U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

Fundamentals of Corrosion

Human Resources
Training & Development

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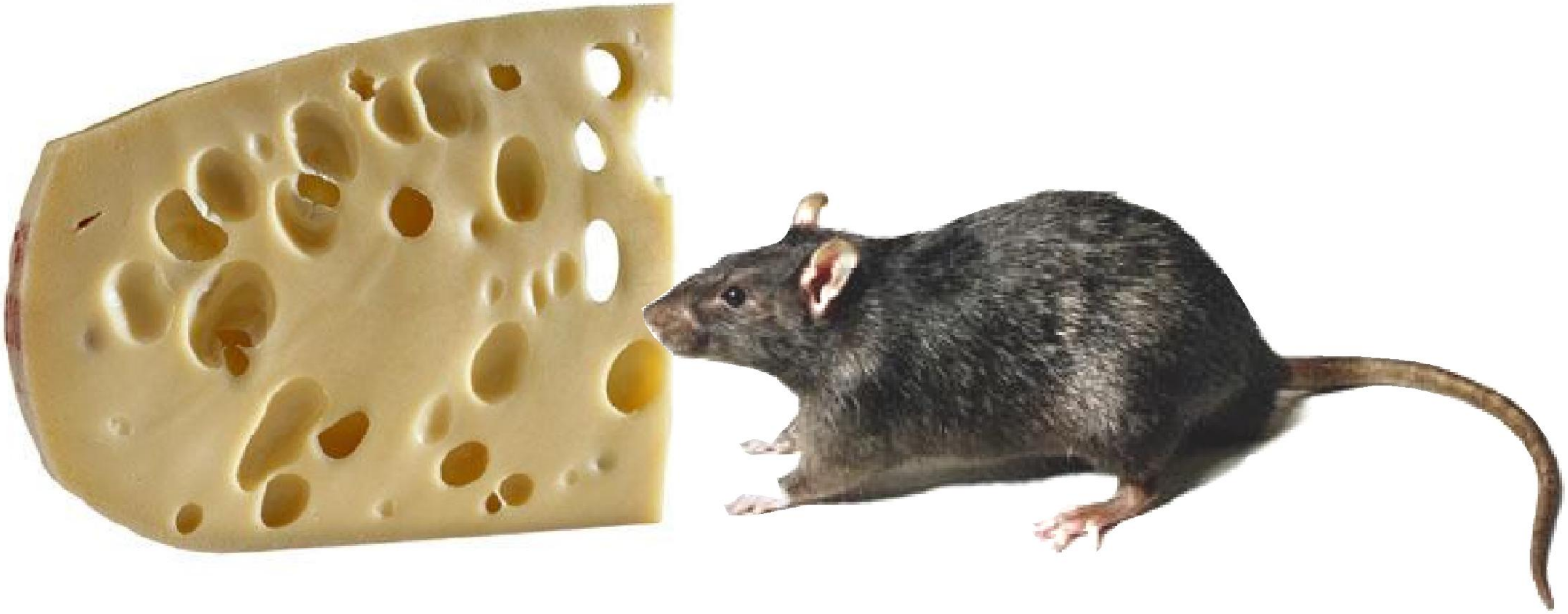
Fundamentals of Corrosion
Learning Objectives

- Understand why metals corrode
- Learn the fundamentals of electrode potential
- Learn components that make up the basic corrosion cell – anode and cathode
- Understand the thermodynamics, i.e., the driving force, of corrosion – Pourbaix Diagrams
- Understand kinetics of corrosion – Evans Diagrams
- Passivity – the key to LWR materials performance

Latin Origin of “Corrosion”



Latin - *Rodere* - To Gnaw

Rodent

Corrode

R. Staehle, Corrosion 2004

What is Corrosion and Why do Metals Corrode?

- Corrosion is the deterioration of a metal or its <u>properties</u> due to a reaction with its environment
- Involves electron transfer, i.e., the loss of its “glue”
- Corrosion is a natural reaction, it’s “green”
  - In the beginning, there were rocks…..
  - Corrosion and Punishment
  - Death, Taxes and Corrosion
  - Rust in Peace
  - Rust’s a Must

Rust's a Must

Mighty ships upon the ocean
Suffer from severe corrosion,
Even those that stay at dockside
Are rapidly becoming oxide
Alas that piling in the sea
Is mostly Fe_2O_3
And where the ocean meets the shore
You'll find there's Fe_3O_4
'Cause when the wind is salty and gusty
Things are getting awful rusty

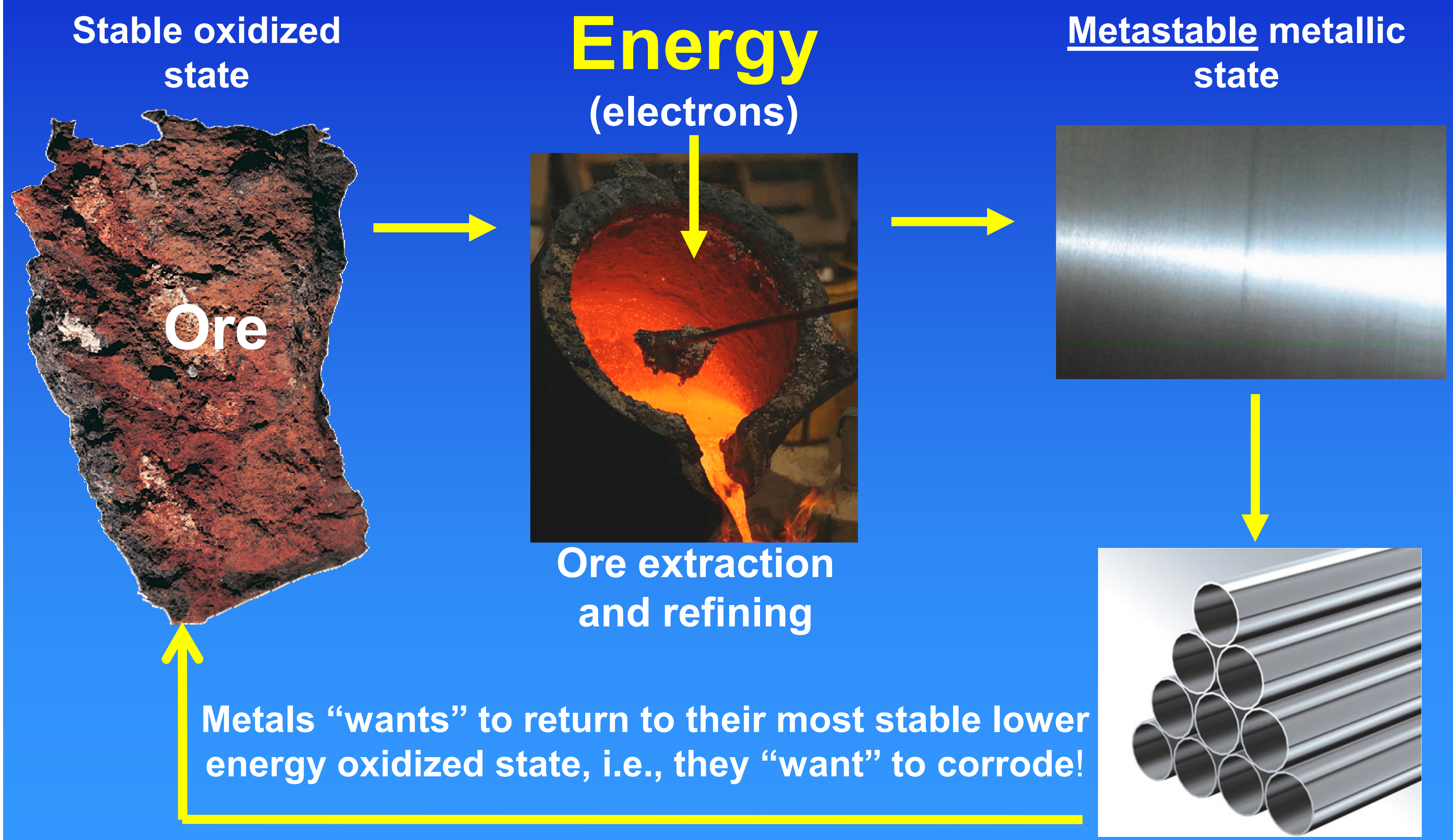
We can measure it we can test it,
We can halt it or arrest it,
We can gather it and weigh it,
We can coat it, we can spray it,
We examine and dissect it,
We cathodically protect it,
We can pick it up and drop it,
But heaven knows, we can never stop it.

