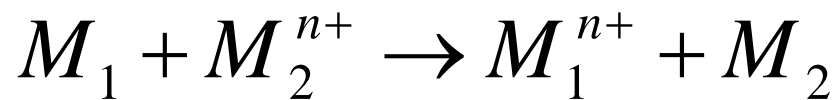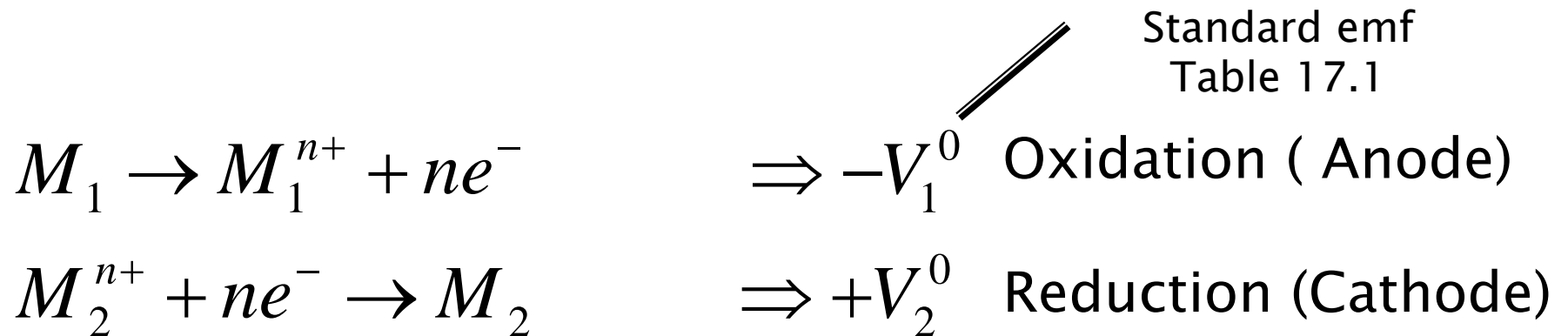# CHAPTER 17:Tutorial CORROSION AND DEGRADATION

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?

Standard Cell: Room temp+1M concentration

Standard emf
Table 17.1

$$M_1 \rightarrow M_1^{n+} + ne^- \qquad \Rightarrow -V_1^0 \quad \text{Oxidation (Anode)}$$

$$M_2^{n+} + ne^- \rightarrow M_2 \qquad \Rightarrow +V_2^0 \quad \text{Reduction (Cathode)}$$

