Chapter (3)

Corrosion Thermodynamics

Sept. 12th , 2017

Thermodynamics:

I. Gibbs Free Energy – van’t Hoff Equation

II. Electrode Potentials (EMF Series and Nernest Equation)

III. Galvanic Series

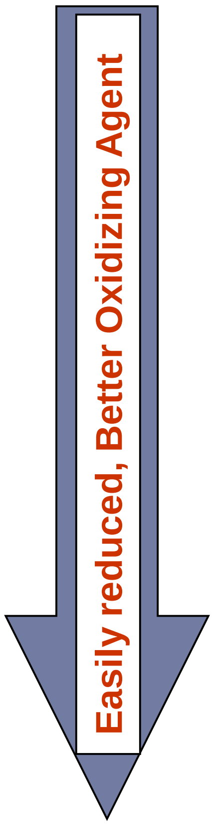
IV. Pourbaix (E-pH) Diagrams

Free Energy

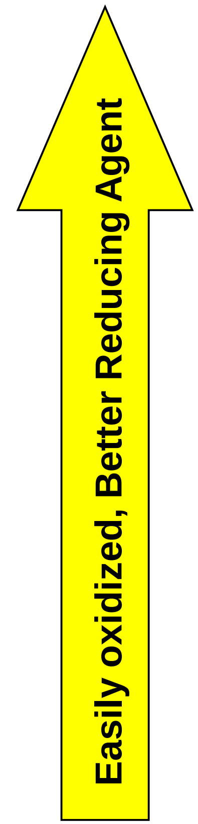
- All interactions between elements and compounds are governed by the free energy changes available to them.
- If individual free energies of species are expressed as G, the net change of energy in a reaction is given by ΔG.
- For a spontaneous reaction to occur, ΔG must be negative.
- Most metals have an inherent tendency to corrode.

Standard Electrode Potentials (EMF series & Nernest Eqn)

As E^o increases → oxidizing ability of half cell reaction increases



Reaction at Interface	Half-cell Potential (E^o)
$Al^{3+} + 3e^- \rightarrow Al$	-1.706 V
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763 V
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.744
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.409V
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.401 V
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.230 V
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126 V
$2H^+ + 2e^- \rightarrow H_2$	0.00 V
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.223 V
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.268 V
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.340 V
$Ag^+ + e^- \rightarrow Ag$	+0.799 V
$Au^+ + e^- \rightarrow Au$	+1.680 V



Electromotive Force Series

	Reaction	Standard Potential, e^o (volts vs. SHE)
Noble	$Au^{3+} + 3e^- = Au$	+1.498
	$Cl_2 + 2e^- = 2Cl^-$	+1.358
	$O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0)	+1.229
	$Pt^{2+} + 3e^- = Pt$	+1.118
	$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$	+0.957
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 7)a	+0.82
	$Ag^+ + e^- = Ag$	+0.799
	$Hg_2^{2+} + 2e^- = 2Hg$	+0.799
	$Fe^{3+} + e^- = Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 14)	+0.401
	$Cu^{2+} + 2e^- = Cu$	+0.342
	$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15
	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	−0.126
	$Sn^{2+} + 2e^- = Sn$	−0.138
	$Ni^{2+} + 2e^- = Ni$	−0.250
	$Co^{2+} + 2e^- = Co$	−0.277
	$Cd^{2+} + 2e^- = Cd$	−0.403
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 7)[a]	−0.413
	$Fe^{2+} + 2e^- = Fe$	−0.447
	$Cr^{3+} + 3e^- = Cr$	−0.744
	$Zn^{2+} + 2e^- = Zn$	−0.762
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 14)	−0.828
	$Al^{3+} + 3e^- = Al$	−1.662
	$Mg^{2+} + 2e^- = Mg$	−2.372
	$Na^+ + e^- = Na$	−2.71
Active	$K^+ + e^- = K$	−2.931

[a]Not a standard state but included for reference.

Source: Handbook of Chemistry and Physics, *71st ed., CRC Press, 1991.*

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

or

$$Zn \rightarrow Zn^{2+} + 2e^-$$

$$2H^+ + 2e^- \rightarrow H_2$$

$$E = e_a + e_c$$

$$E = +0.762 + 0$$

$$E = +0.762V$$

$$\Delta G_o = -nFE_o < 0$$

At standard state, reaction will occur

Electromotive Force Series

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$$3Pb + 2Al^{3+} \rightarrow 3Pb^{2+} + 2Al$$

or

$$Pb^{2+} + 2e^- \rightarrow Pb$$

$$Al^{3+} + 3e^- \rightarrow Al$$

$$E = e_a + e_c$$

$$E = +0.126 + (-1.662)$$

$$E = -1.532V$$

$$\Delta G_o = -nFE_o > 0$$

At standard state, reaction will not occur

Electromotive Force Series

	Reaction	Standard Potential, e° (volts vs. SHE)
Noble	$Au^{3+} + 3e^- = Au$	+1.498
	$Cl_2 + 2e^- = 2Cl^-$	+1.358
	$O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0)	+1.229
	$Pt^{2+} + 3e^- = Pt$	+1.118
	$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$	+0.957
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 7)*a*	+0.82
	$Ag^+ + e^- = Ag$	+0.799
	$Hg_2^{2+} + 2e^- = 2Hg$	+0.799
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Source: Handbook of Chemistry and Physics, *71st ed., CRC Press, 1991.*

The half-cell reaction with the more active (negative) half-cell potential always proceeds as an oxidation.