So here's to rust, no doubt about it,
Most of us would starve without it.

T. R. B. Watson, June 1974

Corrosion was a Big Problem even in the Middle Ages

Reduction of a Mineral to a Metal



Stable oxidized state

Energy

(electrons)

<u>Metastable</u> metallic state

Ore extraction and refining

Metals “wants” to return to their most stable lower energy oxidized state, i.e., they “want” to corrode!

Thermodynamics vs. Kinetics

- All metals/alloys are basically chemicals and can, in some environments, dissolve like table salt in water
- Surprise is not that metals/alloys degrade due to corrosion; the surprise is that they actually work
- Longevity of a metal/alloy depends on the kinetics of the corrosion reaction. Not on thermodynamics!
  - Thermodynamically, you’re screwed!

Corrosion True or False

1. Concentrated acids are more corrosive than dilute acids ☐
2. Acids are more corrosive than bases ☐
3. Hot water is more corrosive than cooler water ☐
4. Increasing the conductivity of the environment will increase the corrosion rate ☐
5. Boric acid is a strong acid ☐
6. Stainless steel is more corrosion resistant than carbon steel ☐
7. Coating a component will increase its life expectancy ☐
8. Corrosion is always undesirable ☐

Metals, Oxides and Cations

- Metal atoms have equal numbers of positive and negative charges, i.e., protons (+) and electrons (-)
- Difference between a metal and its oxide is that a metal has electrically neutral atoms (Fe^0) while oxides have metallic atoms that are positively charged due to the loss of electrons (Fe^{2+})
- An atom that loses an electron is a metal ion (cation) and carries a positive charge. Example: Zn^{2+}

Two metal atoms are walking down the street and meet each other. One says to the other, "Are you OK? "No, I just lost an electron!" "Are you sure?" "Yes. I'm positive!"

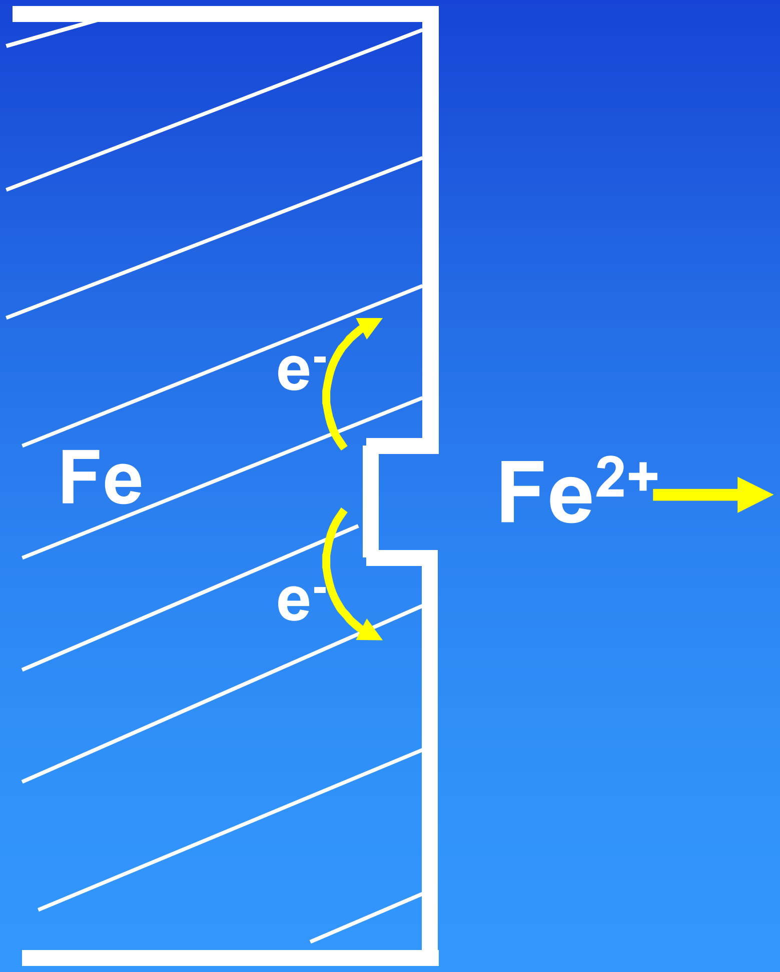
Electrons and Electron Transfer

- Extra electrons are the bonding agent or “glue” that holds metals together
- Metal atoms will attempt to reject this added electron to return to more natural (lower energy) state (an oxide), i.e., a decrease in free energy, ΔG
- If this electron is consumed by an electron acceptor, a corrosion reaction can occur
- This electron transfer process is the essence of the corrosion reaction

Metals in Water

- When a metal is placed in water, there is a thermodynamically-driven tendency for the metal atoms to change into the ionic state, as measured by E, and enter the solution
- Since a continuous flow of metal ions (cations) into the solution is reduced by a mutual repulsion from a boundary layer of cations already in the solution, an equilibrium is established
- Since this boundary layer consists of positive charges, a potential difference will exist between the boundary layer and the metal that now has a net negative charge

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

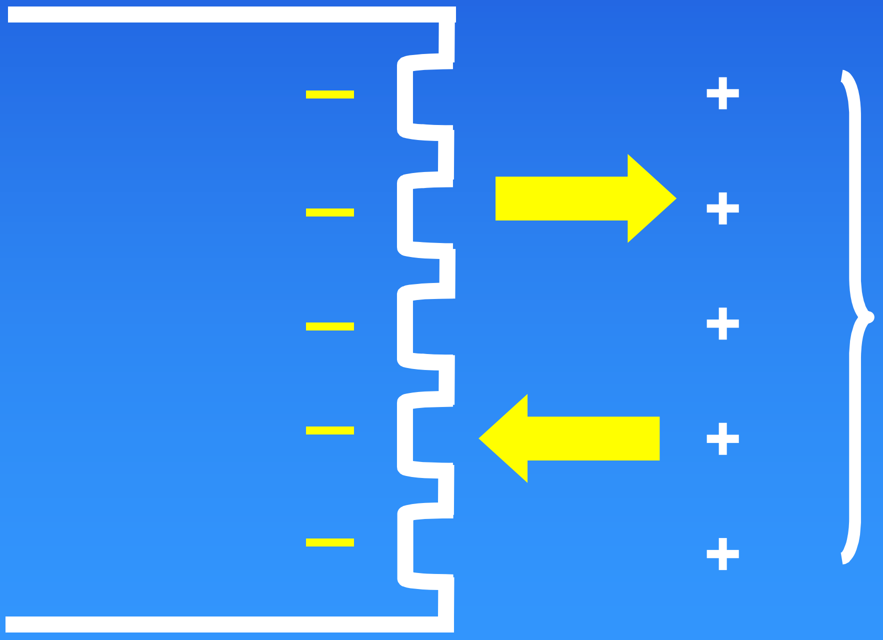


Electrode Potential

- The “electrode potential” (E) is a measure, under certain fixed conditions, of the ***thermodynamic*** tendency of a metal to undergo a corrosion reaction (lose an electron)
- E provides no information concerning kinetics!!
- Five major factors affect electrode potential:
  - Metal purity and condition
  - Metal ion concentration in the electrolyte (Nernst Equation)
  - Other ions in the electrolyte
  - Temperature
  - Current flow

