

# Chapter 17: Corrosion and Degradation of Materials

## ISSUES TO ADDRESS...

- How does corrosion of metals occur?
- Which metals are more likely to corrode and which less?
- How do we prevent or control corrosion?
- How to predict which metal oxidizes under different conditions?
- Polymer degradation



# THE COST OF CORROSION

- **Corrosion:**
  - the destructive chemical (especially electrochemical) attack of a material (metals, in particular) by interactions with its environment.
  - Ex: Al Capone's ship, Sapona, off the coast of Bimini.



Photos courtesy L.M. Maestas, Sandia National Labs. Used with permission.

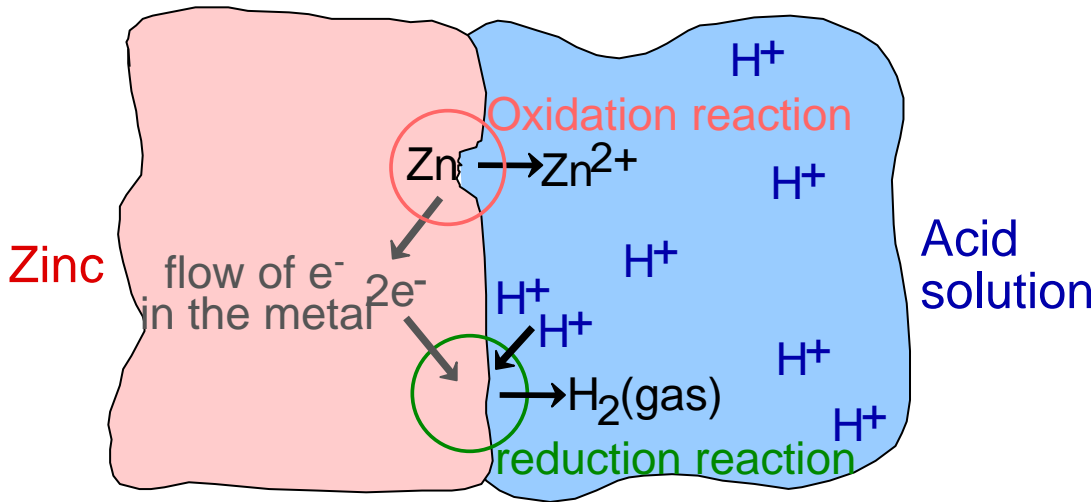
- **Huge loss in economy due to corrosion every year!**
  - 3% of the Gross National Product (GNP)
  - in the U.S. this amounts to ~\$500 billion/yr



# ELECTROCHEMICAL CORROSION

Ex: consider the corrosion of zinc in an aqueous acidic solution

- Two (half cell) reactions happen simultaneously:

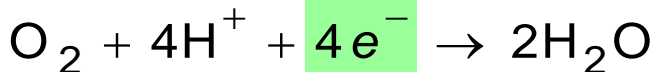


**H<sub>2</sub> evolution if acidic & no O<sub>2</sub>**

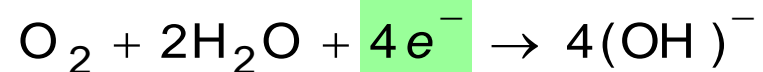
Adapted from Fig. 17.1, *Callister & Rethwisch 8e.* (Fig. 17.1 is from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

- Other reduction reactions possible in solutions with dissolved oxygen:

-- in acidic solution



-- in neutral or basic solution



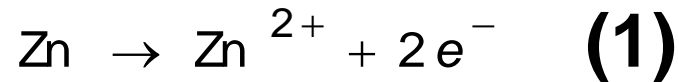
**Oxygen dissolution reaction**



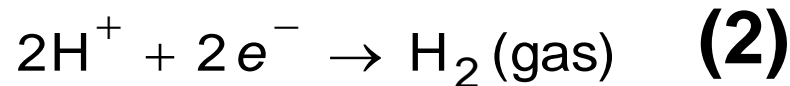
# Half Cell Reactions in Corrosion (1)

Using the example of Zn corrosion in acidic medium without dissolve oxygen

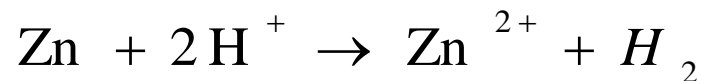
•Anodic reaction/Oxidation (half cell) reaction



•Cathodic reaction/Reduction (half cell) reaction



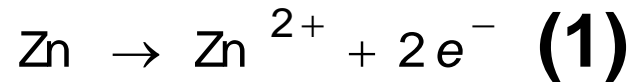
•Overall reaction: (1) + (2)



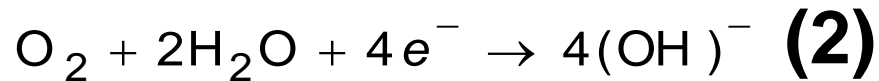
# Half Cell Reactions in Corrosion (2)

Using the example of Zn corrosion in **neutral medium with significant dissolved oxygen**

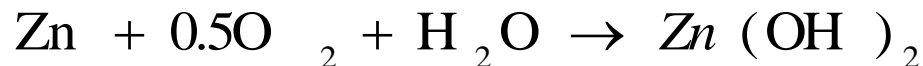
- Anodic reaction or Oxidation (half cell) reaction



- Cathodic reaction or Reduction (half cell) reaction



- Overall reaction: (1) + 0.5(2)