- - - - - - - - - - - - - - - - - - -

$$M_1 + M_2^{n+} \rightarrow M_1^{n+} + M_2$$

$$\Delta V^o = V_2^0 - V_1^0$$

ΔV^o must be positive, if negative means opposite reaction

STANDARD EMF SERIES

- **EMF** series

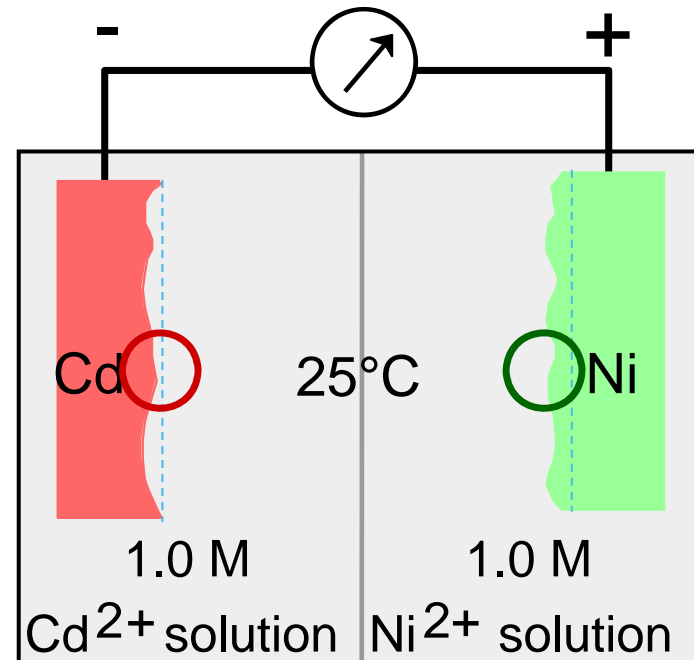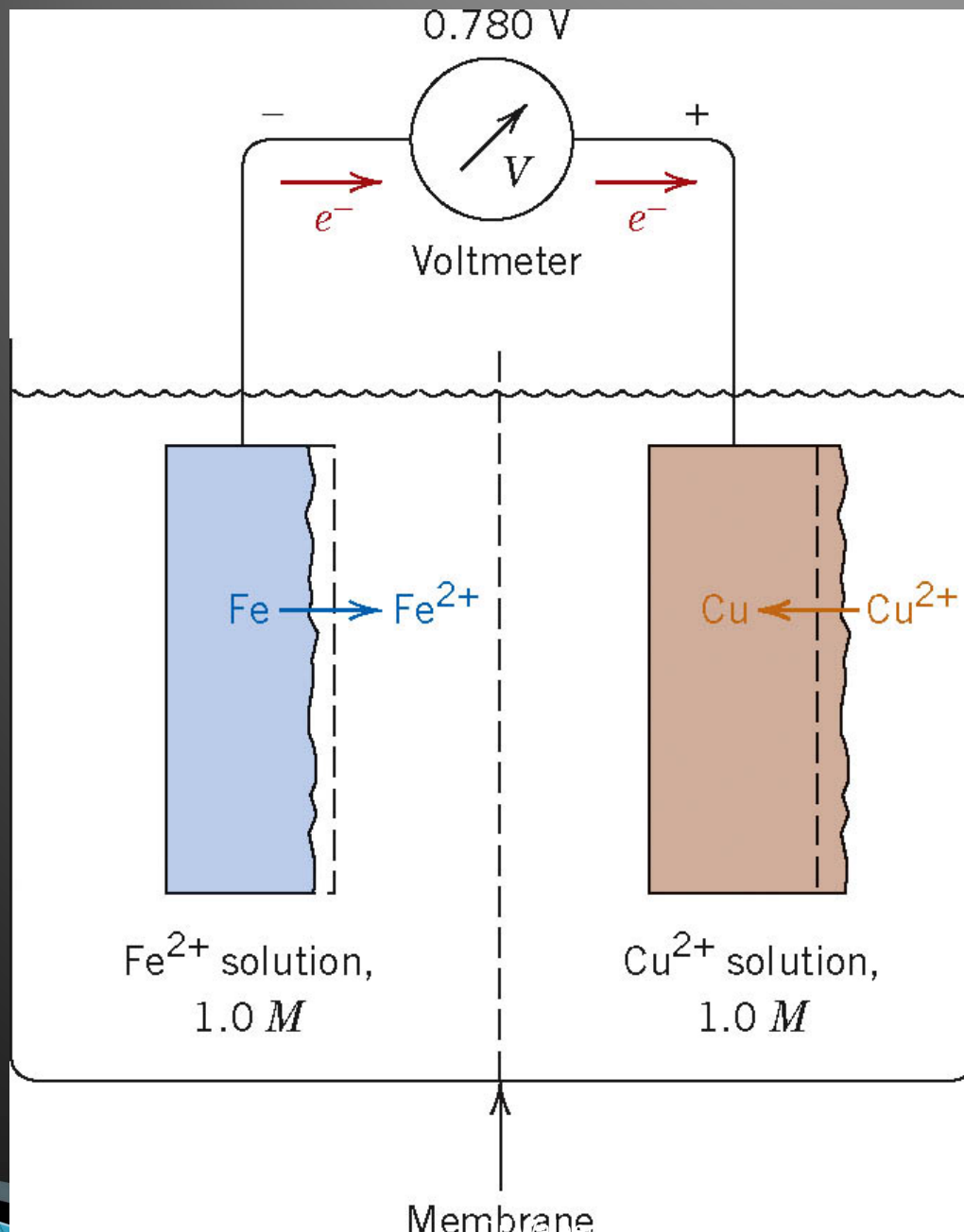| metal	V^o_{metal}
Au	+1.420 V
Cu	+0.340
Pb	- 0.126
Sn	- 0.136
Ni	- 0.250
Co	- 0.277
Cd	- 0.403
Fe	- 0.440
Cr	- 0.744
Zn	- 0.763
Al	- 1.662
Mg	- 2.363
Na	- 2.714
K	- 2.924