Half Cell

The potential difference of this system consisting of the metal and a solution of its ions, known an electrode, can be measured, if combined with another “half cell” electrode forming a battery



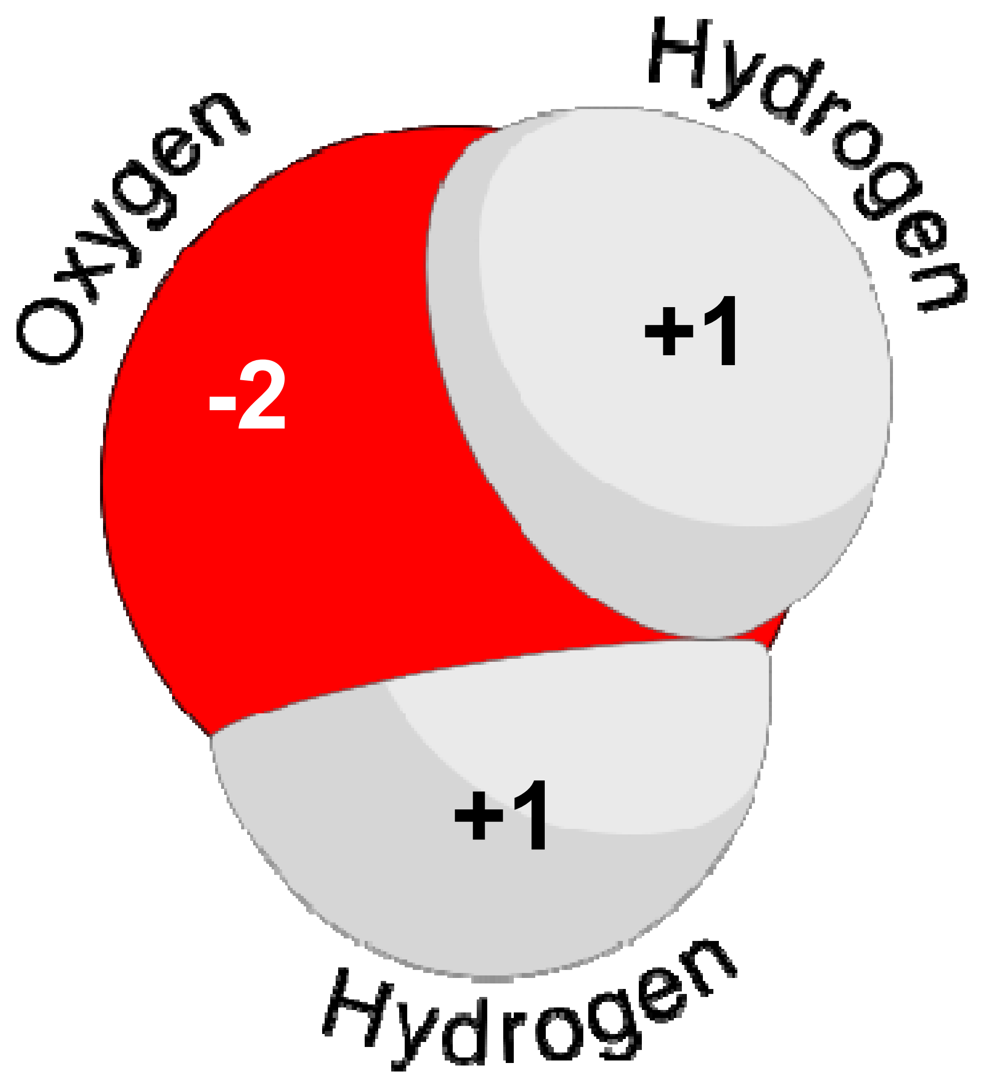
Metal Ions

Example of the Establishment of Ionic Equilibrium in a Solution

Electrode Surface

- Conducting metal surface containing mobile electrons forms a complex interface in contact with water:
  - Charge on cation will attract species of opposite charge
  - Dipoles in the solvent (e.g., water) will align with the cations
  - Forms a layer of charge in both the metal and the electrolyte

Polar Water Molecule



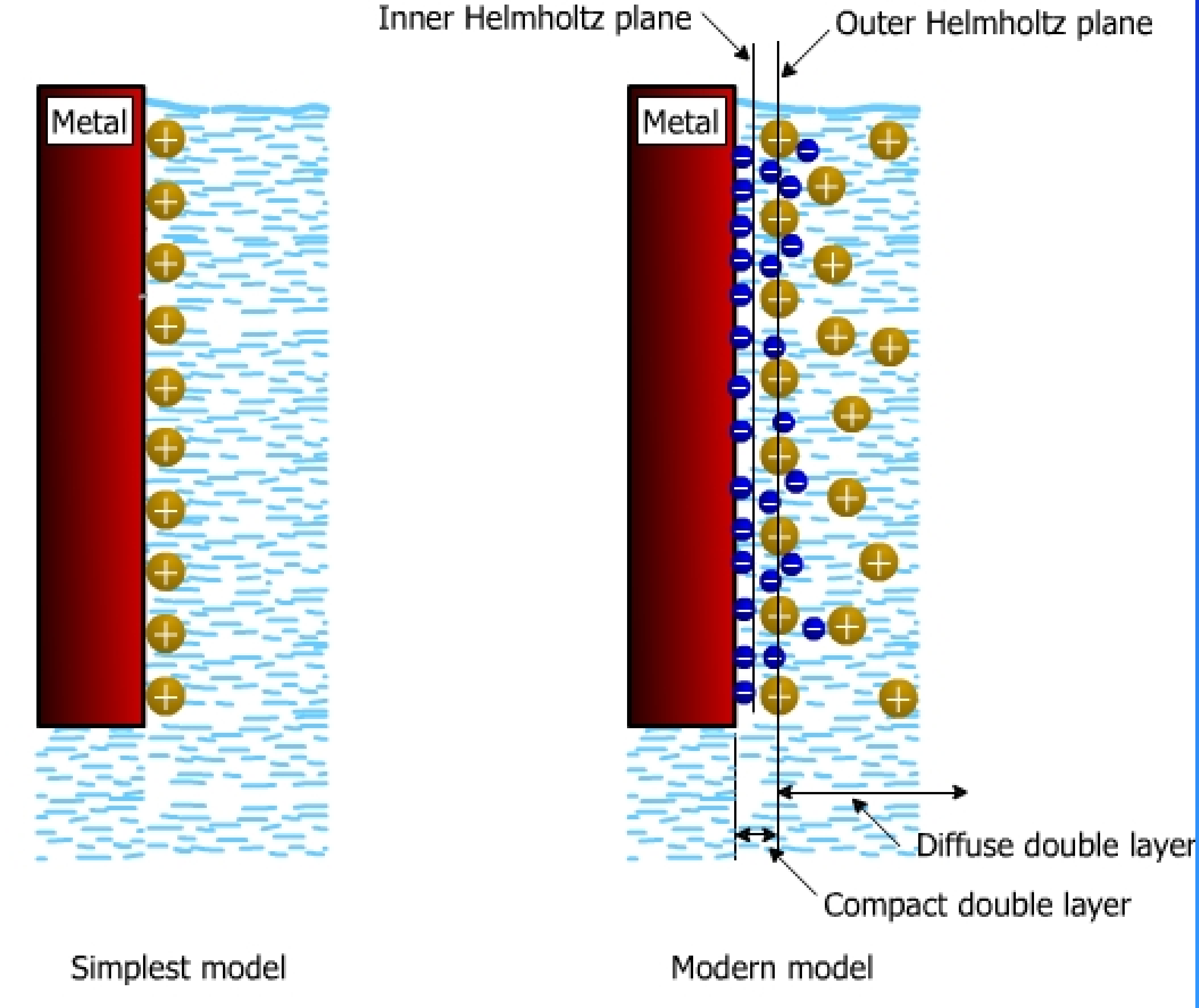
Electrode Surface (continued)

