



## Outline

- Corrosion - *Introduction*
- Corrosion of Metals
  - e.g. *Rusting of iron in water*
- Electrochemical Cell
- Electrode Potential in Electrochemical Cell
- Standard Electromotive Force
- Example
- Relative Corrosion Potential
- Oxidation or Dry Corrosion
- Degradation of Polymers



## CORROSION of Metals

### ISSUES TO ADDRESS...

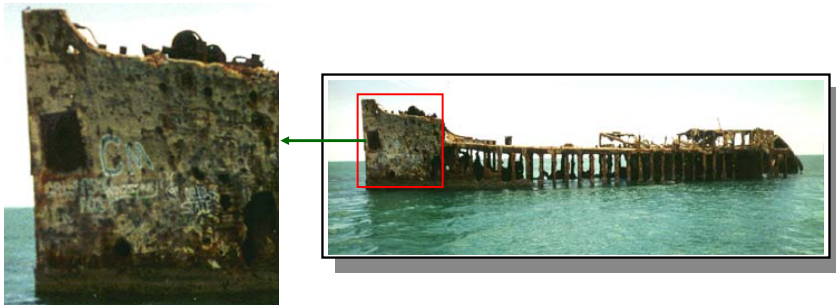
- **Why does corrosion occur?**
- **What metals are most likely to corrode?**
- **How do temperature and environment affect corrosion rate?**
- **How do we suppress corrosion?**



## CORROSION

### • Corrosion:

Is the destruction of a material due to electrochemical attack from the environment.



### • Cost:

- 4 to 5% of the Gross National Product (GNP)
- 2.5 trillion USD global cost of corrosion – *2016 estimate*
- In USA, this amount is about \$400 billion/yr



## CORROSION

### • Corrosion depends on:

- chemicals present
- type of material (metal, ceramic, polymer)
- temperature
- exposure time
- stress .... etc

### Type of material and corrosion

#### • Metals

- *tend to dissolve (Corrosion)*
- *form non-metallic film (Oxidation)*

#### • Ceramics

- *relatively inert, but under certain conditions corrosion may occur.*

#### • Polymers

- *may dissolve in solvents, swell, UV - degradation.*



## CORROSION OF METALS

- Most metals naturally occur as ceramics, (oxides, sulphides etc).
- Metal is extracted from ore (using considerable energy), and then used as metal or alloy.
- But as metals are usually in higher energy state, **more favourable** energetically, to reform **oxides** etc.

Occasionally corrosion process is useful:

- aluminum oxide (*anodizing*)
- etching of microstructures.
- dry-cell batteries



BUT usually it is **undesirable**



## CORROSION OF METALS

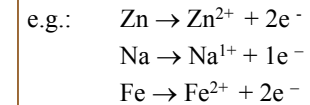
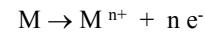
Corrosion of metals takes place through ..... process where:

- **Oxidation - reduction** processes take place and metal atoms lose electrons (become ions) and go into solution.

Often occurs in aqueous medium where moisture can provide electrical circuit to form an **electrochemical cell**.

**OXIDATION REACTION** (*occurs at the ANODE*) - Corrosion (dissolving)

Metals → Ions



*i.e. Metal anode dissolves.*

Electrons transferred to another chemical reaction - Reduction



## CORROSION OF METALS

**REDUCTION reactions** (occur at the cathode - Cathodic Reaction)

• These depend on what is available:

- ✓ If  $H^{+}$  ions are available then:  $2H^{+} + 2e^{-} \rightarrow H_2$
- ✓ If acid solution with dissolved oxygen:  $O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$
- ✓ If basic/neutral with dissolved oxygen:  $O_2 + 2H_2O + 4e^{-} \rightarrow 4(OH^{-})$

• If some metal ions are present they may be reduced by the electrons:



Can get more than one of these occurring at the same time



## CORROSION OF METALS

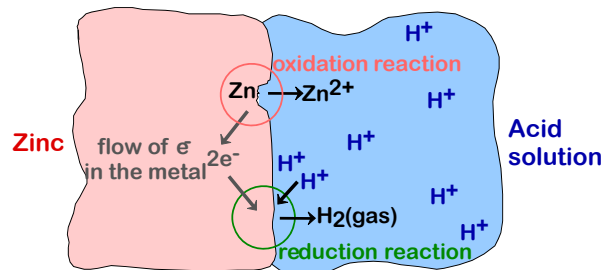
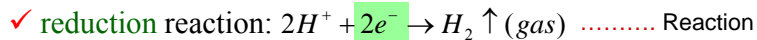
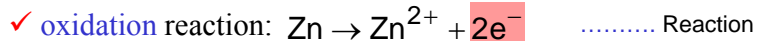
The overall electrochemical reaction consists of at least one oxidation reaction (half-reaction) and at least one reduction half-reaction.