more cathodic

more anodic

$\Delta V^o = 0.153V$

- Metal with smaller V^o_{metal} corrodes.
- Ex: Cd-Ni cell

Data based on Table 17.1, *Callister 7e.*
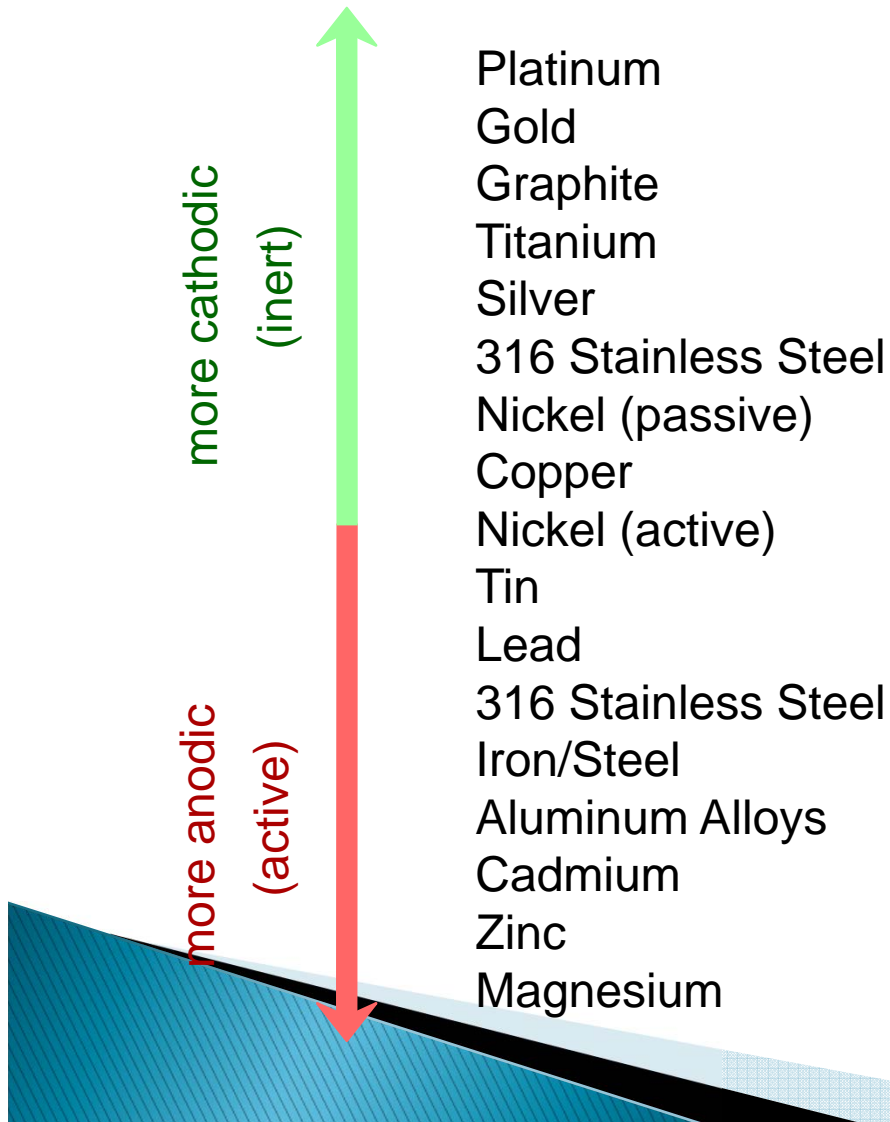
Adapted from Fig. 17.2, *Callister 7e.*

