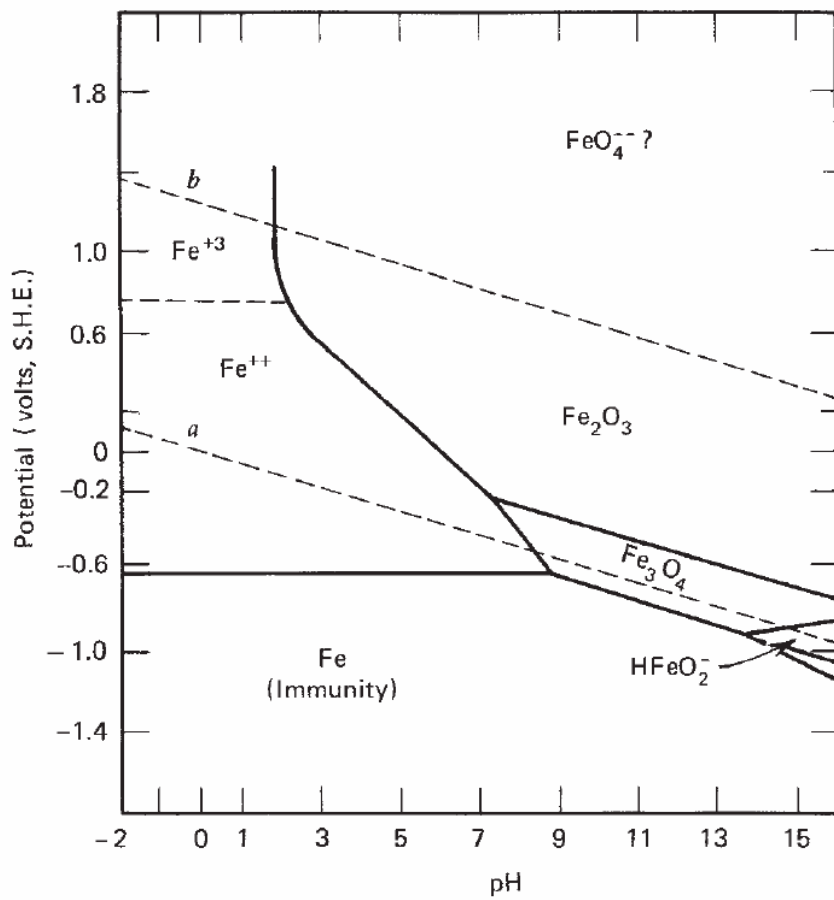
Using the Nernst equation for this equilibrium, the relationship between potential and pH is

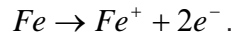$$E = E^\circ - 2.303\frac{RT}{zF}\log\frac{1}{\left[H^+\right]^2} = -0.059\,pH$$

Below line a, represented by this equation, hydrogen gas is evolved from the surface of an immersed electrode. Between lines a, and b, water is stable.
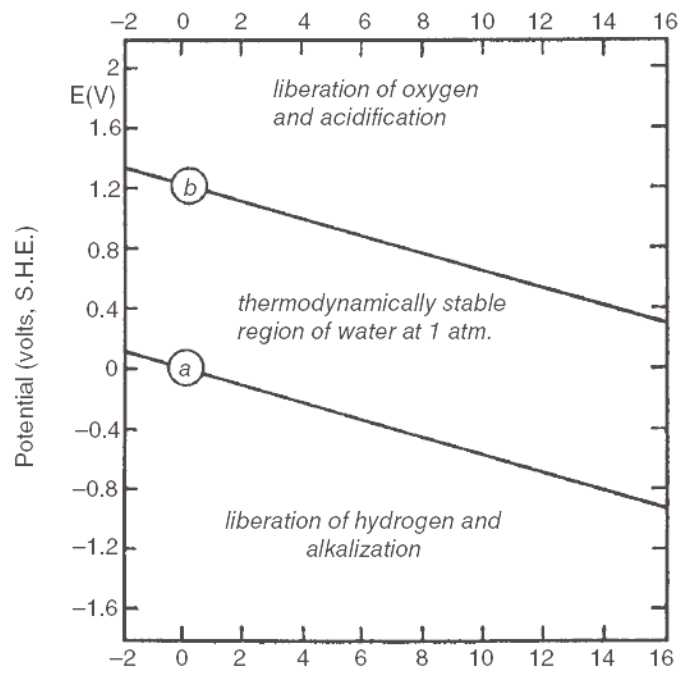
Pourbaix for iron

A horizontal line represents a reaction that does not involve pH; that is, neither H^+ nor OH^- is involved, as in the reaction,
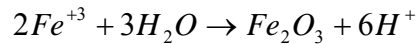
$$Fe \rightarrow Fe^+ + 2e^-.$$

For this equilibrium, using the Nernst equation, we obtain

$$E = E^\circ - 2.303\frac{RT}{zF}\log\frac{1}{\left[Fe^{+2}\right]}$$

If (Fe^{+2}) is taken as $10^{-6}M$, then E= 0.617 V, a horizontal line on the Pourbaix diagram.