- When a metal dissolves, it becomes increasingly negatively charged because of passage of continuous positive ions (cations) in the solution
- Excess negative charge on the metal surface balances the excess positive charge and the solution side of the interface and hence, a separation of charges exists
- Electrons orient themselves opposite a layer of cations of equal and opposite charges on the solution side of the interface
- Electric field that is created consists of two layers of charges, i.e., a double layer
    - Separation of charges in the double layer can be compared to parallel plates in a capacitor as it was done by Helmholtz. The double layer is also called Helmholtz Double Layer.

Helmholtz Double Layer

Hermann von Helmholtz

1821–1894

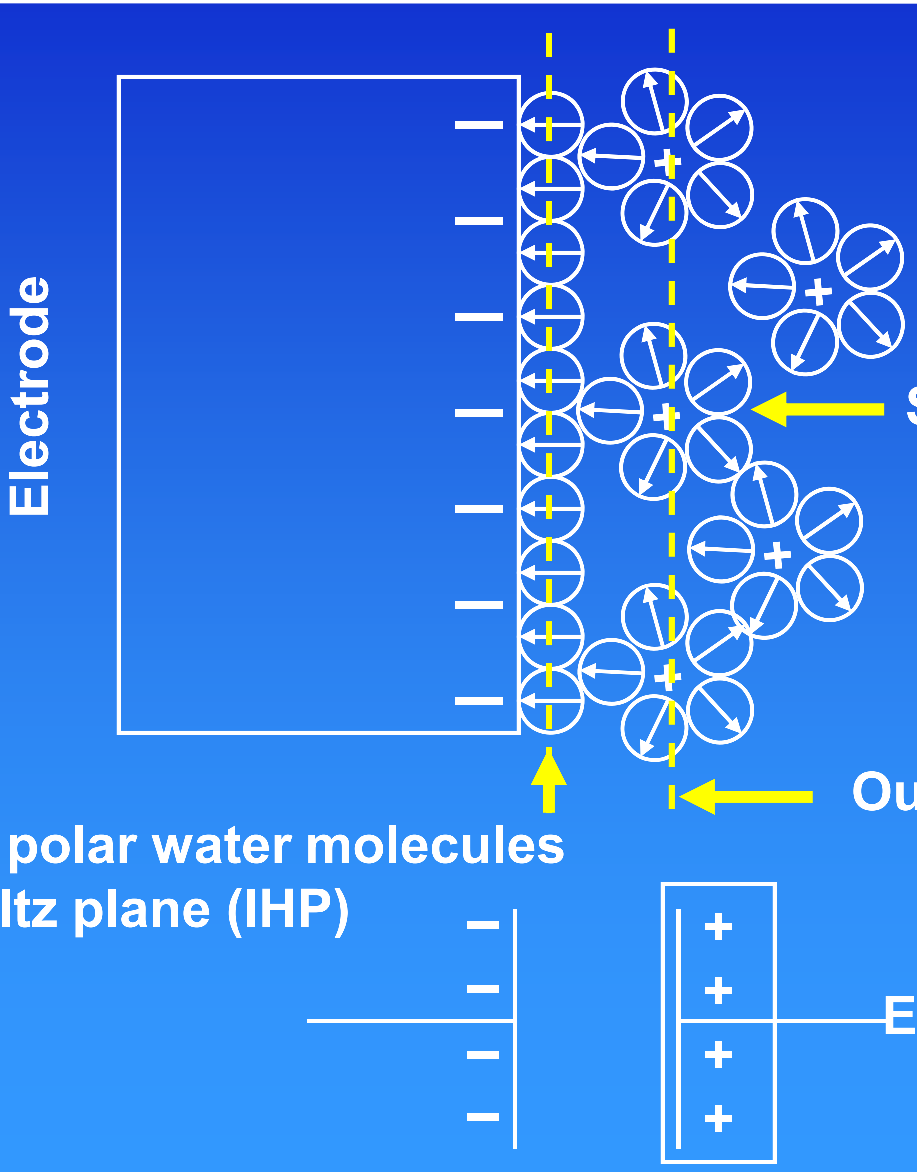


Simplest model

Modern model

The Electric Double Layer

Schematic Electrode Surface



Solvated cations

Outer Helmholtz plane (OHP)

Inner layer of polar water molecules
Inner Helmholtz plane (IHP)

Equivalent capacitor

Final Four of Corrosion

Corrosion in aqueous solutions can occur if, and only if, the following <u>four</u> fundamental parameters are simultaneously present:

1. Anode
2. Cathode

} 2 electrodes

3. Ionic circuit
4. Electrical circuit

} 2 circuits

Which corrosion parameter is the "easiest" to eliminate? How can you do it?

The elimination of any one of these necessary four fundamental parameters absolutely <u>prevents</u> corrosion!

Anode

Anode is the portion of the metal surface that is “corroding” or being oxidized and from which ionic current leaves the metal to enter the electrolyte. Anode characteristics:

- Oxidation, increase in valence ($Fe^0 \rightarrow Fe^{2+} + 2e^-$)
- Loses electrons (loses “glue”)
- Attracts anions (negatively charged ions such as Cl^- and SO_4^{-2})
- Positive (attracts anions) and negative (source of electrons) (See details of basic corrosion cell)
- Anode is the electrode that attracts anions

Cathode

Cathode is the metal surface from which the ionic current leaves the solution and returns to the metal. Cathode characteristics:

- ♦ Reduction, decrease in valance $(2H^+ \rightarrow H_2)$
- ♦ Gains electrons (gains "glue")
- ♦ Attracts cations (positively charged ions such as H^+ and Na^+)
- ♦ Positive (attracts electrons) and negative (attracts cations) (See details of basic corrosion cell)
- ♦ Cathode is the electrode that attracts cations

Keeping Your Electrodes Straight

- Oxidation occurs at the anode (both words begin with vowels)
- Reduction occurs at the cathode (both words begin with consonants)
- LEO the lion roars GER:
  - Lose Electrons → Oxidation
  - Gain Electrons → Reduction

Leo

Electrode Reactions

- Only one basic metal anodic/oxidation/ “corrosion” reaction:
  - $M \rightarrow M^{n+} + ne^-$
- Several possible cathodic reduction reactions in aqueous environments:
  1. Hydrogen gas generation: $2H^+ + 2e^- \rightarrow H_2$
  2. Water decomposition: $2H_2O + 2e^- \rightarrow H_2 + 2(OH)^-$
  3. Hydroxyl formation: $O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$
  4. Water formation: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
  5. Electroplating: $M^{n+} + ne^- \rightarrow M$

What species are being reduced in each one of these reduction reactions?