The reaction with the more noble half-cell potential always proceeds as a reduction in the spontaneous reaction produced by the pair

Electromotive Force Series

	Reaction	Standard Potential, e^0 (volts vs. SHE)
Noble	$Au^{3+} + 3e^- = Au$	+1.498
	$Cl_2 + 2e^- = 2Cl^-$	+1.358
	$O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0)	+1.229
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	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	−0.126
	$Sn^{2+} + 2e^- = Sn$	−0.138
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Question: Is copper (Cu) oxidized (dissolved) by ferric (Fe^{3+}) ions?

Answer: Ferric reduction is more noble relative to copper so copper is oxidized.

Non-Standard Electrode Potential

The **Nernst equation** adjusts for non-standard conditions

e.g. For a reduction potential: $Fe^{2+} + 2\ e^- \rightarrow Fe$

$$E = E^o - \frac{RT}{2F} \ln \frac{[Fe]}{[Fe2+]}$$

at 25°C: $$E = E^o - \frac{0.059}{2} \log \frac{[Fe]}{(Fe2+]}$$

Derivation of Nernst equation from vant't Hoff rquation

- Since ΔG = - nFE , and $\Delta G°$ = - nFE° , then

vant Hoff equation:

$$\Delta G = \Delta G^{o} + RT \ln Q$$

becomes

$$\mathbf{E = E^{0} - 2.303\ (RT/nF)\ log\ Q}$$

- At standard state (298 K),

$$\mathbf{E = E^{0} - (0.059/n)\ log\ Q}$$

which is Nernst equation

Examples of Cases <u>not</u> Predicted by EMF

1. Although iron shows a (–ve) *reduction* potential, it will not corrode if it develops a passive film in certain environments.

2. Although Pb is less noble than hydrogen, Pb does not dissolve in concentrated H_2SO_4 owing to the formation of a protective film of $PbSO_4$ (insoluble salt)

3. Al does not dissolve in concentrated HNO_3 owing to the formation of a protective film of insoluble Al_2O_3.

4. Although Cu and Ag are more noble than hydrogen but they dissolve in KCN with vigorous evolution of H_2 forming the complexes:

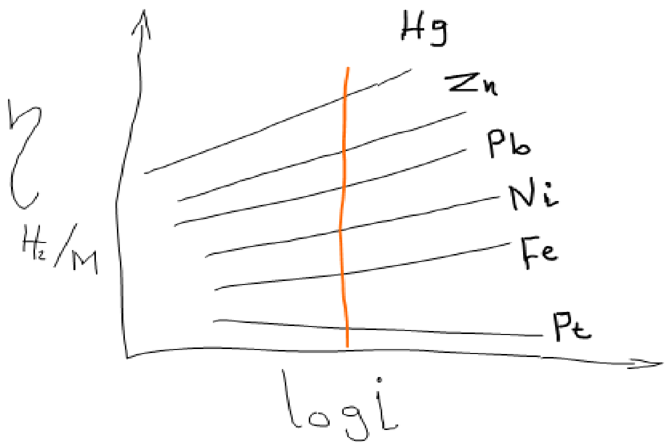
   $K_3\,[Cu(CN)_4]$ and $K\,[Ag(CN)_2]$.

   These complexes have very low ionization constants, e.g Cu^{2+} produced by ionization of copper cyanide complex is extremely small.

   Hence, If we substitute this value in Nernst equation we will find that E_{Cu} is less noble than E_H. Therefore, Cu will dissolve in KCN with H_2 evolution.

Normally in acid media, corrosion (oxidation) of metal occurs coupled with H_2 gas evolution (reduction):

<u>Corrosion reaction takes place if:</u>



$$E_M = E°_M - (0.0592/n) \log [M^{2+}]$$

is less noble than

$$E_{H2} = 0.059 \log [H^+] + \text{activation polarization}$$

Activation polarization means *extra voltage* to allow H_2 gas to evolve from solution at the cathode. This has different values on different metals (see Tafel's equation & plot in the Corrosion Kinetics section).

(e.g. Ecu = -0.1 instead of +0.34 V; *reduction potential*).

Examples of Cases not Predicted by EMF (Cont'd)

5. Although Cu is more noble than hydrogen, it dissolves in HNO_3. In this case, *H_2 plays no role* and the galvanic cell is composed of Cu electrode, and a redox NO_3^- / NO_2^- electrode.

In this cell, the potential of Cu electrode is less noble than the potential of the redox electrode:

The galvanic cell: $Cu / Cu^{2+} // NO_3^- / NO_2^-$

Anode reaction: $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode reaction: $3H^+ + NO_3^- + 2e^- \rightarrow HNO_2 + H_2O$

Accordingly, corrosion will take place with the reduction of the NO_3^- ions to NO_2^- ions instead of H_2 evolution.

(nitrate ions are easier to reduce than hydrogen ions)

Application of EMF Series in Corrosion Science

- Characteristics:
  1. Metals with large +ve E° (reduction) are noble (e.g. Au, Pt, Ag).
  2. Hydrogen is a reference point between more noble & less noble metals.
  3. Metals with large -ve E° (reduction) are active (e.g. Mg, Al, Zn).
  4. E° is a thermodynamic value. It does not consider process kinetics.

Application of EMF Series in Corrosion Science

- Useful Information:

1. Gives indication about tendency of a metal to spontaneously dissolve.
2. Indicates metals with high corrosion resistance in aqueous media (*used to guide materials selection*).
3. Relative tendencies for corrosion; e.g. Mg oxidizes more easily than Zn.
4. Relative tendencies for reduction; e.g. Ag reduced more easily than Cu.
5. Less noble (active, e.g. Zn) will displace more electro noble (e.g. Cu) in their solutions:

$$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$$

Application of EMF Series in Corrosion Science

- Limitations:

1. EMF lists pure metals only. Alloys not included although of major interest in engineering practice.
2. EMF series is based on standard potentials while real corrosion problems occur in ***non-standard*** environments.
3. EMF indicates possibility of metal corrosion but <u>does not confirm</u> if corrosion will actually take place.
4. EMF cannot predict the effect of environment.