Dr.Waleed Khalil Ahmed ERU–FOE–UAEU   Nov.26,2012

0.780 V

Voltmeter

Fe $\longrightarrow$ Fe^{2+} Cu $\longleftarrow$ Cu^{2+}

Fe^{2+} solution, 1.0 M

Cu^{2+} solution, 1.0 M

Membrane

0.323 V

Voltmeter

Fe $\leftarrow$ Fe^{2+} Zn $\rightarrow$ Zn^{2+}

Fe^{2+} solution,
1.0 M

Zn^{2+} solution,
1.0 M

Membrane
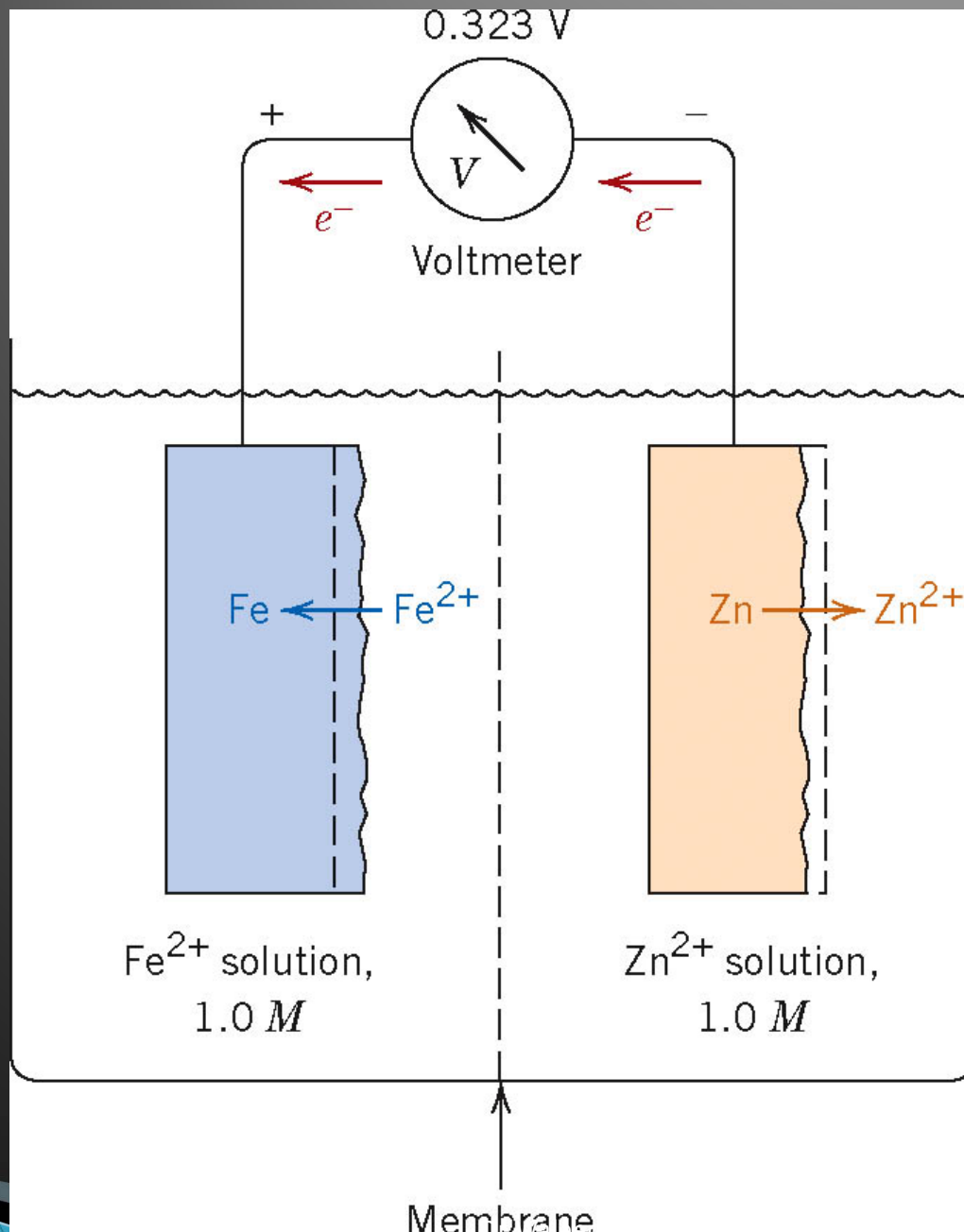
GALVANIC SERIES

- Ranks the reactivity of metals/alloys in seawater

more cathodic (inert)

more anodic (active)

Platinum
Gold
Graphite
Titanium
Silver
316 Stainless Steel
Nickel (passive)
Copper
Nickel (active)
Tin
Lead
316 Stainless Steel
Iron/Steel
Aluminum Alloys
Cadmium
Zinc
Magnesium

Based on Table 17.2, *Callister 7e*. (Source of Table 17.2 is M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

Non Standard Cell

$$\Delta V = \left(V_2^0 - V_1^0\right) - \frac{R.T}{n.F}\ln\left[\frac{M_1^{n+}}{M_2^{n+}}\right]$$