Total oxidation = total reduction (charge balance)

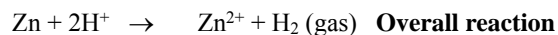


## CORROSION OF ZINC IN ACID

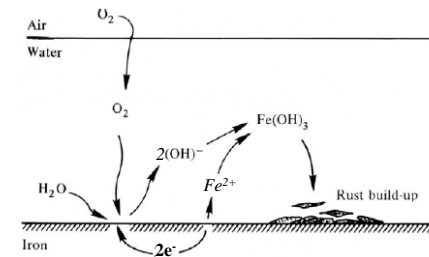
Two reactions are necessary:



Added together:

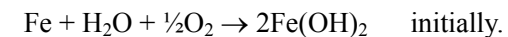
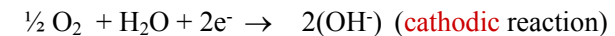


## Rusting of iron in water

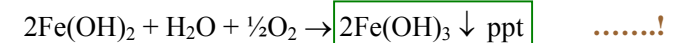


Dissolved oxygen is needed to form  $OH^-$  ions.

Two step process:

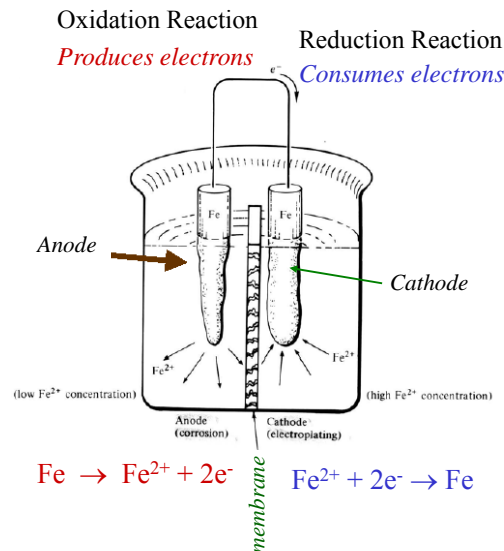


Then:



## Electrochemical cell

- The **anode** gives up electrons to the circuit and corrodes.
- The **cathode** receives electrons from the circuit by means of a chemical or cathode reaction. By-products may form.
- The anode and cathode must be **electrically connected** (usually by physical contact).
- A liquid electrolyte must be in contact with the anode and cathode to **complete the circuit** and allow movement of ions.

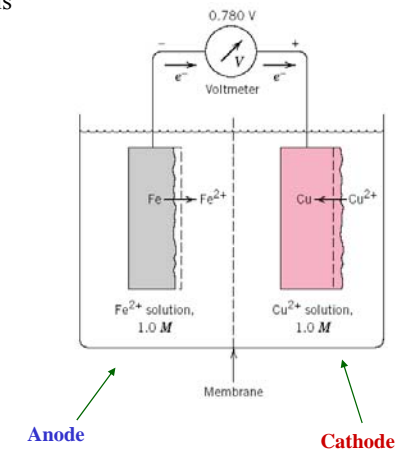
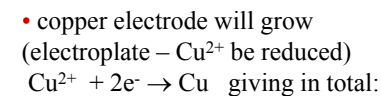


## Electrode Potential In Electrochemical Cells

- For perfect metal in an electrolyte, an Electrode Potential is developed which is related to the tendency of the metal to give up electrons (oxidise).
- Different metals** have **different** tendencies to be oxidised.

**Example:** If iron and copper electrodes in their respective ions are connected electrically:

- iron electrode will dissolve (oxidise)  $Fe \rightarrow Fe^{2+} + 2e^-$  and
- copper electrode will grow (electroplate -  $Cu^{2+}$  be reduced)



A voltage difference of 0.78V is associated with this reaction.



## Electrode Potential In Electrochemical Cells

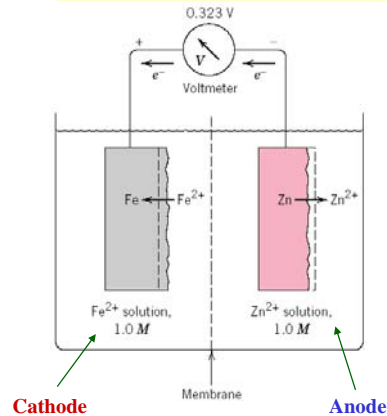
Another **GALVANIC COUPLE** is shown here between iron and zinc.