A vertical line involves H^+ or OH^- but not electrons; for example,

$$2Fe^{+3} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$$

In above figure , the vertical line separating Fe+3 from Fe2O3 corresponds to this reaction .For this equilibrium we have

$$K = \frac{\left(H^+\right)^6}{\left(Fe^{+3}\right)^2}$$

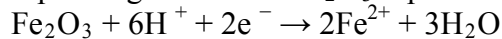$$\log K= 6\log(H^+) - 2\log(Fe^{+3}) = \text{-6 pH -2} \log(Fe^{+3})$$

since $\Delta G^\circ = -RT\ln K$ and $\Delta G^\circ = -8240 J/mole$, we obtain

$$\log K=1.43$$
$$\log(Fe^{+3}) = \text{- 0.72} - 3\text{ pH}$$

Taking (Fe^{+3}) = 10^{-6} M , we obtain pH = 1.76 , and this line at pH= 1.76 represents the equilibrium reaction $2Fe^{+3} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$ .to right of this line Fe_2O_3 is stable phase ; and this oxide as a protective film would be expected to provide some protection against corrosion. To the left of this line (pH<1.76) ferric ions in solution are stable , and corrosion is expected to take place without any protection afforded by a surface oxide film .

A sloping line involves H^+ , OH^- , and electrons. For example, the sloping line separating Fe^{2+} from Fe_2O_3 represents the reaction
$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$
For this reaction, we have

$$E = E^\circ - 2.303\frac{RT}{zF}\log\frac{\left[Fe^{+2}\right]^2}{\left[H^+\right]^6}$$

Since E°= 0.728 v and $z = 2$

$$E = 0.728 - 0.0592(Fe^{+2}) - 0.1776pH$$

Taking (Fe^{+2}) = 10^{-6} M , we obtain

$$E = 1.082 - 0.1776pH$$

This line represents the equilibrium , $Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$.
To the right of this line , Fe_2O_3 is stable phase that is expected to form a surface oxide film that protects the underlying metal from corrosion. To the left of this line Fe^{+2} is a stable species in solution.
The fields marked Fe_2O_3 and Fe_3O_4 are sometimes labeled "passivation" on the assumption that iron reacts in these regions to form protective oxide films. This is correct only insofar as passivity is accounted for by diffusion-barrier oxide layer.

Pourbaix of Aluminum
The pourbaix diagram of aluminum ,indicates that hydrargilite $Al_2O_3.3H_2O$, is the stable phase between about pH 4 and 9 , indeed this film is considered to be responsible for successful use of aluminum in many structural applications. This

diagram also predicts the amphoteric nature of aluminum , with corrosion under highly acidic and highly alkaline conditions and protection by an oxide film
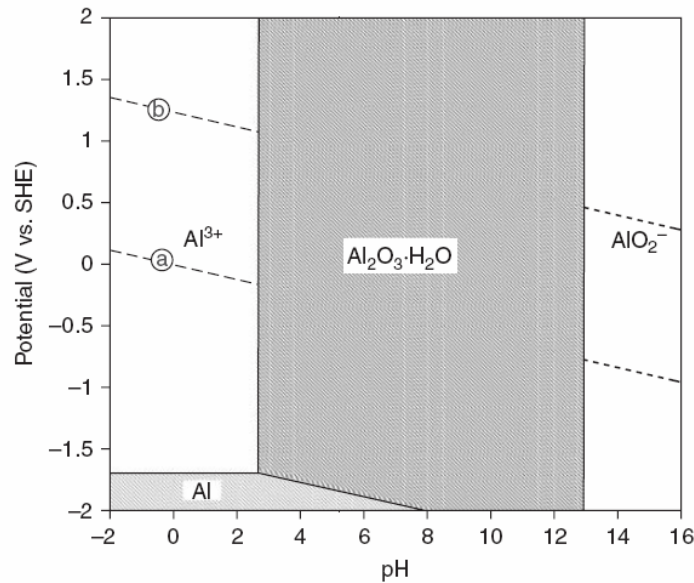
Limitation of Pourbaix diagram
The validity of the diagrams is limited to reactions between pure metals, pure water and the species that can be formed from these. Small amounts of impurities and alloying elements in the metal and dissolved substances in the water do not necessarily influence strongly on the diagram, but in some cases they do.

1-These diagrams are purely based on thermodynamic data and do not provide any information on the reactions.
2-Consideration is given only to equilibrium conditions in specified environment and factors, such as temperature and velocity are not considered which may seriously affect the corrosion rate.
3-The activity of species is arbitrarily selected as 10^{-6} gmol which is not realistic.
4-Pourbaix diagrams deal with pure metals which are not of much interest to the engineers.
5-All insoluble products are assumed to be protective which is not true, as porosity, thickness, and adherence to substrate are important factors

Although the above disadvantages appear to be substantial, the advantages offered by the Pourbaix diagrams far outweigh their limitations