POURBAIX DIAGRAMS

Phase diagrams for corrosion scientists!

Nernst equation again… (different notation)

$$\Delta V = V_2^0 - V_1^0 - \frac{RT}{nF}\ln\frac{[M_1^{n+}]}{[M_2^{n+}]}$$

$\downarrow$

$$\Delta V = \Delta V^0 + \frac{2.3RT}{nF}\log\frac{[M_1^{n+}]}{[M_2^{n+}]}$$

The Pourbaix version

$e = e^0 + \frac{0.059}{n}\ln\frac{[M_1^{n+}]}{[M_2^{n+}]}$ **at 25°C (standard)**

Now pH is defined as pH = -log(H^+)

$\therefore$ for the hydrogen half-cell

- relationship between pH and electropotential

(corrosion susceptibility of a system):

$$e_{H^+/H_2} = e^0_{H^+/H_2} - 0.059\,pH$$

- a simple linear relationship

The basic electrochemical reaction – $2H^+ + 2e^- \rightarrow H_2$ is only valid for low pH values. For wider pH range – need OH- to balance it:

i.e. $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ {a}

However, $e_{H^+/H_2} = e^0_{H^+/H_2} - 0.059\,pH$ **still holds as nothing has formally inbalanced the electrochemical reaction**

so – simple linear relationship for hydrogen production v. pH at all pH values

From {a} – electrochemical evolution of H_2 requires decomposition of H_2O i.e. for water to be thermodynamically unstable

Mechanism:

In an acidic aqueous corrosion system (low pH)
H^+ consumed by $2H^+ + 2e^- \rightarrow H_2$
$\therefore$ H^+ is used up thus increasing pH
increases until {a} is invoked and water consumed

Now, as potential becomes more noble (positive)

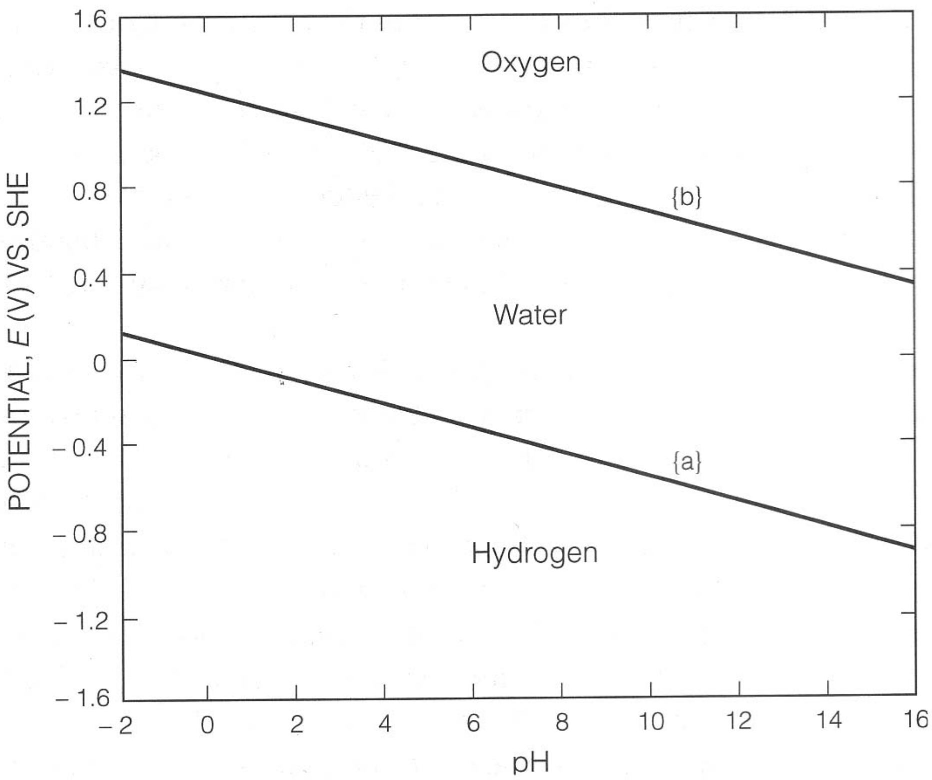
Then
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ becomes thermodynamically more stable

which, at higher pH becomes $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Under standard conditions: $e_{O_2/H_2O} = e^0_{O_2/H_2O} - 0.059\,pH$ **{b}**

again – linear and simple

This gives enough information for a simple Pourbaix diagram



- **below line {a} – water is unstable and must decompose to H_2**
- **above line {a} – water is stable and any H_2 present is oxidised to H^+ or H_2O**
- **above line {b} – water is unstable and must oxidize to give O_2**
- **below line {b} – water is stable and any dissolved O_2 is reduced to H_2O**