TABLE 22-2 ■ *The galvanic series in seawater*

Anodic	Magnesium and Mg alloys	Anodic	Lead
	Zinc		Tin
	Galvanized steel		Cu-40% Zn brass
	5052 aluminum		Nickel-based alloys (active)
	3003 aluminum		Copper
	1100 aluminum		Cu-30% Ni alloy
	Alclad		Nickel-based alloys (passive)
	Cadmium		Stainless steels (passive)
	2024 aluminum		Silver
	Low-carbon steel		Titanium
	Cast iron		Graphite
	50% Pb-50% Sn solder		Gold
	316 stainless steel (active)	Cathodic	Platinum

After ASM Metals Handbook, *Vol. 10, 8th Ed., 1975.*

- PASSIVE – will not corrode – act as cathode. These elements are least likely to give up electrons!
- ACTIVE – will corrode – act as anode. These elements most likely to give up electrons!

Galvanic Series & Corrosion

- **Characteristics:**
  - Metals and alloys are listed according to their relative positions of nobility.
  - Series is based on <u>practical measurement</u> of corrosion potential, E_{CORR} at equilibrium (see Figures next).

- **Useful Information:**
  - Alloys close to each other in the series (e.g. monel & bronze) can be coupled <u>without</u> being corroded.
  - Alloys far from each other in the series (e.g. brass & plated tin) will form a galvanic corrosion cell.
  - Some alloys, particularly stainless steel are present in two places: active and passive (with oxide film). Joining active and passive alloys may lead to galvanic corrosion in a favorable environment.

- **Limitations:**
  - Each environment requires its own Galvanic series (e.g. seawater, acid, alkali, etc.).
  - Position in Galvanic series may not be sufficient to predict corrosion. Galvanic corrosion depends also on polarization of metal in alloy.

Cell for Practical Measurement of Corrosion Potential

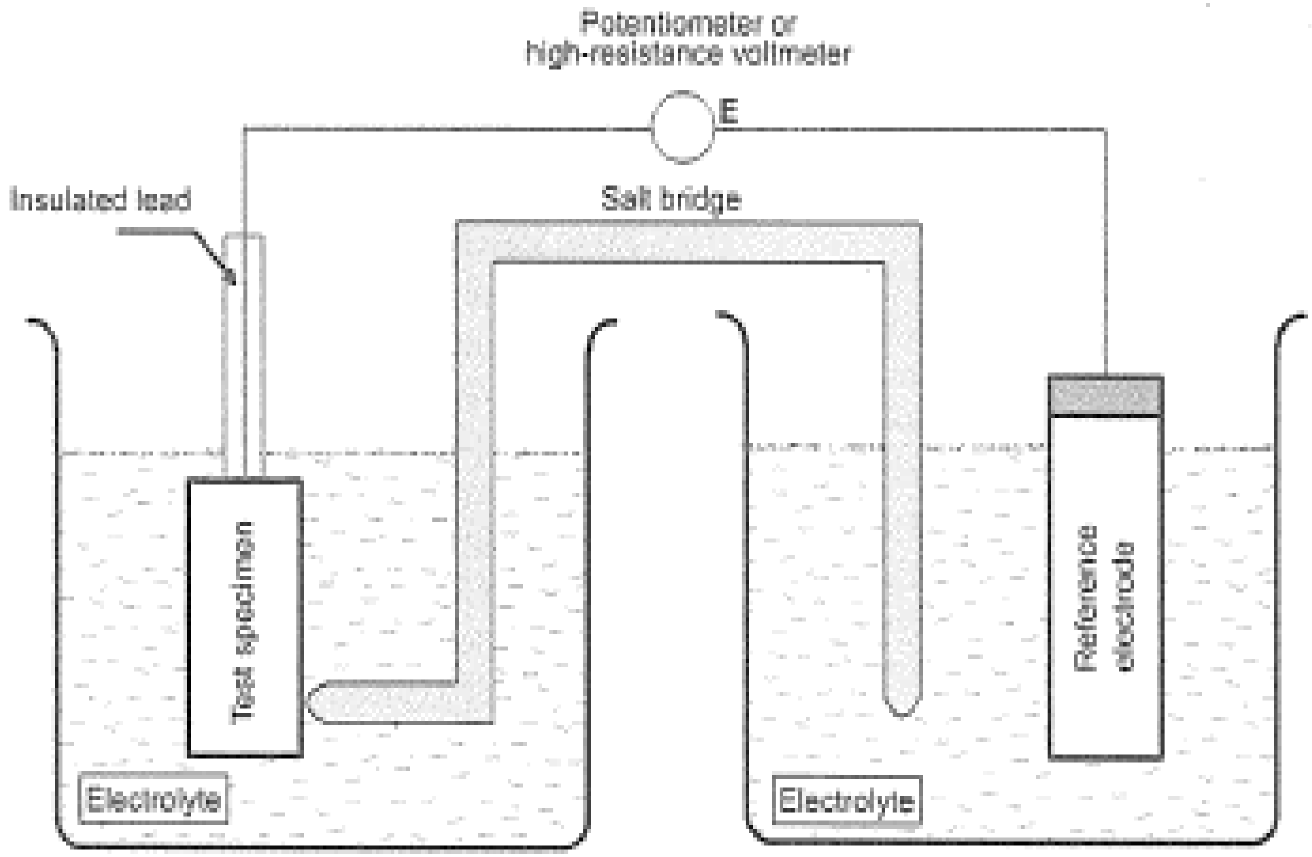


Figure 2.17 Laboratory technique for measuring the single electrode (corrosion) potential E_{corr} of metals and alloys in aqueous environments. Use of salt bridge

Reference Electrodes Used in Practical Measurement of Corrosion Potential

TABLE 2.2 Potential Values for Common Secondary Reference Electrodes. Standard Hydrogen Electrode included for reference.