In this case the iron plates out (iron ions are reduced) and the zinc electrode dissolves (oxidizes) thus:



**Note:** This cell has a different voltage to the Fe - Cu cell

An electrode potential/voltage exists between two cell halves: varies with metals.



## Electrode Potential In Electrochemical Cells

➤ Recall the concept of **electronegativity**?

- ✓ *Electronegativity is a measure of the degree to which an atom attracts a free electron.*
- ✓ *If 2 metals are in contact (either by way of an electrolytic solution or by a wire), they will exchange electrons, according to their electronegativity difference.*
- ✓ *There will be a net flow of electrons from the more electropositive (anode) to the electronegative (cathode) metal.*

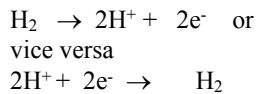
➤ The electrode potential for a **particular metal** (driving force for oxidation - reduction reaction) cannot be measured by itself – need a reference electrode to compare it with.

➤ To get an idea of tendencies to corrode, measure voltage produced by metal reaction, with **standard voltage** of a **reference cell**.



## Standard Electromotive Force (EMF) Series

Reference Cell - **Hydrogen electrode**



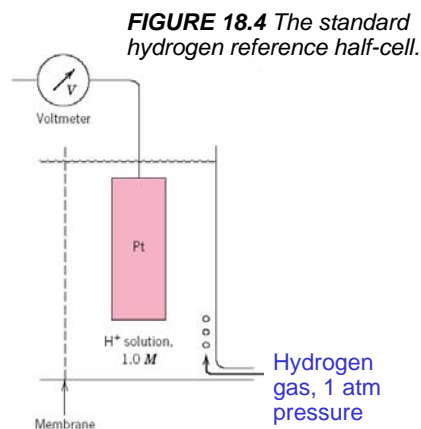
(assigned zero voltage),  $V^0$

So reaction with metal:



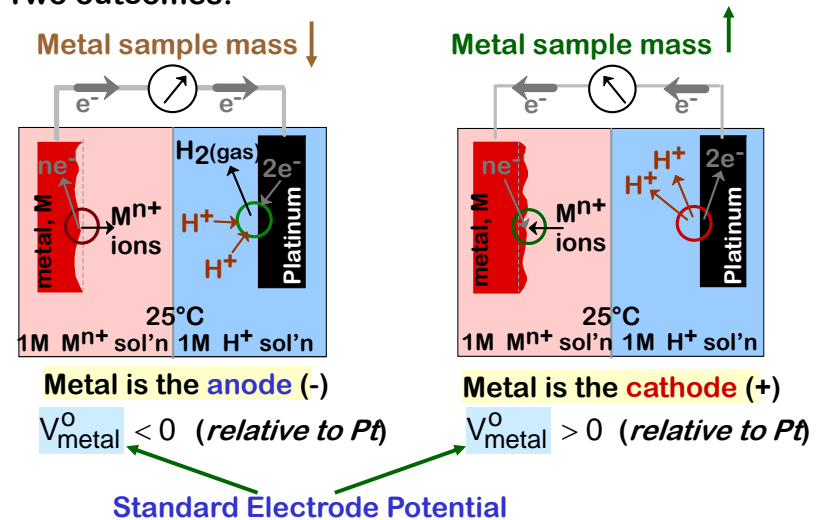
(compare this voltage with standard)

*Pt does not take part in the electrochemical reaction; it acts only as surface on which hydrogen atoms may be oxidized or hydrogen ions may be reduced*



## Standard Hydrogen (Emf) Test

• **Two outcomes:**





## Standard Electromotive Force (EMF) Series

Table 18.1 The Standard emf Series

	Electrode Reaction	Standard Electrode Potential, $V^0$ (V)
Increasingly inert (cathodic)	$Au^{3+} + 3e^- \rightarrow Au$	+1.420
	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^- \rightarrow Pt$	+1.2
	$Ag^+ + e^- \rightarrow Ag$	+0.800
	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.340
	$2H^+ + 2e^- \rightarrow H_2$	0.000
	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.136
Increasingly active (anodic)	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.250
	$Co^{2+} + 2e^- \rightarrow Co$	-0.277
	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.440
	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.744
	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763
	$Al^{3+} + 3e^- \rightarrow Al$	-1.662
	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.363
	$Na^+ + e^- \rightarrow Na$	-2.714
	$K^+ + e^- \rightarrow K$	-2.924

For any given metal, say  $Fe^{2+}$ , anything above it on the table would act as a *cathode* relative to the iron and cause it to corrode. Similarly, anything listed below iron would act as an *anode* relative to iron and cause it to plate out.