BWR Anodic and Cathodic Reactions

- Two Anodic Reactions
  - $M \rightarrow M^{n+} + ne^-$
  - $H_2 \rightarrow 2H^+ + 2e^-$

- Two Cathodic Reactions
  - $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
  - $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

PWR Anodic and Cathodic Reactions

- Two Anodic Reactions
  - ♦ $M \rightarrow M^{n+} + ne^-$
  - ♦ $H_2 \rightarrow 2H^+ + 2e^-$
- One Cathodic Reaction
  - ♦ $2H_2O + 2e^- \rightarrow H_2 + 2(OH)^-$

Why is there only one PWR cathodic reaction while there are two BWR PWR cathodic reactions?

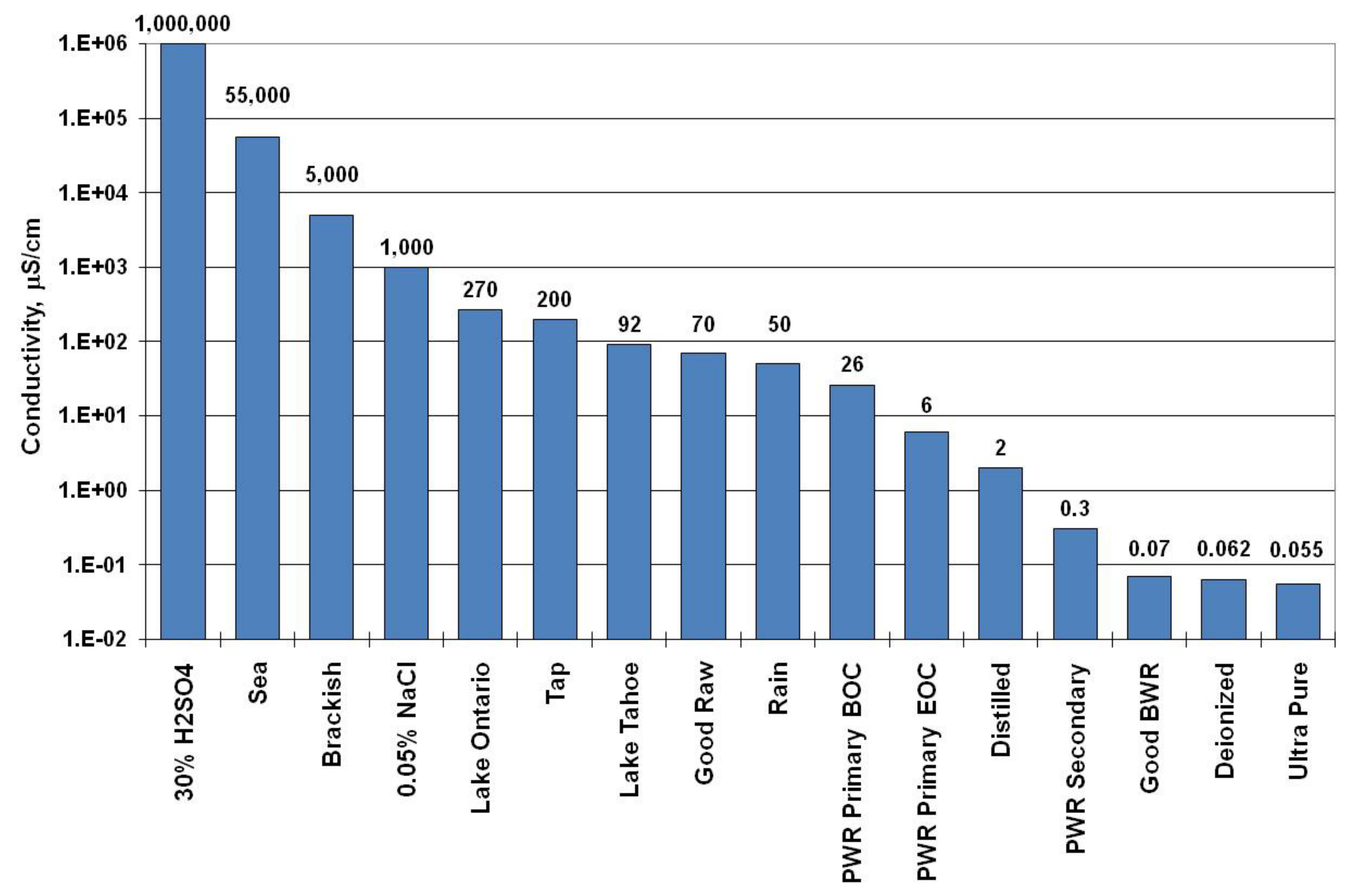
Electrolyte: Conductivity

- Solution or suspension capable of conducting electricity
  - ♦ Does the electrolyte have to be a liquid?
- Its ability to conduct electricity is due to the presence of ions in the solution
- Although water is a low conducting molecular liquid, it does conduct electricity
- Water's conduction is due to the presence of H^+ and OH^-
- Conductivity is expressed in µS/cm (was µmho/cm until the late 1970s)

What are microSiemens/centimeter (µS/cm)?

- Units for electrical conductivity
- Sensor consists of two metal electrodes that are 1.0 cm apart and protrude into the water
- Constant voltage is applied across the electrodes
- Current flows through the water due to this voltage and is proportional to the concentration of dissolved ions in the water
  - More ions = higher conductivity
  - Results in a higher measured electrical current
- Note: Japanese use µS/m