Name	Half-Cell Reaction	Potential V vs. SHE
Mercury-Mercurous Sulfate	$HgSO_4 + 2e^- = Hg + SO_4^{2-}$	+0.615
Copper-Copper Sulfate	$CuSO_4 + 2e^- = Cu + SO_4^{2-}$	+0.318
Saturated Calomel	$Hg_2Cl_2 + 2e^- = 2Hg + 2Cl^-$	+0.241
Silver-Silver Chloride	$AgCl + e^- = Ag + Cl^-$	+0.222
Standard Hydrogen	$2H^+ + 2e^- = H_2$	+0.000

The Electrode Potential in Electrochemical Cells

- Electrode potential - Related to the tendency of a material to corrode. The potential is the voltage produced between the material and a standard electrode.
- emf series - The arrangement of elements according to their electrode potential, or their tendency to corrode.
- Nernst equation - The relationship that describes the effect of electrolyte concentration on the electrode potential in an electrochemical cell.
- Faraday's equation - The relationship that describes the rate at which corrosion or plating occurs in an electrochemical cell.

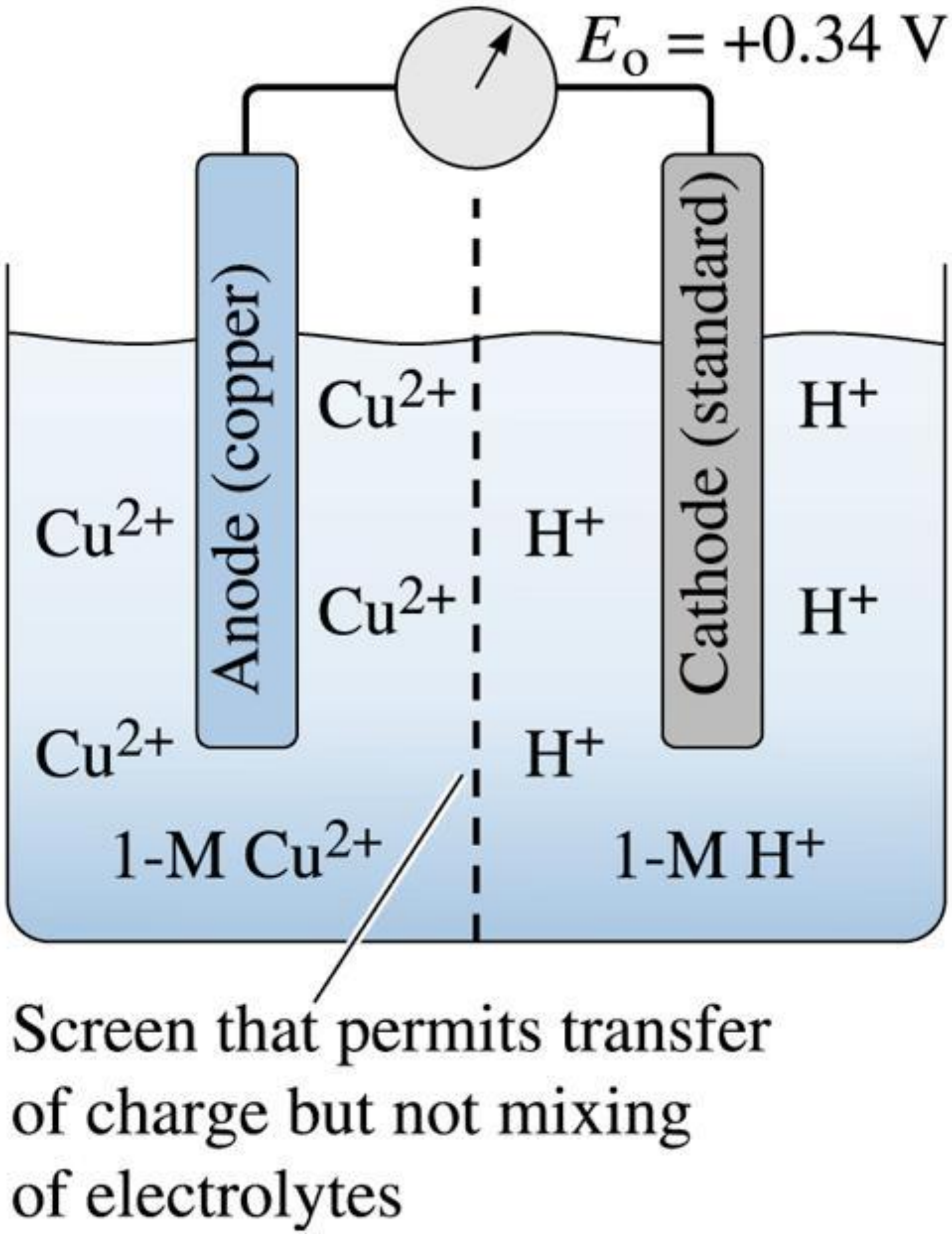


Figure 22.5 The half-cell used to measured the electrode potential of copper under standard conditions. The electrode potential of copper is the potential difference between it and the standard hydrogen electrode in an open circuit. Since E_0 is great than zero, copper is cathodic compared with the hydrogen electrode.