To find the net emf for any given pair of electrodes, simply take the difference between the values listed.

These are for the reduction reactions; for the oxidation reactions, the direction of the reaction is reversed and the sign of the voltage changed.

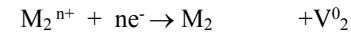
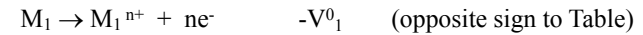
Example: .....



## Reaction's Direction

Example:

Metal  $M_1$  is oxidised and Metal  $M_2$  is reduced thus:



Addition of equations yields:  $M_1 + M_2^{n+} \rightarrow M_1^{n+} + M_2$

and the overall cell potential is:  $\Delta V^0 = V_2^0 - V_1^0$

If this value ( $\Delta V^0$ ) is +ve then reaction occurs spontaneously.

If it is negative, the reaction will go the other way.

**Remember:** When standard half-cells are coupled together, the metal that is lower in the Standard EMF series will oxidize (corrode) and the other will be reduced (electro-deposit).



## Relative corrosion potential

Table 18.2 The Galvanic Series

Increasingly inert (cathodic)	Platinum
	Gold
	Graphite
	Titanium
	Silver
	[316 Stainless steel (passive)]
	[304 Stainless steel (passive)]
	[Inconel (80Ni-13Cr-7Fe) (passive)]
	[Nickel (passive)]
	[Monel (70Ni-30Cu)]
Increasingly active (anodic)	Copper-nickel alloys
	Bronzes (Cu-Sn alloys)
	Copper
	Brasses (Cu-Zn alloys)
	[Inconel (active)]
	[Nickel (active)]
	Tin
	Lead
	[316 Stainless steel (active)]
	[304 Stainless steel (active)]
	[Cast iron]
	[Iron and steel]
	Aluminum alloys
	Cadmium
	Commercially pure aluminum
	Zinc
	Magnesium and magnesium alloys

• Since the preceding table was constructed under highly idealized conditions, it is sometimes more useful to rank the metals according to their general tendency to corrode in *seawater*.

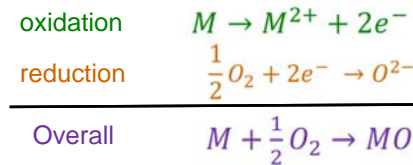
• Metals near the top are ..... **cathodic** (meaning that they resist corrosion and accept electrons), whereas metals near the bottom **corrode rather easily** and act as a source of electrons.

• If metal "A" falls below metal "B" on this list, "A" will most likely corrode and eventually disintegrate when electrically connected to "B"

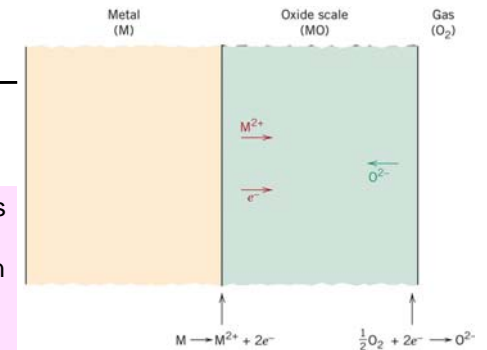


## Oxidation – Dry Corrosion

Degradation of metals in gaseous atmosphere (usually air) by reaction of surface. (*scaling, tarnishing, dry corrosion*) – Also an electrochemical process



The important issue when it comes to oxidation is whether the oxide layer keeps growing after or not. In order for this to happen, oxidising species must diffuse through the oxide layer.





## Oxidation Rate

Rate of oxidation (oxide layer growth rate) is related to the relative volumes:

$$P - B \text{ Ratio} = \frac{A_o \cdot \rho_M}{A_M \cdot \rho_o}$$

Where A is molecular weight  
ρ density  
M denotes metal and O oxide.  
(based on Volume = Mass/Density)

P-B is Pilling-Bedworth Ratio

- For P-B ratio less than 1, oxide film tends to be non-protective and porous and doesn't fully cover the surface.
- For P-B ratio greater than 1, compressive stresses form in oxide film (tend to be protective).
- For P-B ratio greater than 2-3, oxide film may crack and flake off exposing fresh metal (tend to be non-protective).
- This is based on volume change but other factors apply as well

**Table 17.3 Pilling-Bedworth Ratios for a Number of Metals**

Protective		Nonprotective	
Ce	1.16	K	0.45
Al	1.28	Li	0.57
Pb	1.40	Na	0.57
Ni	1.52	Cd	1.21
Be	1.59	Ag	1.59
Pd	1.60	Ti	1.95
Cu	1.68	Ta	2.33
Fe	1.77	Sb	2.35
Mn	1.79	Nb	2.61
Co	1.99	U	3.05
Cr	1.99	Mo	3.40
Si	2.27	W	3.40



## Kinetics of Oxidation

$$W^2 = K_1 t + K_2$$

Rate measured by weight gain per unit area (W) as a function of time (t).

