



Outline

- Brief Review: *Corrosion*
- Concentration and Temperature Effects
- Example
- Corrosion Rates
- Polarization ↔ Corrosion Rate
 - Activation
 - Concentration
- Passive behaviour



Standard Electromotive Force (EMF) Series

Table 18.1 The Standard emf Series

	Electrode Reaction	Standard Electrode Potential, V^0 (V)
	$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$	+1.420
	$\text{O}_2 + 4\text{H}^+ + 4e^- \longrightarrow 2\text{H}_2\text{O}$	+1.229
	$\text{Pt}^{2+} + 2e^- \longrightarrow \text{Pt}$	+1.2
	$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$	+0.800
	$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$	+0.771
Increasingly inert (cathodic)	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4(\text{OH}^-)$	+0.401
	$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.340
	$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.000
	$\text{Pb}^{2+} + 2e^- \longrightarrow \text{Pb}$	-0.126
	$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	-0.136
	$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$	-0.250
	$\text{Co}^{2+} + 2e^- \longrightarrow \text{Co}$	-0.277
	$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.403
	$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.440
	$\text{Cr}^{3+} + 3e^- \longrightarrow \text{Cr}$	-0.744
Increasingly active (anodic)	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	-0.763
	$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.662
	$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.363
	$\text{Na}^+ + e^- \longrightarrow \text{Na}$	-2.714
	$\text{K}^+ + e^- \longrightarrow \text{K}$	-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: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \quad V^0 = -0.340 \text{ V}$

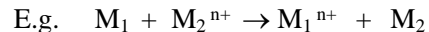


Concentration and Temperature Effects

EMF series is under ideal, standard conditions

- pure metals
- 1M solutions
- 25°C etc.

Changing the purity (.....), temperature or the concentration of ions in the electrolyte changes the potential



Standard cell potential is: $\Delta V^0 = V^0_2 - V^0_1$

General formula is given by Nernst Equation:

$$\Delta V = (V_2^0 - V_1^0) - \frac{RT}{nF} \ln \left(\frac{[\text{M}_1^{n+}]}{[\text{M}_2^{n+}]} \right)$$

Where: n is the number of electrons transferred
 $[\text{M}^{n+}]$ = Molar ion concentrations
 R is the gas constant
 F is the Faraday constant

(96,500 C/mol - charge of 1 mole of electrons). At 25°C, and using \log_{10} rather than natural logs, this becomes:

$$\Delta V = (V_2^0 - V_1^0) - \frac{0.0592}{n} \log \left(\frac{[\text{M}_1^{n+}]}{[\text{M}_2^{n+}]} \right)$$

(Note: If concentrations are 1 M, then Eqn simplifies to $\Delta V^0 = V^0_2 - V^0_1$)



Example

One half of an electrochemical cell consists of a pure nickel electrode in a solution of Ni^{2+} ions; the other is a cadmium electrode immersed in a Cd^{2+} solution.

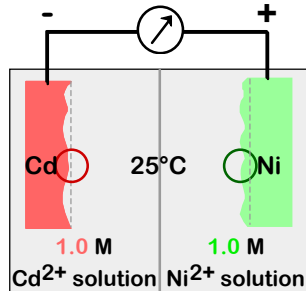
- If the cell is a standard one, write the spontaneous overall reaction and calculate the voltage that is generated.
- Compute the cell potential at 25°C if the Cd^{2+} and Ni^{2+} concentrations are 0.5 and 10^{-3} M, respectively. Is the spontaneous reaction direction still the same as for the standard cell?