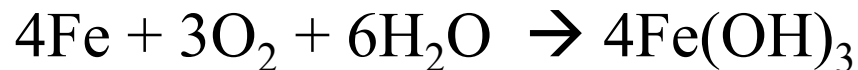
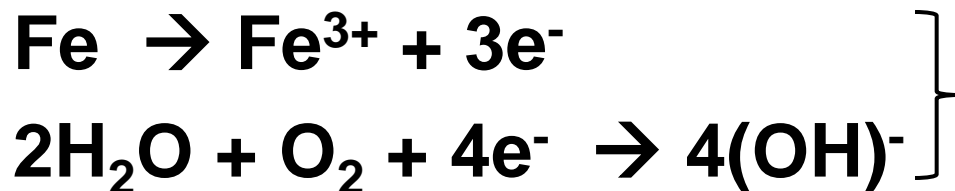
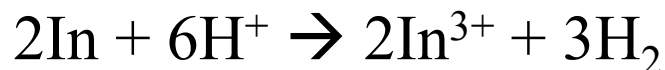
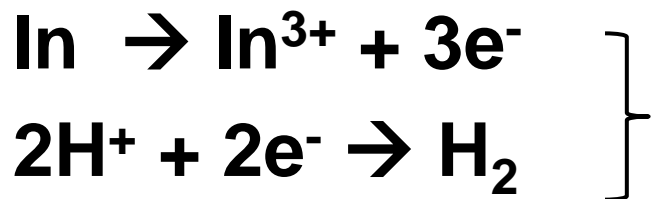
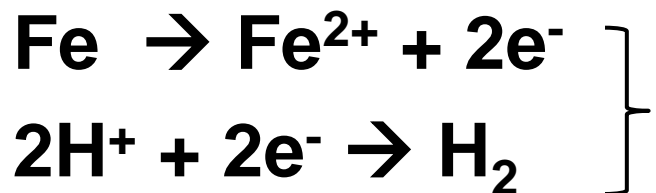


or



## Class Exercise

For the given cathodic and anodic half-cell reactions, write the overall corrosion reaction

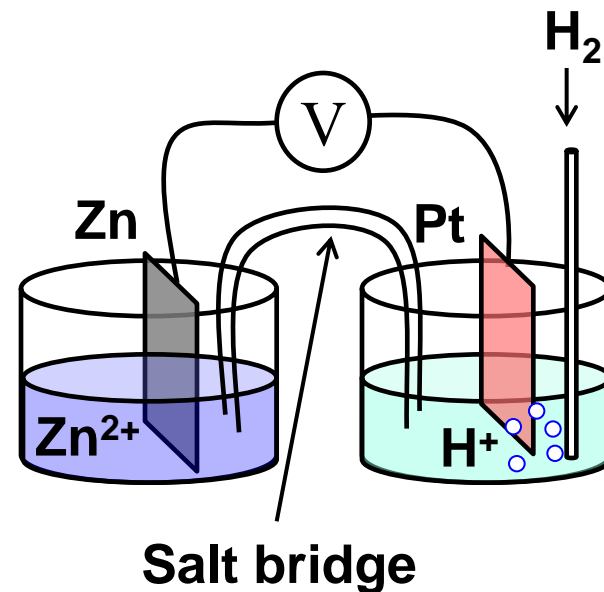


# Electrochemical Cell Potential

- Separate Zn oxidation and H<sub>2</sub> evolution half cell reactions using salt bridge → electrochemical cell
- A stable potential establishes under equilibrium (zero net current):  
Standard cell voltage of Zn/Zn<sup>2+</sup> electrode relative to H<sub>2</sub>/H<sup>+</sup> electrode under equilibrium is

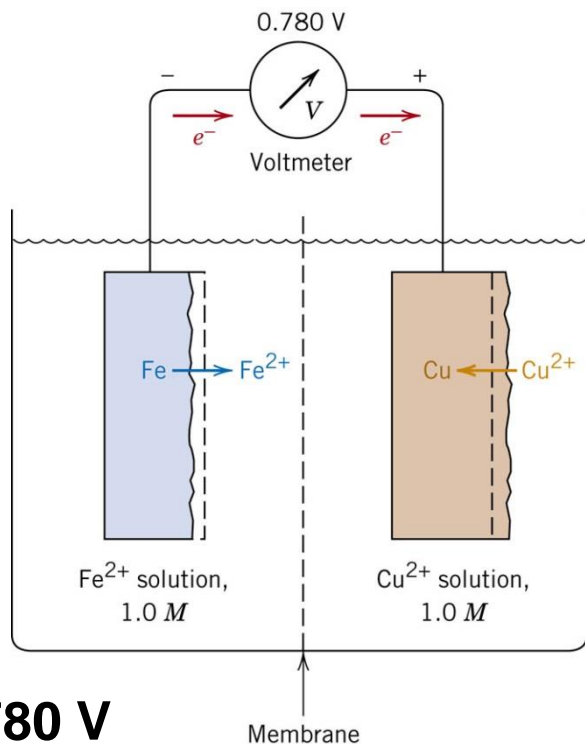
$$E^\circ = -0.763 \text{ V}$$

When connecting Zn/Zn<sup>2+</sup> electrode with H<sub>2</sub>/H<sup>+</sup> (over Pt catalyst) electrode through a small resistor, electrons flow spontaneously from more negative electrode to more positive electrode, i.e., from Zn/Zn<sup>2+</sup> to H<sub>2</sub>/H<sup>+</sup>, accompanied by Zn metal dissolution and H<sub>2</sub> gas evolution



# Electrochemical Cell Potential

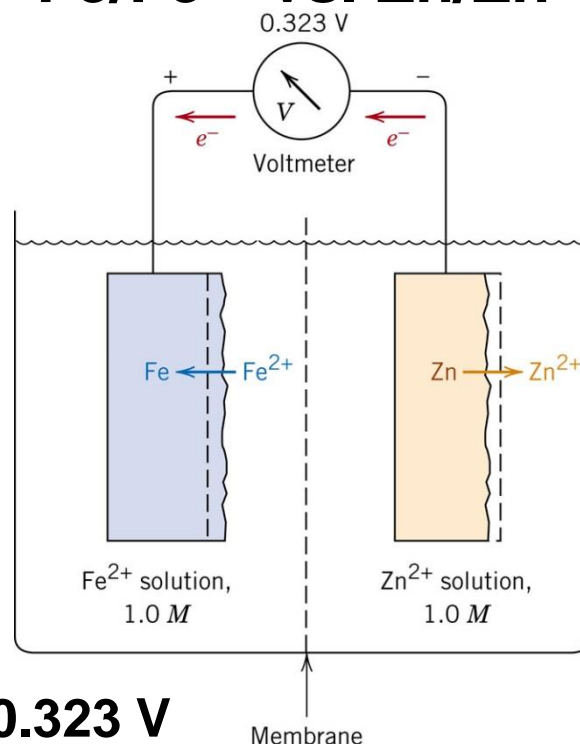
## Fe/Fe<sup>2+</sup> vs. Cu/Cu<sup>2+</sup>



$$E = -0.780 \text{ V}$$

- Fe/Fe<sup>2+</sup> electrode is more negative
- Cu/Cu<sup>2+</sup> electrode is more positive
- Electron flow out of Fe → oxidation (anodic) reaction on Fe/Fe<sup>2+</sup>
- Electron flow in Cu → reduction (cathodic) reaction on Cu/Cu<sup>2+</sup>