TABLE 22-1 ■ ***The electromotive force (emf) series for selected elements and reactions***

		Metal	Electrode Potential E_0 (Volts)
Anodic	↑	$Li \rightarrow Li^{+} + e^{-}$	−3.05
		$Mg \rightarrow Mg^{2+} + 2e^{-}$	−2.37
		$Al \rightarrow A^{3+} + 3e^{-}$	−1.66
		$Ti \rightarrow Ti^{2+} + 2e^{-}$	−1.63
		$Mn \rightarrow Mn^{2+} + 2e^{-}$	−1.63
		$Zn \rightarrow Zn^{2+} + 2e^{-}$	−0.76
		$Cr \rightarrow Cr^{3+} + 3e^{-}$	−0.74
		$Fe \rightarrow Fe^{2+} + 2e^{-}$	−0.44
		$Ni \rightarrow Ni^{2+} + 2e^{-}$	−0.25
		$Sn \rightarrow Sn^{2+} + 2e^{-}$	−0.14
		$Pb \rightarrow Pb^{2+} + 2e^{-}$	−0.13
		$H_2 \rightarrow 2H^{+} + 2e^{-}$	0.00
		$Cu \rightarrow Cu^{2+} + 2e^{-}$	+0.34
		$4(OH)^{-} \rightarrow O_2 + 2H_2O + 4e^{-}$	+0.40
		$Ag \rightarrow Ag^{+} + e^{-}$	+0.80
		$Pt \rightarrow Pt^{4+} + 4e^{-}$	+1.20
		$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-}$	+1.23
Cathodic	↓	$Au \rightarrow Au^{3+} + 3e^{-}$	+1.50

Example: Half-Cell Potential for Copper

Suppose 1 g of copper as Cu^{2+} is dissolved in 1000 g of water to produce an electrolyte. Calculate the electrode potential of the copper half-cell in this electrolyte.

SOLUTION

From chemistry, we know that a standard 1-M solution of Cu^{2+} is obtained when we add 1 mol of Cu^{2+} (an amount equal to the atomic mass of copper) to 1000 g of water. The atomic mass of copper is 63.54 g/mol. The concentration of the solution when only 1 g of copper is added must be:

$$C_{\text{ion}} = \frac{1}{63.54} = 0.0157 \text{ M}$$

From the Nernst equation, with $n = 2$ and $E_0 = +0.34$ V:

$$E = E_0 + \frac{0.0592}{n} \log(C_{\text{ion}}) = 0.34 + \frac{0.0592}{2} \log(0.0157) = 0.29 \text{ V}$$

Pourbaix Diagrams

- A Pourbaix diagram provides information about the stability of a metal as a function of pH and potential. These diagrams are available for over 70 different metals. Pourbaix diagrams have several uses, including in corrosion studies.

- A Pourbaix diagram is also known as a potential / pH diagram or E-pH diagram.

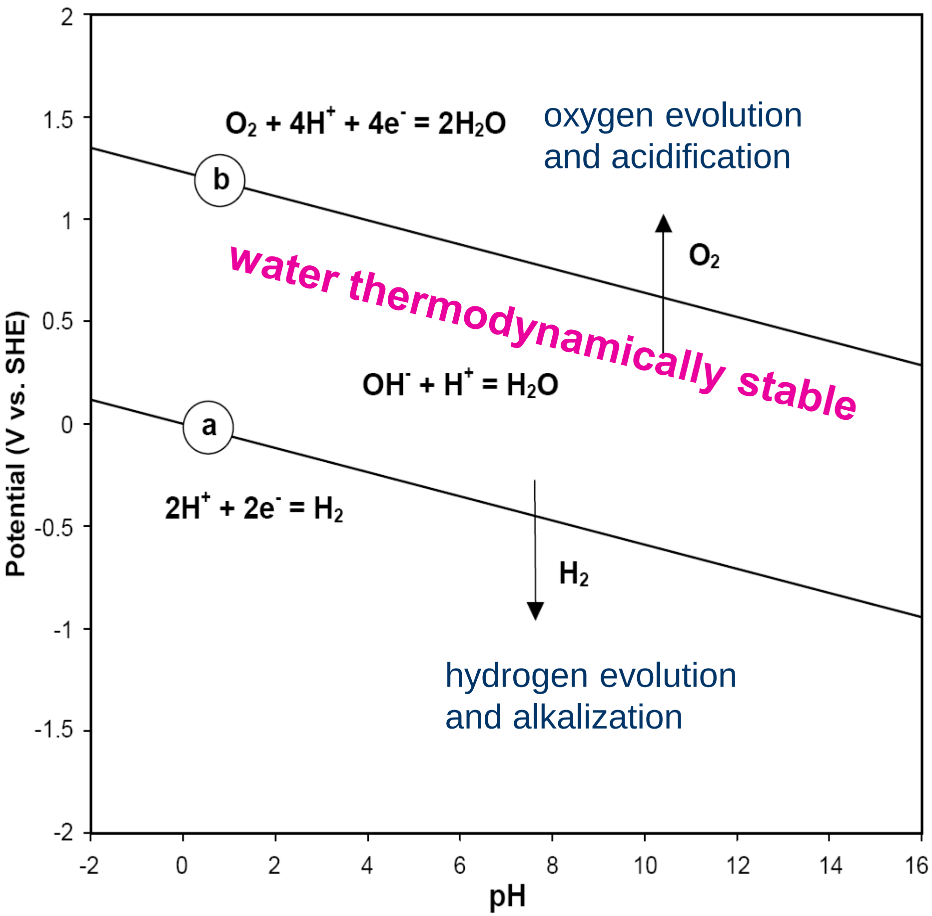
LINES:

1. below line {a} – water is unstable and must decompose to H2.
2. above line {a} – water is stable and any H2 present is oxidised to H+ or H2O.
3. above line {b} – water is unstable and must oxidize to give O2.
4. below line {b} – water is stable and any dissolved O2 is reduced to H2O.