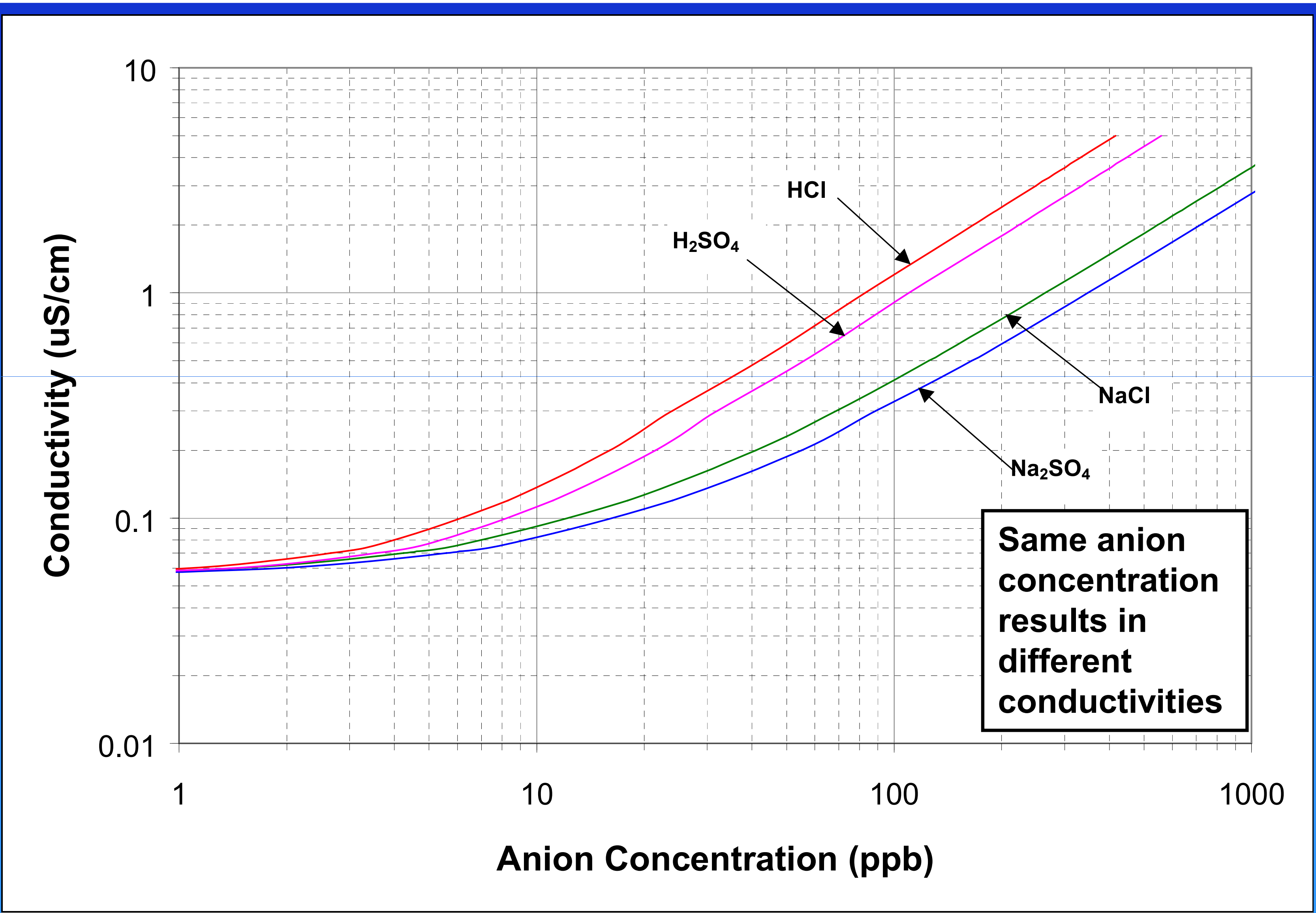
Spectrum of Water Conductivities



Low RH on Aircraft: Why?

- In-flight air is drier than any of the world's deserts!
  - RH is 20-25% in the Sahara or Arabian deserts
  - Optimum comfort is ~50% RH
- In-flight cabin RHs gradually decrease on long-distance, high-altitude flights approaching 1%!
- Two main motivations:
  1. Mitigate bacteria, fungi and molds that can produce/aggravate human respiratory problems
  2. Mitigate corrosion fatigue of structural aircraft components – cannot inspect every component, thus, control the electrolyte!

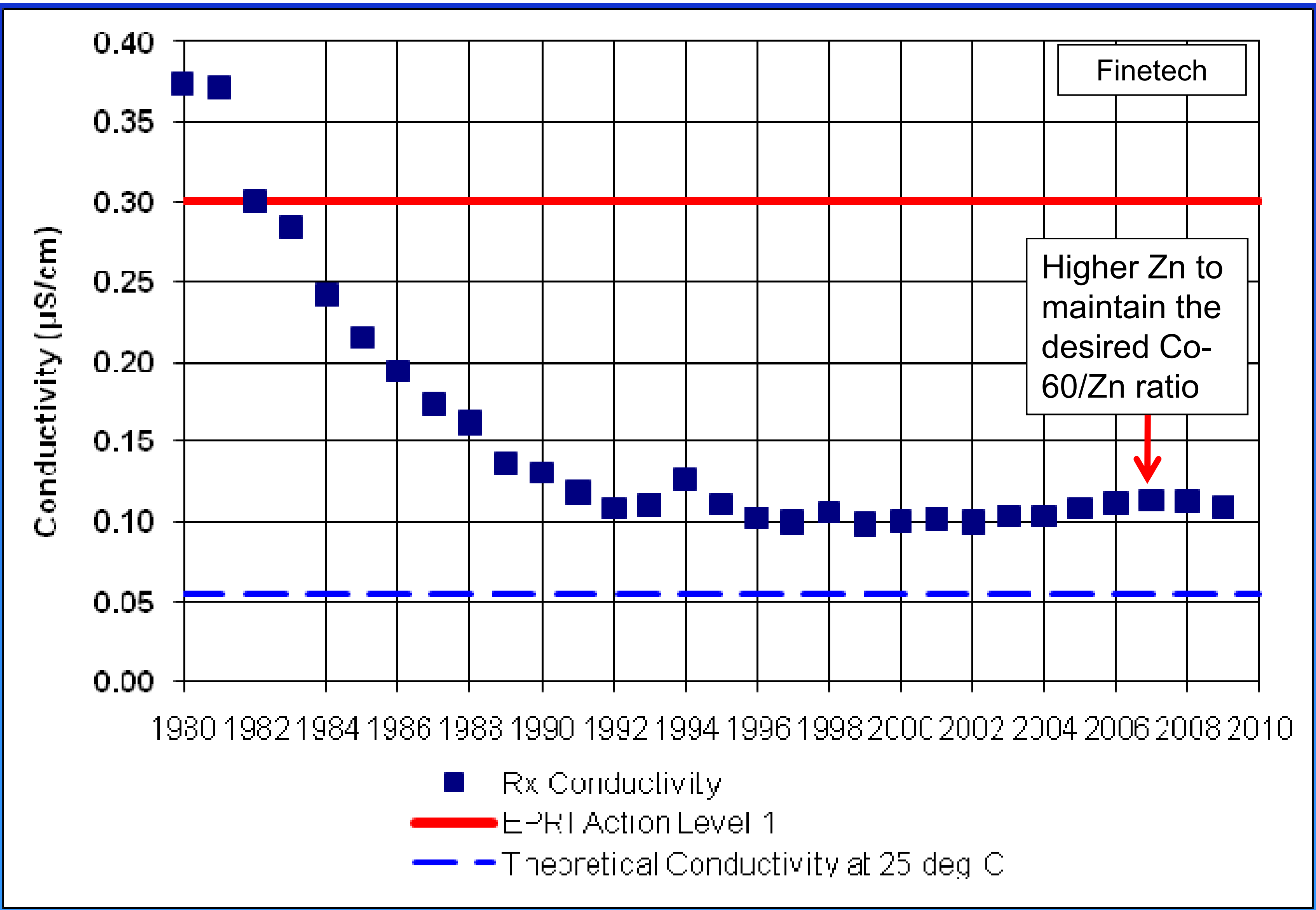
Conductivity as a Function of Cl^- and $SO_4^=$ Concentration at 25°C



Same anion concentration results in different conductivities

Corrosion and Corrosion Control in LWRs

Mean BWR Reactor Water Conductivity



Electrolyte: pH

- 1909 - Sören Sörensen (Denmark) invented the pH scale for measuring acidity
- pondus hydrogenii (Latin), pouvoir hydrogène (French), power of hydrogen = the log of the reciprocal of hydrogen ion concentration in moles per liter, i.e., $pH = -\log[H^+]$
- Provides a handy means, typically on a scale from 0 to 14, of the relative acidity or alkalinity of a solution
- In neutral water, the concentrations of $H^+ = OH^- = 10^{-7}$ moles/L (molarity = moles of solute/liter of solvent)
  - 7 is neutral at 25ºC
  - <7 is acidic at 25ºC
  - >7 is basic at 25ºC