## Fe/Fe<sup>2+</sup> vs. Zn/Zn<sup>2+</sup>



$$E = +0.323 \text{ V}$$

- Fe/Fe<sup>2+</sup> electrode is more positive
- Zn/Zn<sup>2+</sup> electrode is more negative
- Electron flow out of Zn → Oxidation (anodic) reaction on Zn/Zn<sup>2+</sup>
- Electron flow into Fe → reduction (cathodic) reaction on Fe/Fe<sup>2+</sup>

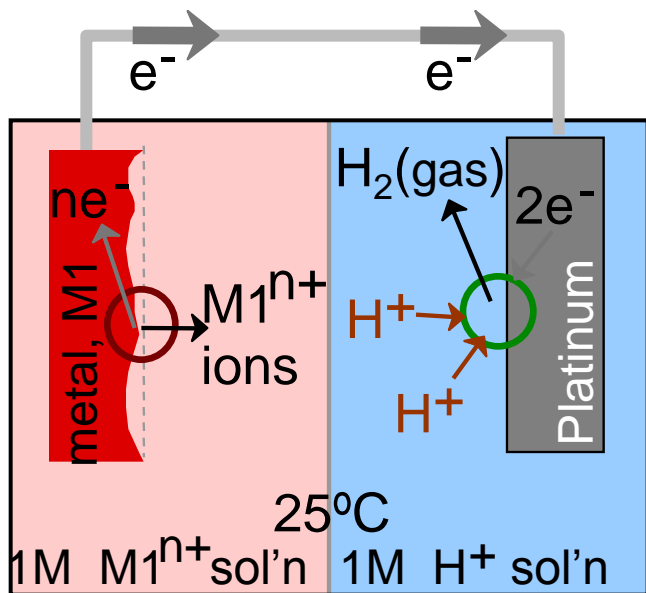




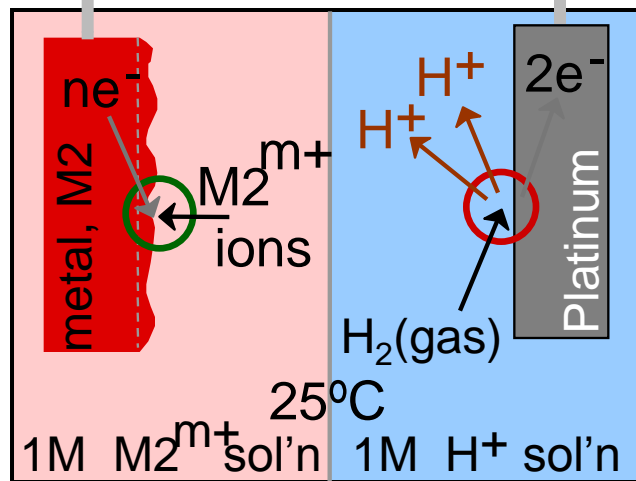
# STANDARD HYDROGEN ELECTRODE

- Using  $H_2/H^+$  as standard electrode and compare the voltage for other half cell reactions (e.g.,  $Zn/Zn^{2+}$ ) against this standard

Adapted from Fig. 17.2,  
Callister & Rethwisch 8e.



$$E_{M1/M1^{n+}}^{\circ} < 0 \text{ (relative to } H_2/H^+)$$



$$E_{M2/M2^{m+}}^{\circ} > 0 \text{ (relative to } H_2/H^+)$$

Standard Electrode Potential

- Electrons flow from  $M1/M1^{n+}$  electrode to  $H_2/H^+$  electrode
- $M1$  oxidizes and dissolves
- $M1$  is the anode where oxidation happens

- Electron flow from  $H_2/H^+$  electrode to  $M2/M2^{m+}$  electrode
- $M2$  deposits from solution
- $M2$  is the cathode where reduction happens



# STANDARD Electrode Potential SERIES

- Standard electrode potential  $E^\circ$  (vs.  $H_2/H^+$  electrode)

Redox pair	$E^\circ$
Au/Au <sup>3+</sup>	+1.520 V
Cu/Cu <sup>2+</sup>	+0.340
H <sub>2</sub> /H <sup>+</sup>	0.000
Pb/Pb <sup>2+</sup>	- 0.126
Sn/Sn <sup>2+</sup>	- 0.136
Ni/Ni <sup>2+</sup>	- 0.250
Co/Co <sup>2+</sup>	- 0.277
Cd/Cd <sup>2+</sup>	- 0.403
Fe/Fe <sup>2+</sup>	- 0.440
Cr/Cr <sup>3+</sup>	- 0.744
Zn/Zn <sup>2+</sup>	- 0.763
Al/Al <sup>3+</sup>	- 1.662
Mg/Mg <sup>2+</sup>	- 2.363
Na/Na <sup>+</sup>	- 2.714
K/K <sup>+</sup>	- 2.924

More difficult to give out electron

Easier to give out electron

When connecting two half cells together

- The half cell (or redox pair) with **more negative** standard electrode potential will go through **oxidation (or anodic) reaction**
- The half cell (or redox pair) with **more positive** standard electrode potential will go through **reduction (or cathodic) reaction**