Three Regions:

1. upper: H2O electrolyzed anodically to O2
2. lower: H2O electrolyzed cathodically to H2
3. middle: H2O stable and won't decompose.

Pourbaix (or Stability) Diagrams



For hydrogen evolution at a fixed potential

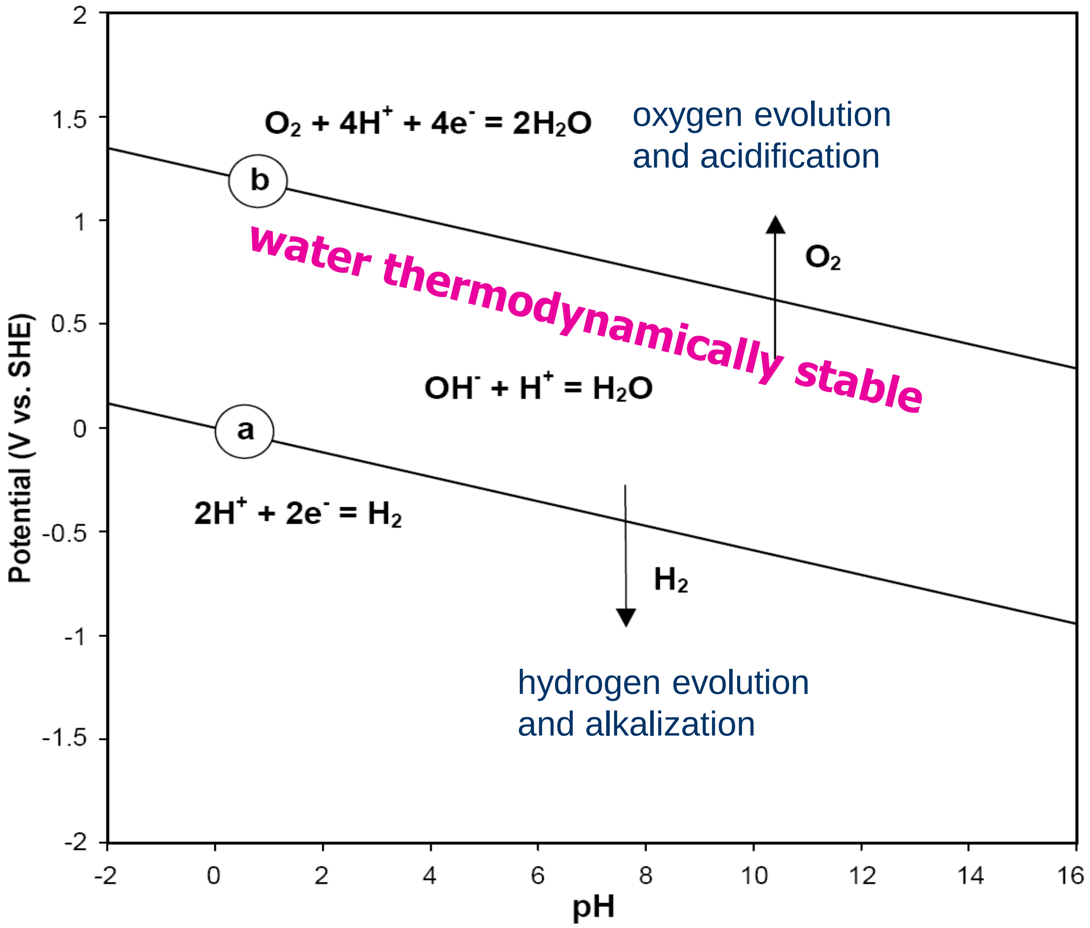
$$2H^+ + 2e^- = H_2$$

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

as pH increases (H^+ concentration decreases), it is less likely to form H_2 gas

Note that, consistent with the half-cell potential definitions, the **hydrogen line** goes through zero potential at zero pH

Pourbaix (Stability) Diagram for water



At higher potential

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Oxygen absorption is feasible

$$e_{O_2/H_2O} = e^0_{O_2/H_2O} - 0.059\,pH$$

Note that, consistent with the half-cell potential definitions, the **oxygen line** goes through 1.229V at zero pH and 0.401V at pH=14. This reaction is the basis for water electrolysis

Role of Oxygen in Metal Corrosion

From kinetic considerations, the oxygen content will be an important factor in determining corrosion rates.

The oxygen content of water is usually minimal, since the solubility of oxygen in water decreases with increasing temperature (see Figure), and any oxygen remaining in the water is consumed over time by the cathodic corrosion reaction.

Typically, oxygen concentrations stabilize at very low levels (around 0.3 ppm), where the cathodic oxygen reduction reaction is hindered and further corrosion is negligible.