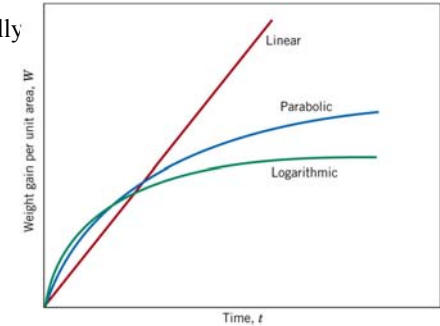
- For non-porous, well-attached oxide, growth is related to ionic diffusion giving a parabolic rate, ( $K_1$  and  $K_2$  are constants for a given temperature).  
- Examples: iron, cobalt, copper

- For porous, flaky oxide, growth is usually linear. - Examples: Na, K, Ta

$$W = K_3 t$$

- For some very thin oxide films, growth at low temperatures can be logarithmic.  
- Examples: Al, Fe, Cu at ambient temperature

$$W = K_4 \log(K_5 t + K_6)$$



## Degradation of Polymers

- Not electrochemical corrosion. (Physio-chemical)
  - Swelling and degradation, bond rupture are some common mechanisms.
  - Liquid/solute diffuses into polymer and between large molecules. Swells polymer making it weaker.

**Table 17.5 Resistance to Degradation by Various Environments for Selected Elastomeric Materials<sup>a</sup>**

Material	Weather-Sunlight Aging		Ozone Oxidation Cracking		Alkali Dilute/ Concentrated	Acid Dilute/ Concentrated	Chlorinated Hydrocarbons, Degreasers	Aliphatic Hydrocarbons, Kerosene, Etc.	Animal, Vegetable Oils
	D	B	NR	A/C-B	A/C-B	NR	NR	D-B	
Polyisoprene (natural)	D	B	NR	A/C-B	A/C-B	NR	NR	D-B	
Polyisoprene (synthetic)	NR	B	NR	C-B/C-B	C-B/C-B	NR	NR	D-B	
Butadiene	D	B	NR	C-B/C-B	C-B/C-B	NR	NR	D-B	
Styrene-butadiene	D	C	NR	C-B/C-B	C-B/C-B	NR	NR	D-B	
Neoprene	B	A	A	A/A	A/A	D	C	B	
Nitrile (high)	D	B	C	B/B	B/B	C-B	A	B	
Silicone (polysiloxane)	A	A	A	A/A	B/C	NR	D-C	A	

<sup>a</sup> A = excellent, B = good, C = fair, D = use with caution, NR = not recommended.  
Source: Compound Selection and Service Guide, Seals Eastern, Inc., Red Bank, NJ, 1977.



## Degradation of Polymers

**Table 17.4 Resistance to Degradation by Various Environments for Selected Plastic Materials<sup>a</sup>**

Material	Nonoxidizing Acids (20% H <sub>2</sub> SO <sub>4</sub> )	Oxidizing Acids (10% HNO <sub>3</sub> )	Aqueous Salt Solutions (NaCl)	Aqueous Alkalis (NaOH)	Polar Solvents (C <sub>2</sub> H <sub>5</sub> OH)	Nonpolar Solvents (C <sub>6</sub> H <sub>6</sub> )	Water
	Polytetrafluoroethylene	S	S	S	S	S	S
Nylon 6,6	U	U	S	S	Q	S	S
Polycarbonate	Q	U	S	U	S	U	S
Polyester	Q	Q	S	Q	Q	U	S
Polyetheretherketone	S	S	S	S	S	S	S
Low-density polyethylene	S	Q	S	—	S	Q	S
High-density polyethylene	S	Q	S	—	S	Q	S
Poly(ethylene terephthalate)	S	Q	S	S	S	S	S
Poly(phenylene oxide)	S	Q	S	S	S	U	S
Polypropylene	S	Q	S	S	S	Q	S
Polystyrene	S	Q	S	S	S	U	S
Polyurethane	Q	U	S	Q	U	Q	S
Epoxy	S	U	S	S	S	S	S
Silicone	Q	U	S	S	S	Q	S

<sup>a</sup> S = satisfactory; Q = questionable; U = unsatisfactory.

Source: Adapted from R. B. Seymour, Polymers for Engineering Applications, ASM International, Materials Park, OH, 1987.



*Next time:*  
*Continue Corrosion*