Overall, standard cell potential

$$E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{an}}$$

Standard electrode potential for cathodic and anodic half cell reactions

In general, for any electrochemical cell,

If  $E_{\text{cell}} > 0$ , reaction proceeds

If  $E_{\text{cell}} < 0$ , reverse reaction proceeds



# Example: Cd/Cd<sup>2+</sup> electrode connected with Ni/Ni<sup>2+</sup> electrode

Standard electrode potential

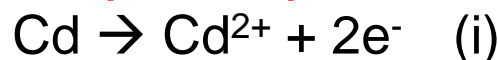
Redox pair

$$E^\circ(\text{Ni}/\text{Ni}^{2+}) = -0.250 \text{ V}$$

$$E^\circ(\text{Cd}/\text{Cd}^{2+}) = -0.403 \text{ V}$$

$$E^\circ(\text{Cd}/\text{Cd}^{2+}) \text{ more negative} \rightarrow$$

**Oxidation (anodic)** reaction for Cd/Cd<sup>2+</sup> electrode



**Reduction (cathodic)** reaction for Ni/Ni<sup>2+</sup> electrode



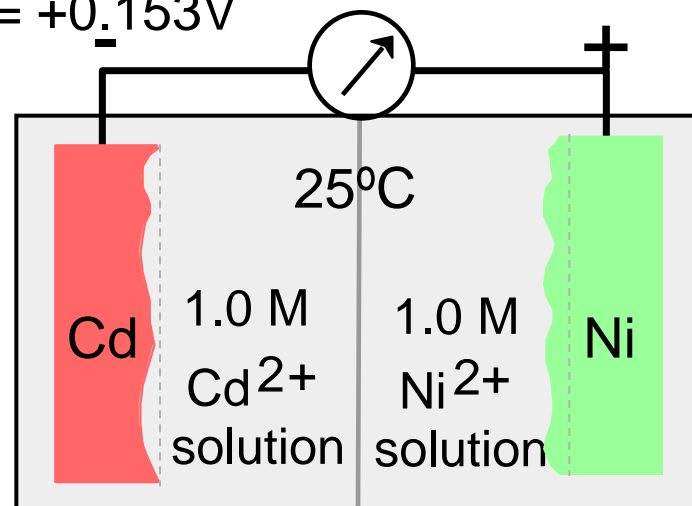
Overall reaction = (i) + (ii): **Cd + Ni<sup>2+</sup> → Cd<sup>2+</sup> + Ni**

$$E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{an}} = E^\circ(\text{Ni}/\text{Ni}^{2+}) - E^\circ(\text{Cd}/\text{Cd}^{2+}) = -0.250 - (-0.403) = +0.153 \text{ V}$$

↑ More difficult to give out electron

↓ Easier to give out electron

Au/Au <sup>3+</sup>	+1.520 V
Cu/Cu <sup>2+</sup>	+0.340
H <sub>2</sub> /H <sup>+</sup>	0.000
Pb/Pb <sup>2+</sup>	-0.126
Sn/Sn <sup>2+</sup>	-0.136
Ni/Ni <sup>2+</sup>	-0.250
Co/Co <sup>2+</sup>	-0.277
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Zn/Zn <sup>2+</sup>	-0.763
Al/Al <sup>3+</sup>	-1.662
Mg/Mg <sup>2+</sup>	-2.363
Na/Na <sup>+</sup>	-2.714
K/K <sup>+</sup>	-2.924



Adapted from Fig. 17.2,  
Data based on Table 17.1, Callister & Rethwisch 8e.



# Class Exercise

For an electrochemical cell connecting Cu/Cu<sup>2+</sup> (1 M) electrode with Zn/Zn<sup>2+</sup> (1 M) electrode through a membrane

**Q1: On which electrode does oxidation reaction (metal dissolution) and reduction (metal deposition) reaction happen, respectively? Write half cell as well as overall reactions. Knowing**

**$E^\circ(\text{Zn}/\text{Zn}^{2+}) = -0.763\text{V}$  and  $E^\circ(\text{Cu}/\text{Cu}^{2+}) = +0.340\text{V}$**

$E^\circ(\text{Zn}/\text{Zn}^{2+})$  is more negative than  $E^\circ(\text{Cu}/\text{Cu}^{2+})$

Zn/Zn<sup>2+</sup> electrode:

anodic/oxidation half cell reaction:  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

Cu/Cu<sup>2+</sup> electrode:

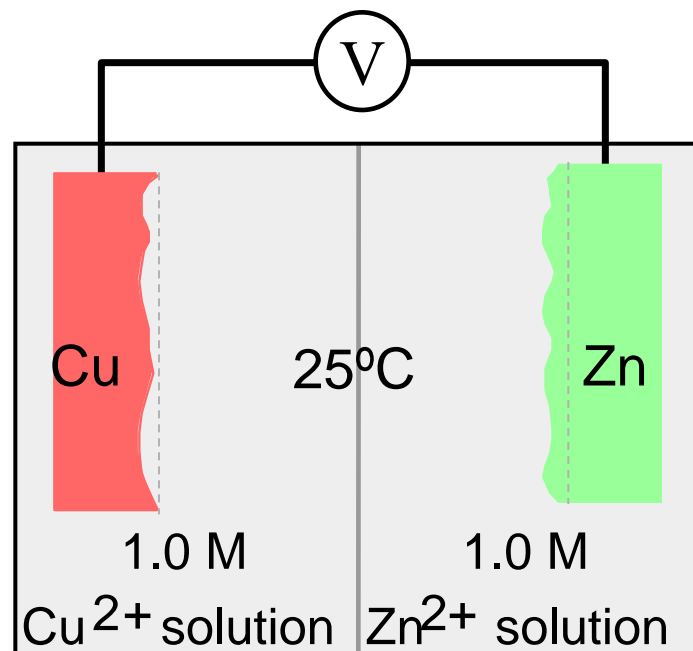
cathodic/reduction half cell reaction:  $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$

Overall reaction:  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

**Q2 Determine the standard cell potential for such a cell?**

**$E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{an}} = E^\circ(\text{Cu}/\text{Cu}^{2+}) - E^\circ(\text{Zn}/\text{Zn}^{2+}) =$**

**$0.340\text{V} - (-0.763\text{V}) = 1.103\text{V}$**



# Class Exercise

Between copper and aluminum, when each of them is immersed in an acidic aqueous solution WITHOUT dissolved oxygen (two separate experiments), which metal will corrode and which one will not? Please also write down the half cell reactions and the overall corrosion reaction and standard cell potential.