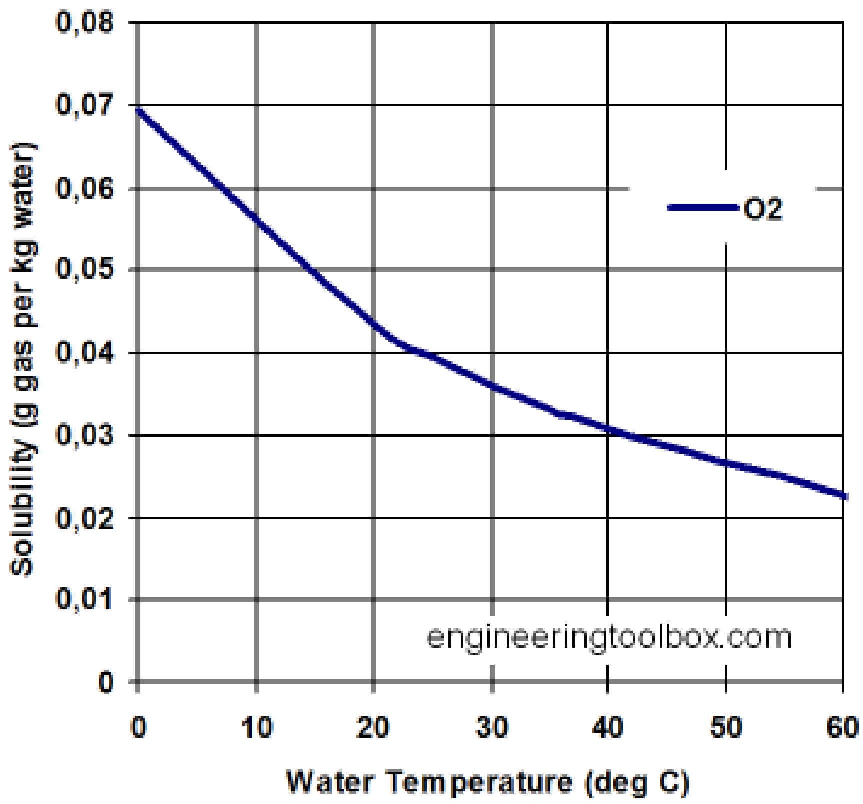


Figure
Solubility of oxygen in water in equilibrium with air at different temperatures.

Pourbaix (or Stability) Diagram for Water

- Sloping straight lines (a,b) give redox potentials of solution in equilibrium with O_2 and H_2 gases, respectively.

- This diagram has special relevance to electro-chemical corrosion of metals.
  - Metals less noble than hydrogen in the EMF series undergo oxidation (corrosion) by reducing H^+ ions in water.
  - The reduction of H^+ or absorption of oxygen occur on the corroding metal surface.

Pourbaix Diagram for Fe: Regions

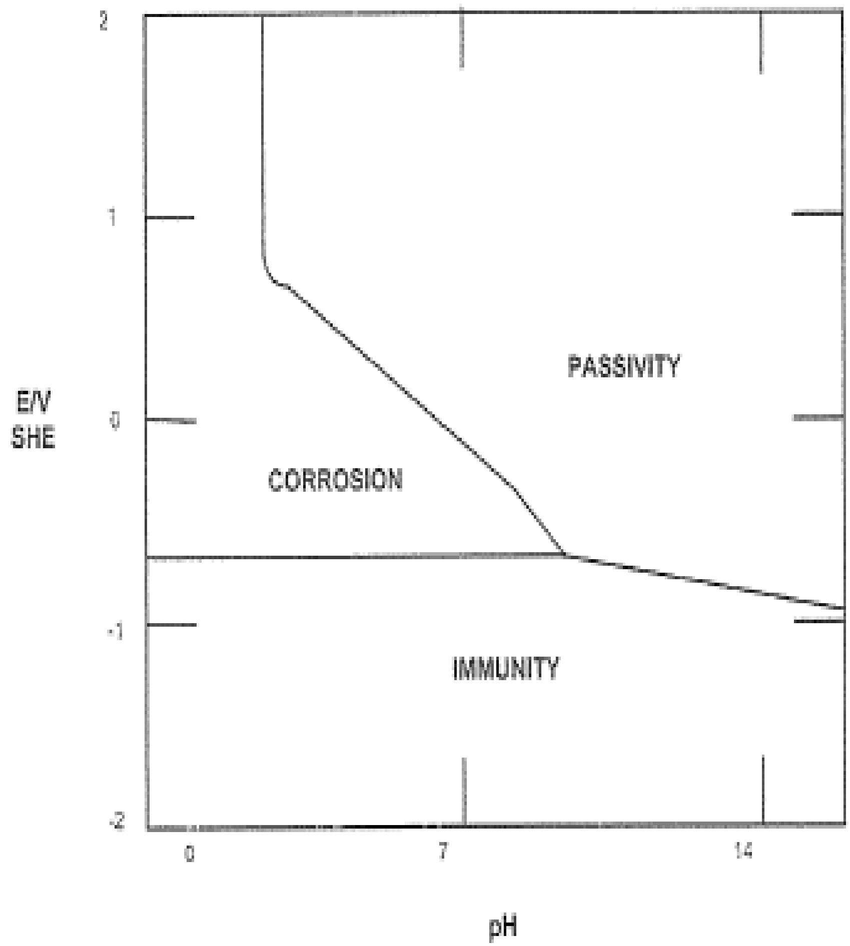


Figure 2.20 Pourbaix diagram for the iron–water system at 25°C showing nominal zones of immunity

1. Corrosion: Soluble ions of the metal are stable

2. Passivation: Oxides are stable

3. Immunity: Reduced form of the metal is stable

Conditions / factors:

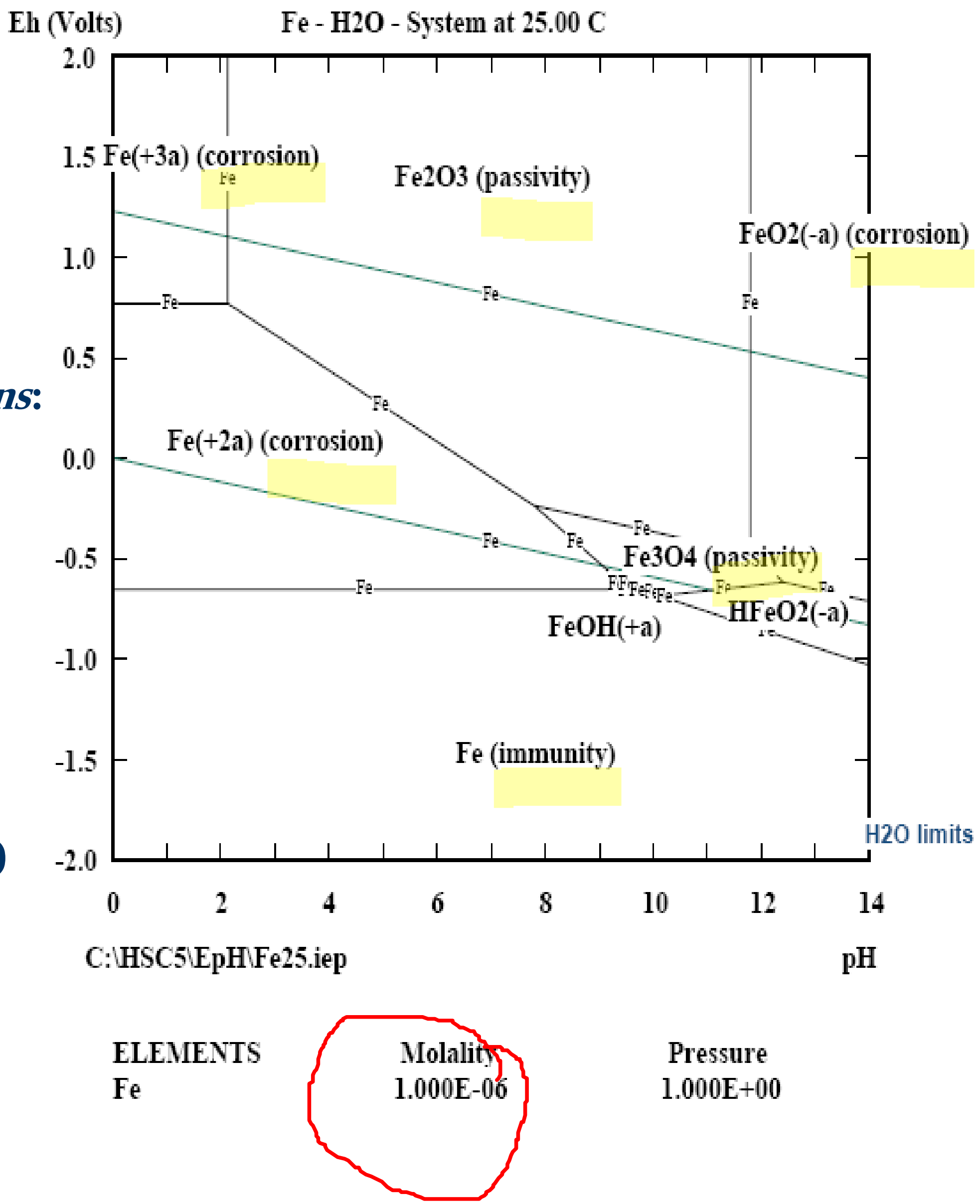
T, % Composition, solubility of metal species, actual Nernst potentials

Detailed Pourbaix Diagram for Iron (Fe)

- **Horizontal lines:** reactions are *involved with electrons (potential), but independent of pH:*
  $Fe^{2+}=Fe^{3+}+e$
  $E_e=0.771+0.0591\cdot\log(a_{Fe}{}^{3+}/a_{Fe}{}^{2+})$
  $Fe=Fe^{2+}+2e$
  $E_e=0.771+0.0591\cdot\log(a_{Fe}{}^{2+}/a_{Fe})$

- **Vertical lines:** reactions are *involved with pH, but independent of electrons*:
  $Fe^{3+}+H_2O=FeOH^{2+}+H^+$
  $\log(a_{FeOH}{}^{2+}/a_{Fe}{}^{3+})=-2.22+pH$
  $Fe^{2+}+2H_2O=Fe(OH)_2+2H^+$
  $\log(a_{Fe}{}^{2+})=13.37-2pH$

- **Diagonal lines:** reactions are *involved both pH and electrons*:
  $Fe^{2+}+H_2O=FeOH^{2+}+H^++e$
  $E_e=0.877-0.0591pH+0.0591\cdot\log(a_{Fe(OH)}{}^{2+}/a_{Fe}{}^{2+})$
  $Fe^{2+}+3H_2O=Fe(OH)_3+3H^++e$
  $E_e=0.748-0.1773pH-0.0591\cdot\log a_{Fe}{}^{2+}$
  $Fe+2H_2O=Fe(OH)_2+2H^++2e$
  $E_e=-0.045-0.0591pH$



NOTES:

1. Pourbaix diagrams may be constructed for any metal.
2. Pourbaix diagrams can be complex. This is because there are many reactions that can be considered.
3. For corrosion considerations, a metal ion concentration of 10^{-6} M (10^{-6} mol/L) is considered as indicative of conditions that apply in the liquid film next to the metal surface with no extraneous source of those ions. Most Pourbaix diagrams consider this concentration for corrosion.
4. Limitations of Pourbaix Diagrams:
    1. Tell us what can happen, not necessarily what will happen
    2. No information on rate of reaction
    3. Can only be plotted for pure metals and simple solutions, not for alloys