3 regions:

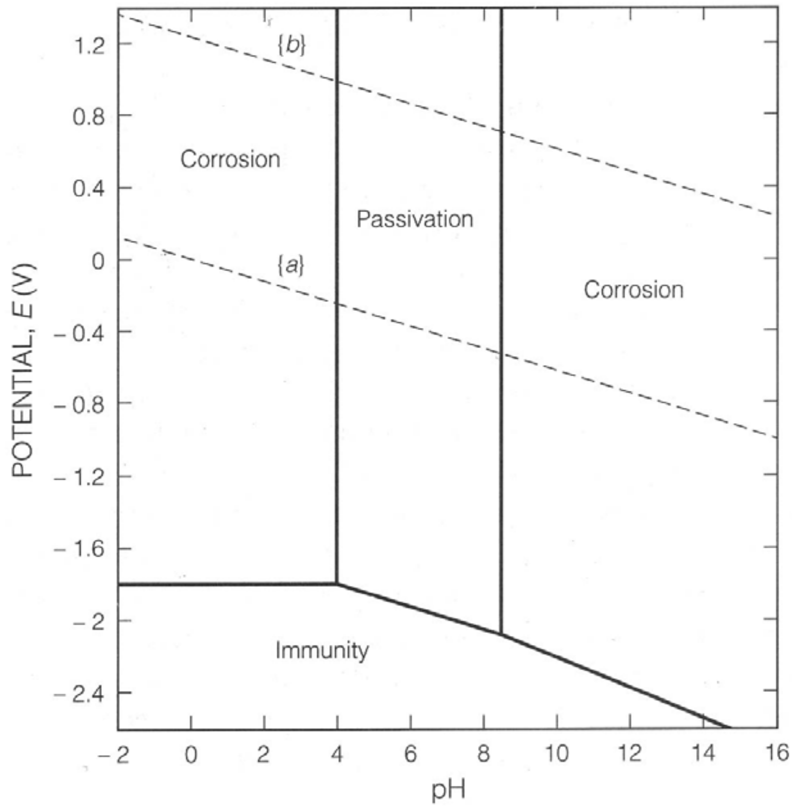
upper: - H_2O electrolysed anodically to O_2
lower: - H_2O electrolysed cathodically to H_2
middle: - H_2O stable and won't decompose

This example – basic oxidation/reduction reactions for aqueous systems

Can be superimposed on a metal one to give a corrosion system!
- will show under what conditions, a metal will corrode

POURBAIX DIAGRAM FOR ALUMINIUM

In aqueous environments:



3 regions: corrosion, passivation, immunity

In regions where:

Al^{+++} is stable	**– corrosion is possible**
aluminium oxide is stable	**– resistance or passivity is possible**
Al is stable	**– thermodynamically immune to corrosion**

Passivity?

Caused by thin hydroxide layer forming on metal surface, protecting the metal from anodic dissolution
However, oxide will itself corrode under certain conditions

Aluminium = *amphoteric* metal = acid and alkali reactions
as does the passive oxide layer