← Oxidation (Anode)

← Reduction (Cathode

R:Gas constant 8.31J/mol-K
T:Temperature in K
n: No. of electrons in half cell
F:faraday no. 96500C/mol

If T=25 C°

$$\Delta V = \left(V_2^0 - V_1^0\right) - \frac{0.0592}{n}\log\left[\frac{M_1^{n+}}{M_2^{n+}}\right]$$

17.5 An Fe/Fe^{2+} concentration cell is constructed in which both electrodes are pure iron. The Fe^{2+} concentration for one cell half is $0.5\ M$, for the other, $2 \times 10^{-2}\ M$. Is a voltage generated between the two cell halves? If so, what is its magnitude and which electrode will be oxidized? If no voltage is produced, explain this result.

17.5 This problem calls for us to determine whether or not a voltage is generated in a Fe/Fe^{2+} concentration cell, and, if so, its magnitude. Let us label the Fe cell having a 0.5 *M Fe^{2+} solution as cell 1, and the other as cell 2. Furthermore, assume that oxidation occurs within cell 2, wherein $[Fe_2^{2+}]$ = 2 x 10–2* *M.*
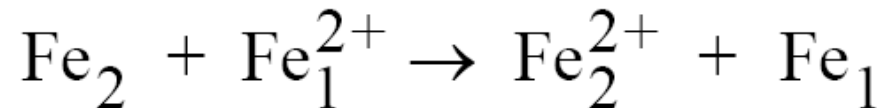
$$Fe_2 + Fe_1^{2+} \rightarrow Fe_2^{2+} + Fe_1$$

$$\Delta V = -\frac{0.0592}{2} \log \frac{[Fe_2^{2+}]}{[Fe_1^{2+}]}$$

$$= -\frac{0.0592}{2} \log \left| \frac{2 \times 10^{-2} \, M}{0.5 \, M} \right| = +0.0414 \, V$$

Therefore, a voltage of 0.0414 V is generated when oxidation occurs in the cell 2, the one having a Fe^{2+} concentration of 2 x 10^{-2} *M.*

17.6 An electrochemical cell is composed of pure copper and pure cadmium electrodes immersed in solutions of their respective divalent ions. For a $6.5 \times 10^{-2} M$ concentration of Cd^{2+}, the cadmium electrode is oxidized yielding a cell potential of 0.775 V. Calculate the concentration of Cu^{2+} ions if the temperature is 25°C.

17.6 We are asked to calculate the concentration of Cu^{2+} ions in a copper-cadmium electrochemical cell. The electrochemical reaction that occurs within this cell is:
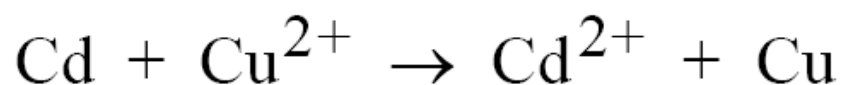
$$Cd + Cu^{2+} \rightarrow Cd^{2+} + Cu$$

while $\Delta V = 0.775$ V and $[Cd2+] = 6.5 \times 10^{-2}$ M. Thus, Equation 17.20 is written in the form:

$$\Delta V = \left(V^{\circ}_{Cu} - V^{\circ}_{Cd} \right) - \frac{0.0592}{2} \log \frac{[Cd^{2+}]}{[Cu^{2+}]}$$

This equation may be rewritten as

$$-\frac{\Delta V - (V_{Cu}^{\circ} - V_{Cd}^{\circ})}{0.0296} = \log \frac{[Cd^{2+}]}{[Cu^{2+}]}$$

Solving this expression for $[Cu^{2+}]$ gives

$$[Cu^{2+}] = [Cd^{2+}] \exp + \left[(2.303) \frac{\Delta V - (V_{Cu}^{\circ} - V_{Pb}^{\circ})}{0.0296} \right]$$

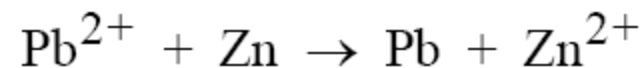The standard potentials from Table 17.1 are $V_{Cu}^{\circ} = +0.340$ V and $V_{Cd}^{\circ} = -0.403$ V. Therefore,

$$[Cu^{2+}] = (6.5 \times 10^{-2} \ M) \exp + \left[(2.303) \frac{0.775 \ V - \{0.340 \ V - (-0.403 \ V)\}}{0.0296} \right]$$

$$= 0.784 \ M$$

17.7 An electrochemical cell is constructed such that on one side a pure Zn electrode is in contact with a solution containing Zn^{2+} ions at a concentration of 10^{-2} M. The other cell half consists of a pure Pb electrode immersed in a solution of Pb^{2+} ions that has a concentration of 10^{-4} M. At what temperature will the potential between the two electrodes be $+0.568$ V?