Effect of Solution Concentration

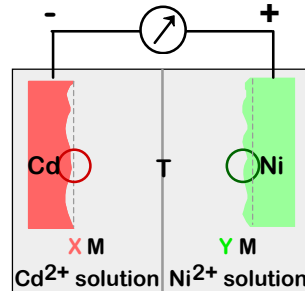
- Ex: Cd-Ni cell with standard 1M solutions

$$V_{Ni}^0 - V_{Cd}^0 = 0.153$$



- Ex: Cd-Ni cell with non-standard solutions

$$V_{Ni} - V_{Cd} = V_{Ni}^0 - V_{Cd}^0 - \frac{RT}{nF} \ln \frac{X}{Y}$$



$n = \#e^-$
per unit
oxid/red
reaction
(=2 here)

- Reduce " $V_{Ni} - V_{Cd}$ " by
 - increasing X
 - decreasing Y



Corrosion Rates

- Real systems are not at equilibrium and short-circuiting often occurs.
- EMF potentials give indication of relative tendencies to dissolve etc but no information on
- Corrosion rates can be measured as Corrosion Penetration Rate (CPR), or *thickness of material lost per unit time*.

For most applications a CPR of **0.5mm/yr** is acceptable (*uniform corrosion*).

$$CPR = \frac{KW}{\rho At}$$

Where:

- ✓ K is a constant (For SI units, $K = 87.6$ and then CPR is given in mm/yr)
- ✓ W is weight loss (mg) after time, t (hrs).
- ✓ ρ is the material density (gcm^{-3})
- ✓ A is the area (cm^2) exposed.

We can also express corrosion rate in terms of current density (*current/unit surface area corroding*).

$$r = \frac{i}{nF}$$

Where:

r is corrosion rate in $\text{mol.m}^{-2}.\text{s}^{-1}$

F is Faraday's constant

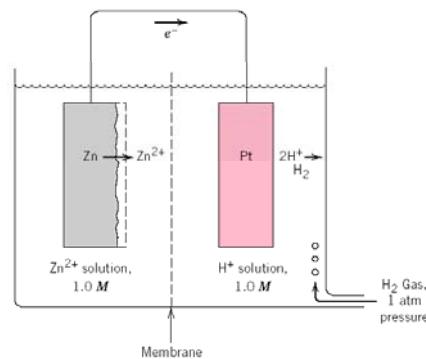
i is current density in A.m^{-2}

n is the number of valence electrons involved.



Corrosion rates and Polarization

- Because of short-circuiting these cells will not be at equilibrium and will not have the standard emf values.
- The difference between standard and real value is called and the value is called the **overvoltage** (η).
- E.g. if actual potential of zinc electrode is -0.621 and standard value is -0.763, η is +0.142 V.



Electrochemical cell consisting of standard zinc and hydrogen electrodes that has been short-circuited.

This difference in voltage can take place by two mechanisms:

- **Activation polarization**
- **Concentration polarization**

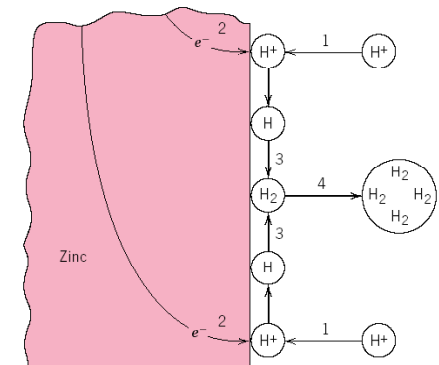


Activation Polarization

- This refers to condition when reaction rate is controlled by the **slowest** step in the process.

I.e. there is an energy barrier related to this slowest step.

- This may be affected by the composition of the metal, etc.



Schematic representation of possible steps in the hydrogen reduction reaction, the rate of which is controlled by activation polarization.