Knowing  $E^\circ(\text{Cu}/\text{Cu}^{2+}) = 0.340\text{V}$  and  $E^\circ(\text{Al}/\text{Al}^{3+}) = -1.662\text{V}$ ,  $E^\circ(\text{H}_2/\text{H}^+) = 0.0\text{V}$ ,  $E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.229\text{V}$

$E^\circ(\text{Cu}/\text{Cu}^{2+}) = 0.340\text{V}$  more positive than  $E^\circ(\text{H}_2/\text{H}^+) = 0\text{V}$

$E^\circ(\text{Al}/\text{Al}^{3+}) = -1.662\text{V}$  more negative than  $E^\circ(\text{H}_2/\text{H}^+) = 0\text{V}$

Therefore, Al will oxidize with respect to  $\text{H}_2/\text{H}^+$ , while Cu will NOT

Anodic (oxidation) half cell reaction:  $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$

Cathodic (reduction) half cell reaction:  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Overall reaction:  $2\text{Al} + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2$

Standard cell potential:  $E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{an}} = E^\circ(\text{H}_2/\text{H}^+) - E^\circ(\text{Al}/\text{Al}^{3+}) = 0 - (-1.662\text{V}) = 1.662\text{V}$



# Class Exercise

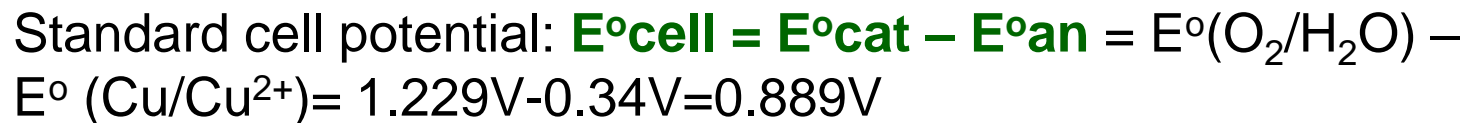
Knowing standard potential  $E^\circ$  for the following reaction



When copper metal ( $E^\circ(\text{Cu}/\text{Cu}^{2+}) = 0.340\text{V}$ ) is immersed in acidic aqueous solution containing significant dissolved oxygen, will copper corrode? If yes, write down the overall reaction as well as the anodic and cathodic half cell reactions and give the standard cell voltage. If not, explain why.

Copper standard electrode potential  $E^\circ(\text{Cu}/\text{Cu}^{2+})=0.34\text{V}$ , which is more negative compared with  $E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.229 \text{ V}$

Therefore, oxidation (anodic) reaction happen for  $\text{Cu}/\text{Cu}^{2+}$  half cell (pair).





# Common Forms of Corrosion

- **Uniform Attack**

Oxidation & reduction reactions occur uniformly over surfaces (oxidation of steel or Ag or Cu tarnish)

- **Selective Leaching**

Preferred corrosion of one element/constituent [e.g., Zn loss from brass].

- **Intergranular**

Corrosion along grain boundaries, often where precip. particles form.

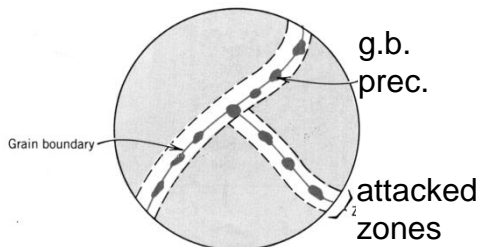


Fig. 17.18, Callister & Rethwisch 8e.

- **Stress corrosion**

Corrosion at crack tips when a tensile stress is present.

- **Erosion-corrosion**

Combined chemical attack and mechanical wear (e.g., pipe elbows).

- **Pitting**

Downward propagation of small pits and holes.

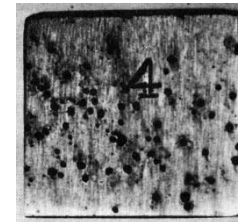


Fig. 17.17, Callister & Rethwisch 8e. (Fig. 17.17 from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

- **Galvanic**

Dissimilar metals are physically joined in the presence of an electrolyte. The metal with more negative electrode potential corrodes (e.g., Fe-Cu)

- **Crevice** Narrow and confined spaces.

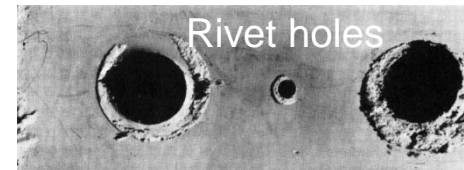
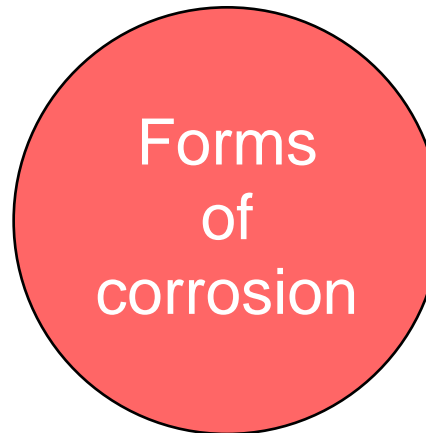


Fig. 17.15, Callister & Rethwisch 8e. (Fig. 17.15 is courtesy LaQue Center for Corrosion Technology, Inc.)





# Passivation

- Under certain condition (especially in terms of pH value), initial corrosion product does not dissolve and form a dense protective layer over metal surface, preventing further corrosion

Examples:

- Al in neutral water
- Cr in very weakly acidic to strongly basic solutions
- Ni in basic solutions
- ...



# CORROSION PREVENTION (i)

- **Materials selection**

- Use metals that are relatively unreactive (more noble) in the corrosion environment -- e.g., Au or Pt

- Use metals that **passivates**

- These metals form a thin, adhering oxide layer that slows corrosion.



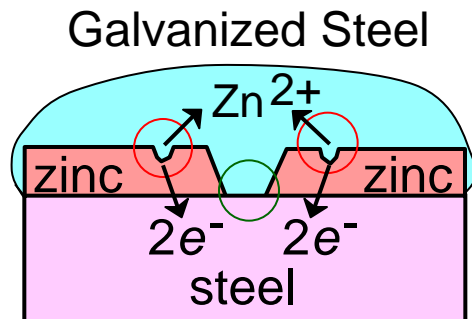
Metal oxide  
Metal (e.g., Al,  
stainless steel)

- **Lower the temperature** reduces rates of oxidation and reduction)
- Apply **physical barriers** -- e.g., protective films and coatings



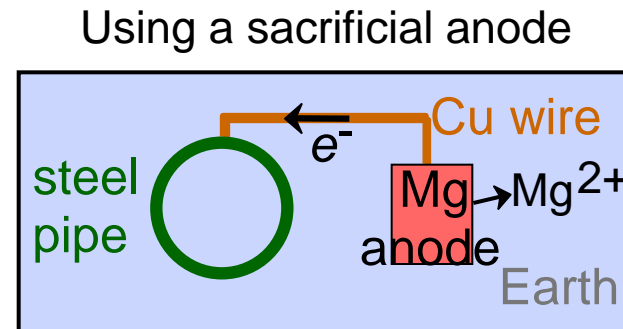
# CORROSION PREVENTION (ii)

- Add **inhibitors** (substances added to solution that decrease its reactivity) – usually used in closed system
  - Slow oxidation/reduction reactions by removing reactants (e.g., remove  $O_2$  gas by reacting it w/an inhibitor).
- Engineering design
- **Cathodic (or sacrificial) protection**
  - Attach a more anodic material to the one to be protected.



e.g., zinc-coated nail

Adapted from Fig. 17.23, Callister & Rethwisch 8e.



e.g., Mg Anode

Adapted from Fig. 17.22(a), Callister & Rethwisch 8e.