Sören Sörensen
1868–1939

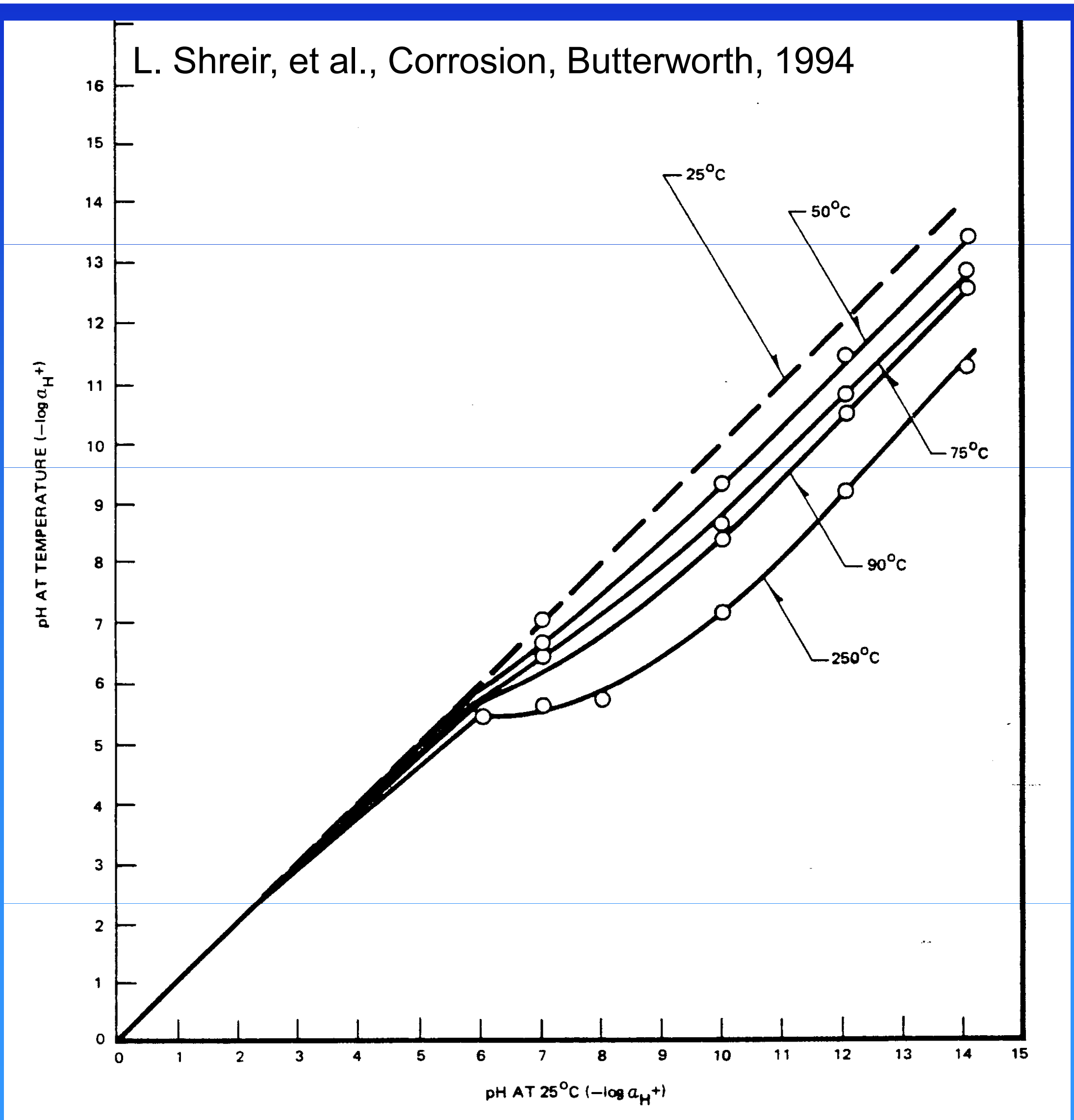
pH affects the stability of surface oxides

pH Examples

	$[H^+]$	pH	Example
Acids	1×10^{0}	0	HCl
	1×10^{-1}	1	Stomach acid
	1×10^{-2}	2	Lemon juice
	1×10^{-3}	3	Vinegar
	1×10^{-4}	4	Soda, Boric Acid
	1×10^{-5}	5	Rainwater
	1×10^{-6}	6	Milk
Neutral	1×10^{-7}	7	Pure water
Bases	1×10^{-8}	8	Egg whites
	1×10^{-9}	9	Baking soda
	1×10^{-10}	10	Tums® antacid
	1×10^{-11}	11	Ammonia
	1×10^{-12}	12	Mineral lime - $Ca(OH)_2$
	1×10^{-13}	13	Drano®
	1×10^{-14}	14	NaOH

pH of Coca-Cola Classic® = 2.5!

Effect of Temperature on pH in Pure H_2O



L. Shreir, et al., Corrosion, Butterworth, 1994

- Equilibrium/dissociation constant:

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

- pH = log $1/[H^+]$ = $-\log[H^+]$
- pH + pOH = 14
- pH changes with T because K_w decreases from 1×10^{-14} (e.g., $K_w = 1 \times 10^{-11.2}$ at 288°C)

What is neutral pH at 288°C?

Acids and Bases

- 1884 definition of Svante Arrhenius (Sweden)
  - An acid is a material that can release a proton or hydrogen ion (H+) (e.g., HCl)
  - A base, or alkali, is a material that can donate a hydroxide ion (OH-) (e.g., NaOH)


1859 - 1927

Properties of Acids

- Acids release H^+ into water
- Acids neutralize bases in a neutralization reaction
  - An acid and a base combine to make a salt + water
  - A salt is any ionic compound that could be made with the anion of an acid and the cation of a base
- Acids turn blue litmus paper red
- Acids taste sour
  - “Sauer” in German means acid