The slowest of these steps determines the rate of the overall reaction



Activation Polarization

For activation polarization: $\eta_a = \pm \beta \log \frac{i}{i_o}$

Where β and i_o are constants for the particular halfcell

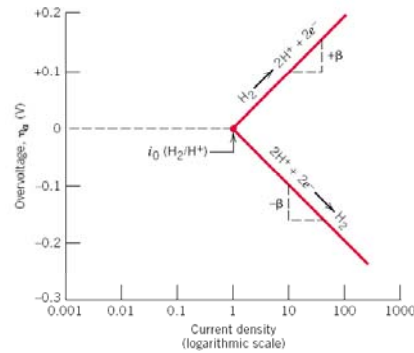
i_o is the **exchange current density**

At equilibrium: $r_{red} = r_{oxid} = \frac{i_o}{n F}$

i_o is determined experimentally and it varies from system to system

Slope = $+\beta \rightarrow$ oxidation

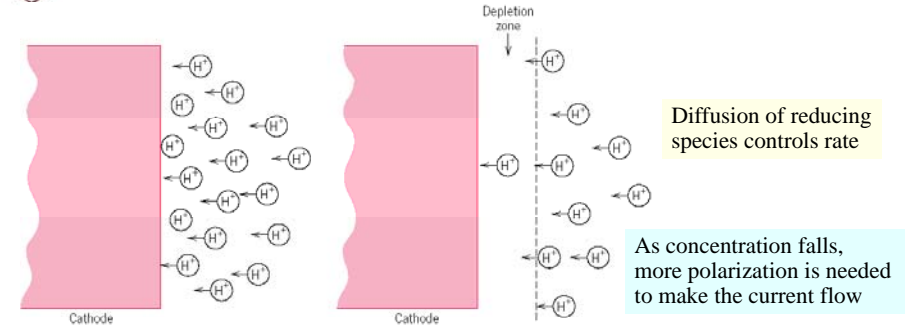
Slope = $-\beta \rightarrow$ reduction



For a hydrogen electrode, plot of activation polarization overvoltage versus logarithm of current density for both oxidation and reduction reactions.



Concentration Polarization



- Build-up or depletion of ions near electrode can affect reactions because the current density is reduced.
- If reaction rate is **low** and/or **concentration** of ions is **high** then there is always a **good supply of H⁺** ions near the electrode surface.
- If reaction rate is **high** and /or concentrations are **low**, will get a around electrode so **reduction** reaction is slowed down (if reduction reaction is slowed - so must be the oxidation reaction)



Corrosion Rates from Polarization Data

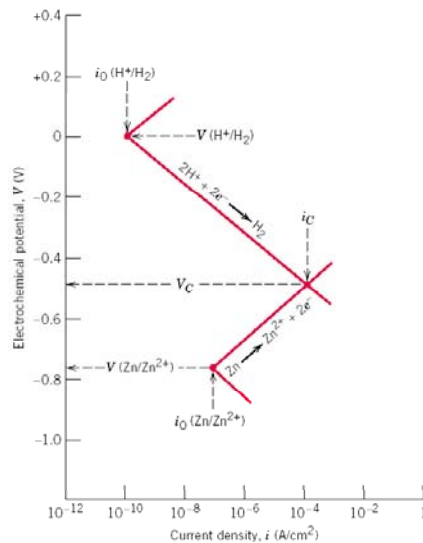
• Rates of oxidation and reduction so only possible where two lines intersect.

• This is the corrosion potential, V_C , and the corrosion current density, i_C .

• These values can then be used to predict **corrosion rate**.

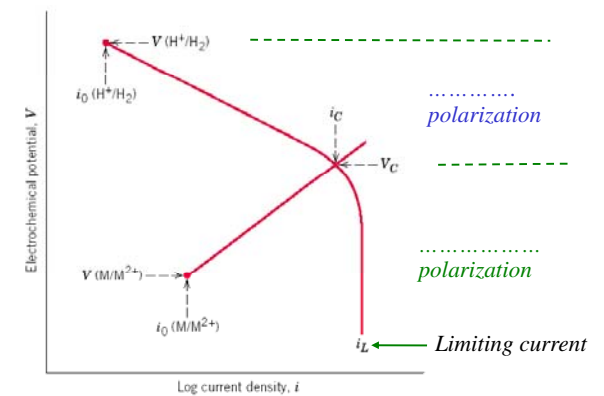
Recall that corrosion rate is proportional to current density. (So the higher i_C is, the faster the corrosion rate.)

$$r = \frac{i}{nF}$$



Corrosion Rates from Polarization Data

Both concentration and activation polarization are possible for reduction reactions. Under these circumstances, the **total overvoltage** is just the **sum** of both overvoltage contributions.