# Oxidation

- Generally, oxidation of metal in gas atmosphere, can also be viewed as a type of corrosion. It is also called scaling, tarnish, or dry corrosion
- Oxidizing agent often gaseous species of  $O_2$ ,  $H_2O$  vapor, sulfur vapor,  $H_2S$ ,  $SO_2$ , etc.
- Overall reaction using example of  $O_2$  as oxidizing agent:  
$$xM + y/2 O_2 \rightarrow M_xO_y$$
- Whether a metal oxidizes under certain condition thermodynamically, depends on metal type, temperature, and (gas) atmosphere, etc.
  - Fe oxidizes easily in air
  - Au or Pt does not oxidize in air



# Ellingham Diagram

- Determine **equilibrium**  $pO_2$  for  $M/M_xO_y$  at given temperature

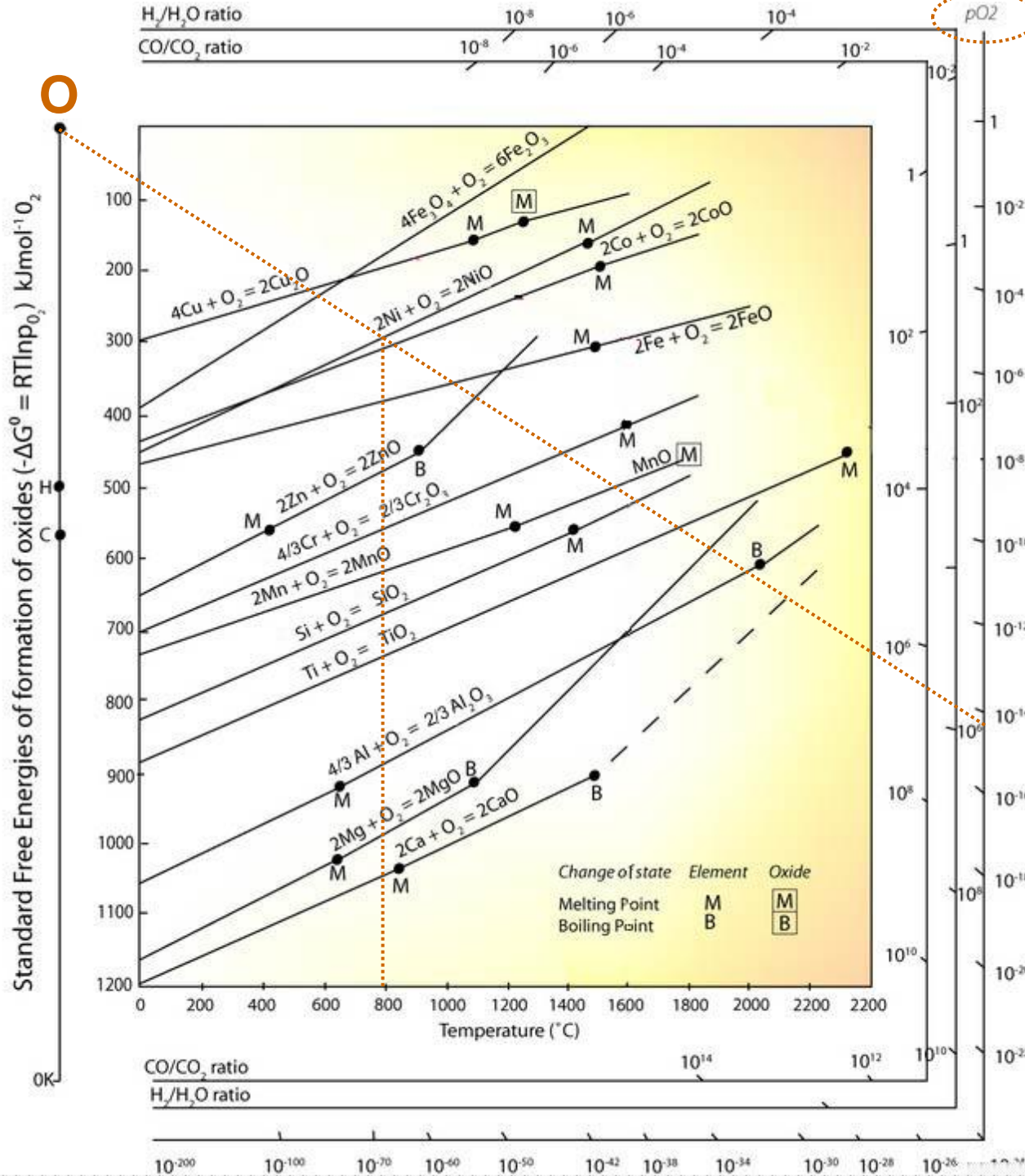
e.g., for



At 800 °C,  
 $pO_2^{eq} \sim 10^{-14}$  atm

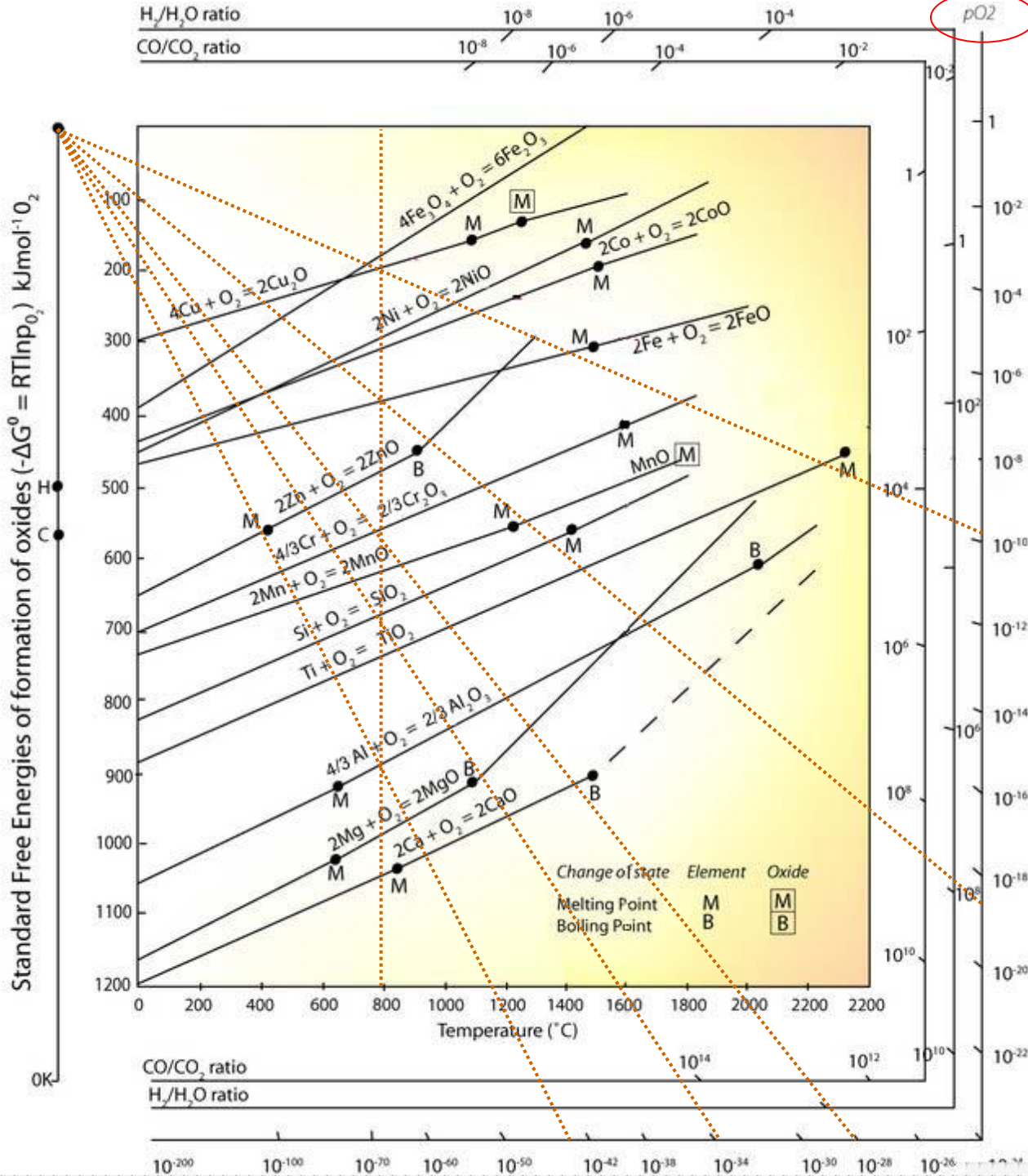
Determined by connecting **O** point with the appropriate temperature (800 °C in this case) intercept point on the line (Ni/NiO in this case) and read the intercept with the  $pO_2$  axis (scale)

Question: at 800 °C, if actual  $pO_2 = 10^{-10}$  atm, will Ni oxidize to NiO? What if actual  $pO_2 = 10^{-20}$  atm?



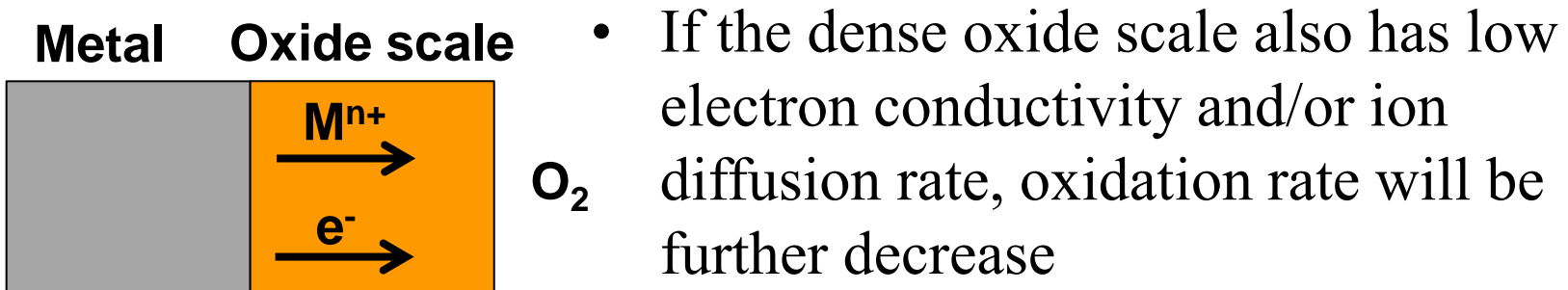