17.7 This problem asks for us to calculate the temperature for a zinc–lead electrochemical cell when the potential between the Zn and Pb electrodes is +0.568 V. On the basis of their relative positions in the standard emf series (Table 17.1), assume that Zn is oxidized and Pb is reduced. Thus, the electrochemical reaction that occurs within this cell :

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

Thus, Equation 17.20 is written in the form

$$\Delta V = (V_{Pb}^{\circ} - V_{Zn}^{\circ}) - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Pb^{2+}]}$$

Solving this expression for T gives

$$T = -\frac{nF}{R}\left|\frac{\Delta V - (V^{\circ}_{Pb} - V^{\circ}_{Zn})}{\ln\dfrac{[Zn^{2+}]}{[Pb^{2+}]}}\right|$$

The standard potentials from Table 17.1 are $V^{\circ}_{Zn} = -0.763$ V and $V^{\circ}_{Pb} = -0.126$ V. Therefore,

$$T = -\frac{(2)(96,500\ C/mol)}{8.31\ J/mol\text{-}K}\left|\frac{0.568\ V - \{-0.126\ V - (-0.763\ V)\}}{\ln\left(\dfrac{10^{-2}\ M}{10^{-4}\ M}\right)}\right|$$

$$= 348\ K = 75°C$$

Corrosion Rate CPR

$$CPR = \frac{K.W}{\rho.A.t}$$

CPR: Corrosion Penetration Rate

K:Constant

W:Wieght loss

ρ:Density

A:Area

t:time

CPR-units

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mpy (mils per year)                    mm/year
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1/1000 in

K=534

W=milligrams

ρ=g/ cm³

A=in²

t=hr

K=87.6

W=milligrams

ρ=g/ cm³

A=cm²

t=hr

Question

- Prove that for the CPR in mm/year, the constant k is equal to 87.6?

17.11 A piece of corroded metal alloy plate was found in a submerged ocean vessel. It was estimated that the original area of the plate was 800 cm^2 and that approximately 7.6 kg had corroded away during the submersion. Assuming a corrosion penetration rate of 4 mm/yr for this alloy in seawater, estimate the time of submersion in years. The density of the alloy is 4.5 g/cm^3.

_17.11_ This problem calls for us to compute the time of submersion of a metal plate. In order to solve this problem, we must first rearrange Equation 17.23, as

$$t = \frac{KW}{\rho A \, (\text{CPR})}$$

Thus, using values for the various parameters given in the problem statement

$$t = \frac{(87.6)(7.6 \times 10^6 \text{ mg})}{(4.5 \text{ g/cm}^3)(800 \text{ cm}^2)(4 \text{ mm/yr})}$$

$$= 4.62 \times 10^4 \text{ h} = 5.27 \text{ yr}$$

17.12 A thick steel sheet of area 100 in.^{2} is exposed to air near the ocean. After a one-year period it was found to experience a weight loss of 485 g due to corrosion. To what rate of corrosion, in both mpy and mm/yr, does this correspond?

17.12 This problem asks for us to calculate the CPR in both mpy and mm/yr for a thick steel sheet of area 100 in.2 which experiences a weight loss of 485 g after one year. Employment of Equation 17.23 leads to:

$$CPR(mm/yr) = \frac{KW}{\rho A t}$$

$$= \frac{(87.6)(485 \ g)(10^3 \ mg/g)}{(7.9 \ g/cm^3)(100 \ in.^2)(2.54 \ cm/in.)^2(24 \ h/day)(365 \ day/yr)(1 \ yr)}$$

$$CPR(mpy) = \frac{(534)(485 \ g)(10^3 \ mg/g)}{(7.9 \ g/cm^3)(100 \ in.^2)(24 \ h/day)(365 \ day/yr)(1 \ yr)}$$

$$= 37.4 \ mpy$$