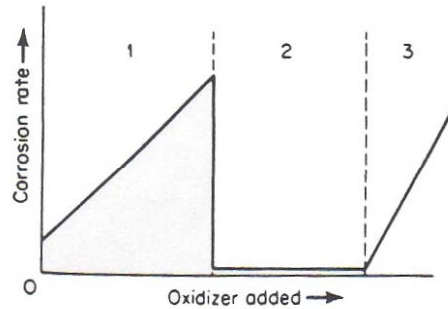
Schematic electrode kinetic behavior for metal M ; the reduction reaction is under combined activation-concentration polarization control.



Passive Behavior

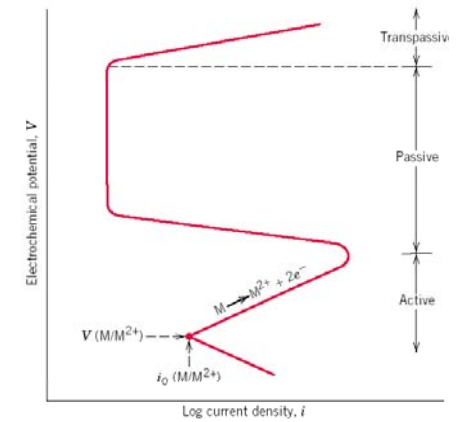
Some metals cease to be reactive under the right conditions

1. Active Behavior
2. Passive Behavior
3. Transpassive



Passivity

- Under certain environments some metals/alloys become inert (passive).
- E.g. **Chromium**, nickel, titanium, iron... Usually by formation of thin, protective, surface oxide film. **Stainless steels** (>11%Cr) develop Cr_2O_3 layer which in many environments is protective. **Aluminum** forms Al_2O_3 layer. If damaged (scratched etc) normally reforms rapidly.
- In some environments this layer **breaks** down and material becomes “**active**” again.

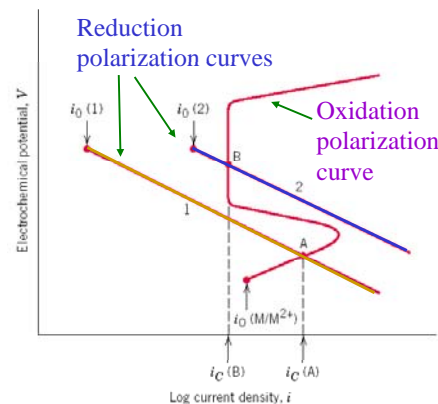


Schematic polarization curve for a metal that displays an active-passive transition.



Passivity

- **Curve 1** intersects the oxidation polarization curve in the **active region** at point A, yielding a corrosion current density $i_C(A)$.
- The intersection of **curve 2** at point B is in the **passive region** and at current density $i_C(B)$.
- The corrosion rate of metal M in solution 1 is **greater** than in solution 2 since $i_C(A)$ is greater than $i_C(B)$
- This difference in corrosion rate between the two solutions may be **significant** (several orders of magnitude) when one considers that the current density scale in is scaled **logarithmically**.



Demonstration of how an active-passive metal can exhibit both active and passive corrosion behavior.



Example - Corrosion of Iron

An iron container 10 cm × 10 cm at its base is filled to a height of 20 cm with a corrosive liquid. A current is produced as a result of an electrolytic cell, and after 4 weeks, the container has decreased in weight by 70 g. Calculate (1) the current and (2) the current density involved in the corrosion of the iron.

SOLUTION:

1. The total exposure time is:



Example - Copper-Zinc Corrosion Cell

Suppose that in a corrosion cell composed of copper and zinc, the current density at the copper cathode is 0.05 A/cm^2 . The area of both the copper and zinc electrodes is 100 cm^2 . Calculate (1) the corrosion current, (2) the current density at the zinc anode, and (3) the zinc loss per hour.

SOLUTION

1. The corrosion current is:
2. The current in the cell is the same everywhere. Thus:
3. The atomic mass of zinc is 65.38 g/mol . From Faraday's equation:



Next time:
Continue Corrosion