# Class Exercise

- Determine, at 800 °C and  $pO_2$  of  $10^{-14}$  atm, which of the following metals will oxidize: Cu, Fe, Cr, Si, Al
- Metals that will oxidize  $pO_2 = 10^{-14} > pO_2^{eq}$ 
  - Fe:  $pO_2^{eq}$  (Fe/FeO)  $\sim 10^{-18}$
  - Cr:  $pO_2^{eq}$  (Cr/Cr<sub>2</sub>O<sub>3</sub>)  $\sim 10^{-28}$
  - Si:  $pO_2^{eq}$  (Si/SiO<sub>2</sub>)  $\sim 10^{-34}$
  - Al:  $pO_2^{eq}$  (Al/Al<sub>2</sub>O<sub>3</sub>)  $\sim 10^{-43}$
- Metal that will be stable against oxidation:  $pO_2 = 10^{-14} < pO_2^{eq}$ 
  - Cu:  $pO_2^{eq}$  (Cu/CuO)  $\sim 10^{-10}$



# Kinetics in Oxidation

- Metals such as Al and Cr has extremely low  $pO_2^{eq}$  - Why can metal still exist at certain conditions?
- Oxidation kinetics (or rate) plays a role
- Most oxide scale are solids. For oxidation of metal to continue,
  - If oxide scale is porous or have cracks or peels off → overall oxidation rate will be high  
Examples of Fe, Mo, W
  - If oxide scale is dense (i.e., impermeable to  $O_2$ ), metal ion and electrons have to diffuse through the oxide scale if the scale dense → oxidation rate slow after forming protective oxide scale  
Examples of Ni, Cr, Al, Si etc.