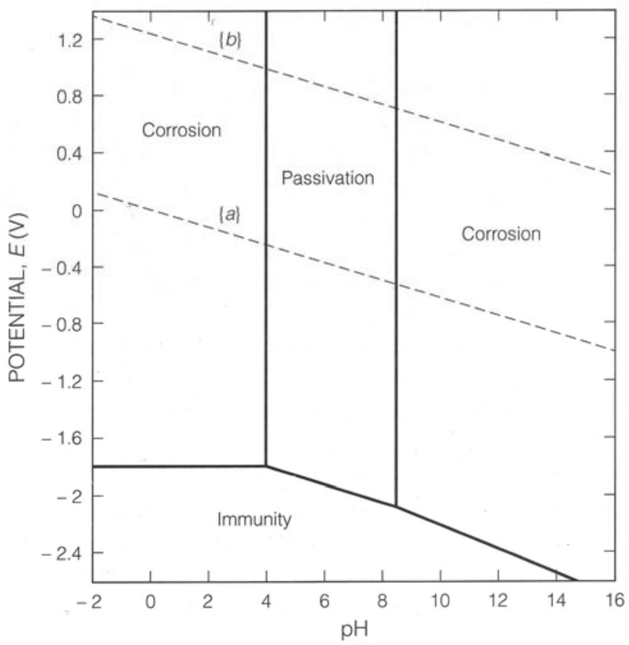
if pH < 4 - Al^{+++} stable
if pH > 8.3 - $Al_2O_2^-$ stable
if 4 < pH < 8.3 - Al_2O_3 stable and thus protects the metal

If the potential is sufficiently low – aluminium itself is immune to corrosion

Boundaries define transition from one stable phase to another

Not fixed – e.g. vary with solubility of Al^{+++} bearing ions

HOW TO READ A POURBAIX DIAGRAM



Vertical lines **– separate species that are in acid/alkali equilibrium**
Non-vertical lines **– separate species at redox equilibrium where:**

horizontal lines separate redox equilibrium species not involving hydrogen or hydroxide ions

diagonal lines separate redox equilibrium species involving hydrogen or hydroxide ions

Dashed lines **enclose the practical region of stability of the aqueous solvent to oxidation or reduction i.e. the region of interest in aqueous systems**

Outside this region, it is the water that breaks down, not the metal

Redox equilibria:

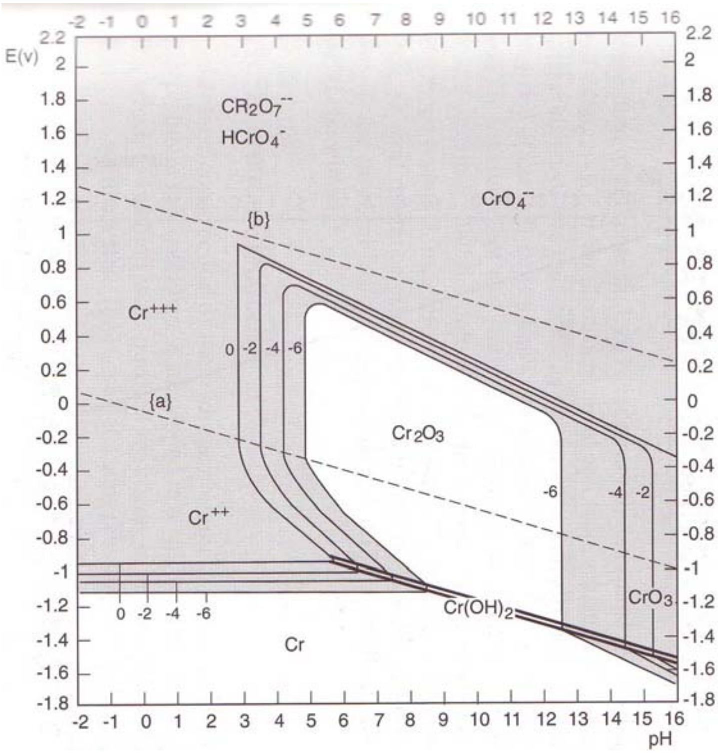
where oxidation and reduction could equally occur and are completely reversible

Any point of the diagram – the most thermodynamically stable (hence, abundant) form of the metal can be found for any given potential or pH

Strong oxidizing agents (forms of the metal) occur at the top of the diagram. Strong reducing agents at the bottom

A species that ranges from the top to the bottom of the diagram at a given pH will have no oxidizing/reducing properties whatsoever at that pH.

e.g chromium



Chromium – reducing agent

Cr_2O_7—(chromate ion) – very strong oxidizing agent

in aqueous environments – Cr not stable

READING TOPICS

Construction of iron and aluminium Pourbaix diagrams (on web site)

Investigate the difference in Pourbaix characteristics between a normal steel and a stainless steel