- Oxidation rate increases dramatically as temperature increases



# Degradation of Polymers

## Physical

- Swelling and dissolution by interaction with solvents especially between similar chemicals

## Chemical - Bond rupture

- Chemical reactions with  $O_3$ ,  $O_2$ ,  $H_2O$ , and other species
- Thermal degradation at elevated temperatures
- Radiation by X-ray, UV, etc.





# SUMMARY

- Metallic corrosion involves electrochemical reactions: electrons are given up by metals in an anodic or **oxidation** reaction while consumed in a cathodic or **reduction** reaction
- Electrode potential for different metals are compared with standard hydrogen electrode to give standard electrode potential.
- Solution composition affect electrode potential.
- Some metals experience passivation when the corrosion product form protective layer over its surface preventing further corrosion
- Forms of corrosion are classified according to mechanism
- Different ways exist for corrosion control including proper materials selection, applying protective coating, adding inhibitors, and cathodic protection
- Oxidation of metals can be viewed as a type of corrosion. Whether a metal oxidizes depend on metal type, gas atmosphere, and temperature, and could be predicted using Ellingham diagrams



# Homework

- Read chapter 11-17 and give statement confirm reading ALL the chapters.
- Calister 8ed, 17.2(a)
- When connecting copper and iron together and immersed in salt water without oxygen, which metal corrode first and why? If the two half cell reaction can be separated by salt bridge, what is the standard electrode potential for such a cell?
- Additional problem using Ellingham diagram (See next page)



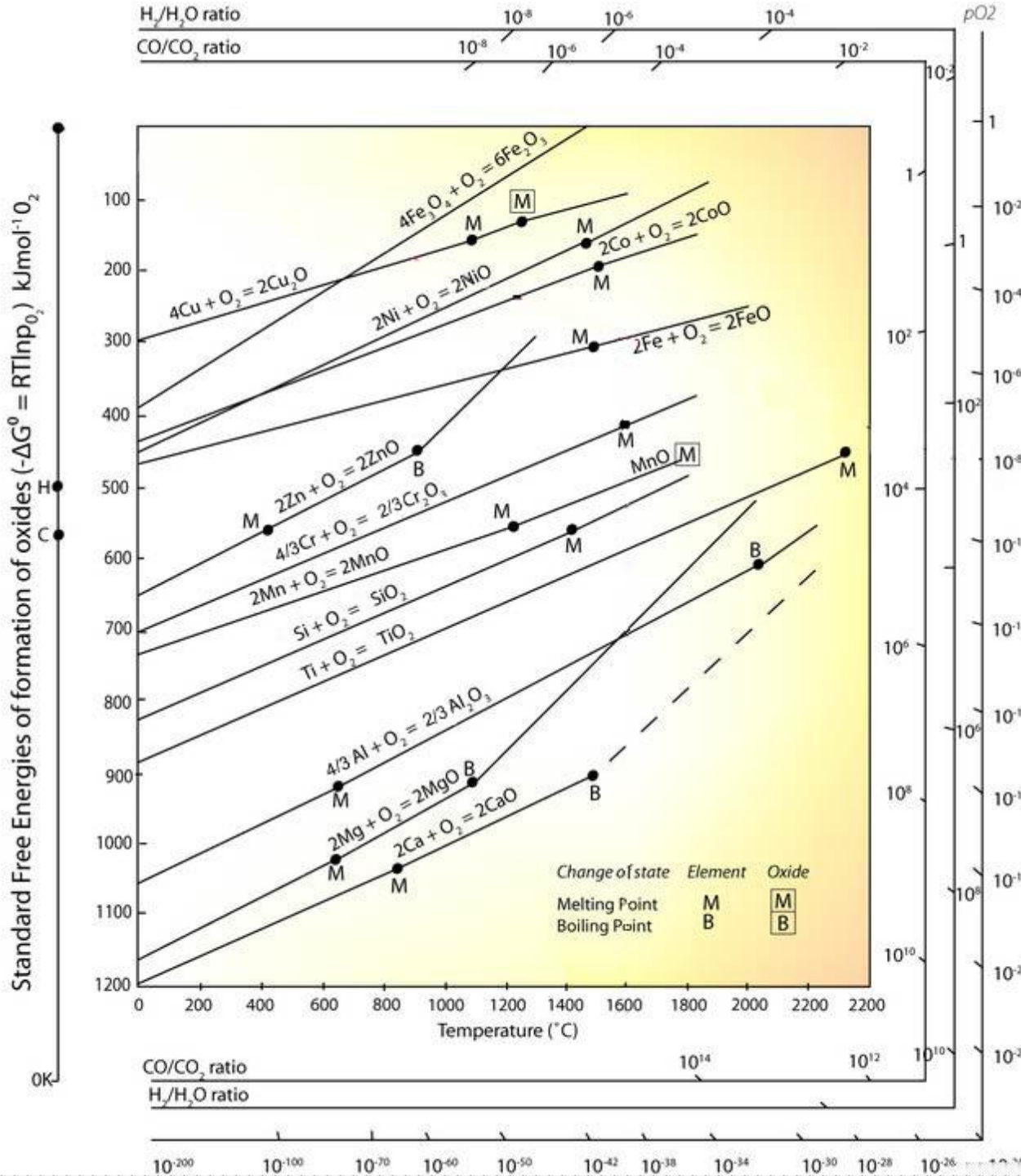
# Homework

- **17.2(a) Write the possible oxidation and reduction half-reaction that occur when magnesium is immersed in each of the following solutions: (i) HCl, (ii) an HCl solution containing dissolved oxygen**



# Homework

Use Ellingham diagram on the right to determine the equilibrium oxygen partial pressure for Fe/FeO at 800 °C. Also determine if a gas mixture with  $pO_2$  of  $10^{-6}$  could reduce FeO to Fe?



[http://www.doitpoms.ac.uk/tlplib/ellingham\\_diagrams/ellingham.php](http://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/ellingham.php)