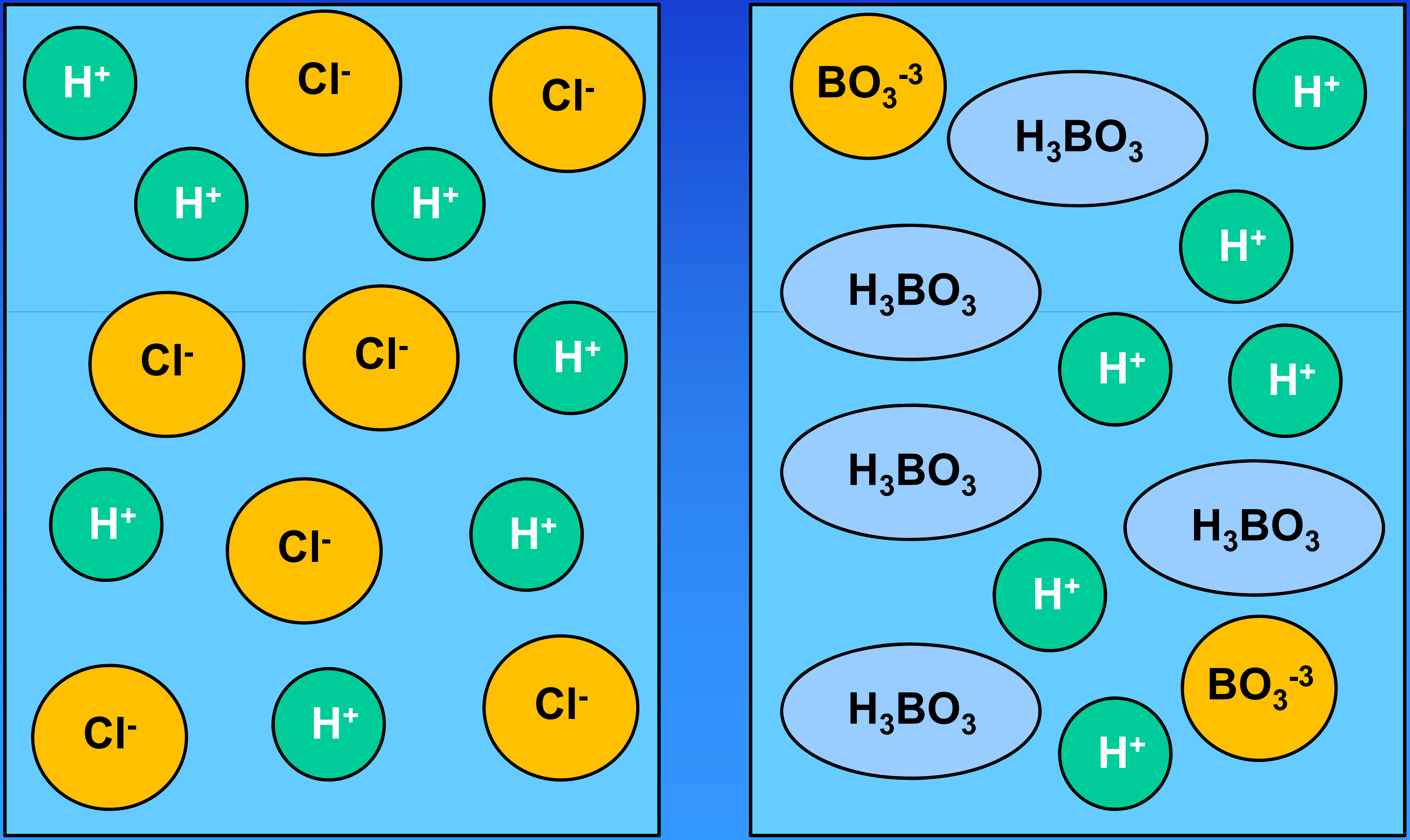
Strong and Weak Acids

- Strong acids are acids that are almost 100% ionized. There are only 6 strong acids:
  - HNO_3 - nitric acid HCl - hydrochloric acid
  - H_2SO_4 - sulfuric acid $HClO_4$ - perchloric acid
  - HI - hydroiodic acid HBr - hydrobromic acid
  - Do not confuse strong acids with concentrated acids
- All other acids are weak acids, i.e., are incompletely ionized
  - Do not confuse weak acids with dilute acids
  - H_3BO_3 - boric acid is a weak acid!

Strong vs. Weak Acids

Strong Acid HCl

Weak Acid H_3BO_3



Properties of Bases

- Bases release OH^- into water
- Bases neutralize acids in a neutralization reaction to form a salt + water
- Bases turn red litmus paper blue
- Bases taste bitter
- Bases detrimentally alter protein
  - ♦ Accounts for the “slippery” feeling on hands when exposed to base
  - ♦ Strong bases are very dangerous because human beings are made of protein
    - ○ Drāno®

Strong and Weak Bases

- Strong bases are bases that are almost 100% ionized. There are only 9 strong bases:
  - LiOH - lithium hydroxide
  - KOH - potassium hydroxide
  - $Ca(OH)_2$ - calcium hydroxide
  - CsOH - cesium hydroxide
  - $Ba(OH)_2$ - barium hydroxide
  - NaOH - sodium hydroxide
  - $Mg(OH)_2$ - magnesium OH
  - RbOH - rubidium OH
  - $Sr(OH)_2$ - strontium OH
  - Do not confuse strong bases with concentrated bases
- All other bases are weak bases, i.e., are incompletely ionized
  - Do not confuse weak bases with dilute bases

Drāno® Corrosion Chemistry

- $NaOH + NaNO_3 + NaCl + Al$ (Harry Drackett 1923)
  - $NaOH$, $NaNO_3$ and $NaCl$ dissolve
  - $NaOH$ removes Al's passive film!
  - Machined shards of Al react with $NaOH + H_2O \rightarrow H_2$ + heat → boiling:
    - $2NaOH + 2Al + 2H_2O \rightarrow 2H_2 + 2NaAlO_2$
  - H_2 reduces NO_3 to NH_3 (BWR!), removing the fire and explosion hazard posed by free H_2 gas:
    - $2NO_3^- + 9H_2 \rightarrow 2NH_3 + 6H_2O$
- Sharp Al shards in the hot churning solution physically cut hair and dislodge deposits

Tutorial on ppm, ppb and ppt

- LWRs typically measure additives and impurities in ppm or ppb
  - ppm is part per million by weight
  - 1 ppm = 10^{-6} = 0.0001%
  - 1 ppm = 1 mg/liter = 1 mg/kg

  - ppb is part per billion by weight
  - 1 ppb = 10^{-9} = 0.0000001%
  - 1 ppb = 1 μg/liter = 1 μg/kg
  - 1000 ppb = 1 ppm

  - ppt is part per trillion by weight
  - 1 ppt = 10^{-12} = 0.0000000001%
  - 1 ppt = 1 ng/liter = 1 ng/kg
  - 1000 ppt = 1 ppb

PWR LiOH + H_3BO_3

- LiOH is a strong base (to mitigate general corrosion of Fe-base alloys)
- H_3BO_3 is a weak acid (a chemical shim to control of core reactivity)
- Since H_3BO_3 is such a weak acid, it is present in much higher concentrations compared to LiOH in the PWR:
  - ~1400 ppm boron as H_3BO_3
  - ~2 ppm lithium as LiOH

LWR Gas Units

- BWRs add hydrogen to mitigate IGSCC
  - As measured by ppm in reactor coolant
  - As measured standard cubic meter/second (SCMS) or standard cubic feet/minute (SCFM) in the feedwater
- PWRs add hydrogen to enhance the nuclear reaction physics and (now) to mitigate PWSCC
  - As measured by cc H_2/kg water
  - 1 cc/kg H_2 = 0.089 ppm H_2
  - 1 cc/kg O_2 = 1.43 ppm O_2

Two BWR Electrolytes

- Normal water chemistry (NWC) – “abnormal WC”
  - 288°C (550°F), <0.1 μS/cm conductivity
  - No additives, pH 5.6 (neutral at 288°C [550°F])
  - ~200 ppb dissolved O_2 + ~20 ppb dissolved H_2 in piping
  - SS corrosion potential ~ +100 mV(SHE)
- Hydrogen water chemistry (HWC)
  - 288°C (550°F), <0.1 μS/cm conductivity
  - pH 5.6 (neutral at 288°C [550°F])
  - <20 ppb dissolved O_2 + ~200 ppb dissolved H_2 in piping
  - SS corrosion potential <-230 mV(SHE)
  - Typically catalytic noble metal additions (NMCA)
- 36 of 36 North American BWRs operate on HWC
- 32 of 36 North American BWRs operate on NMCA/OLNC

Two PWR Electrolytes

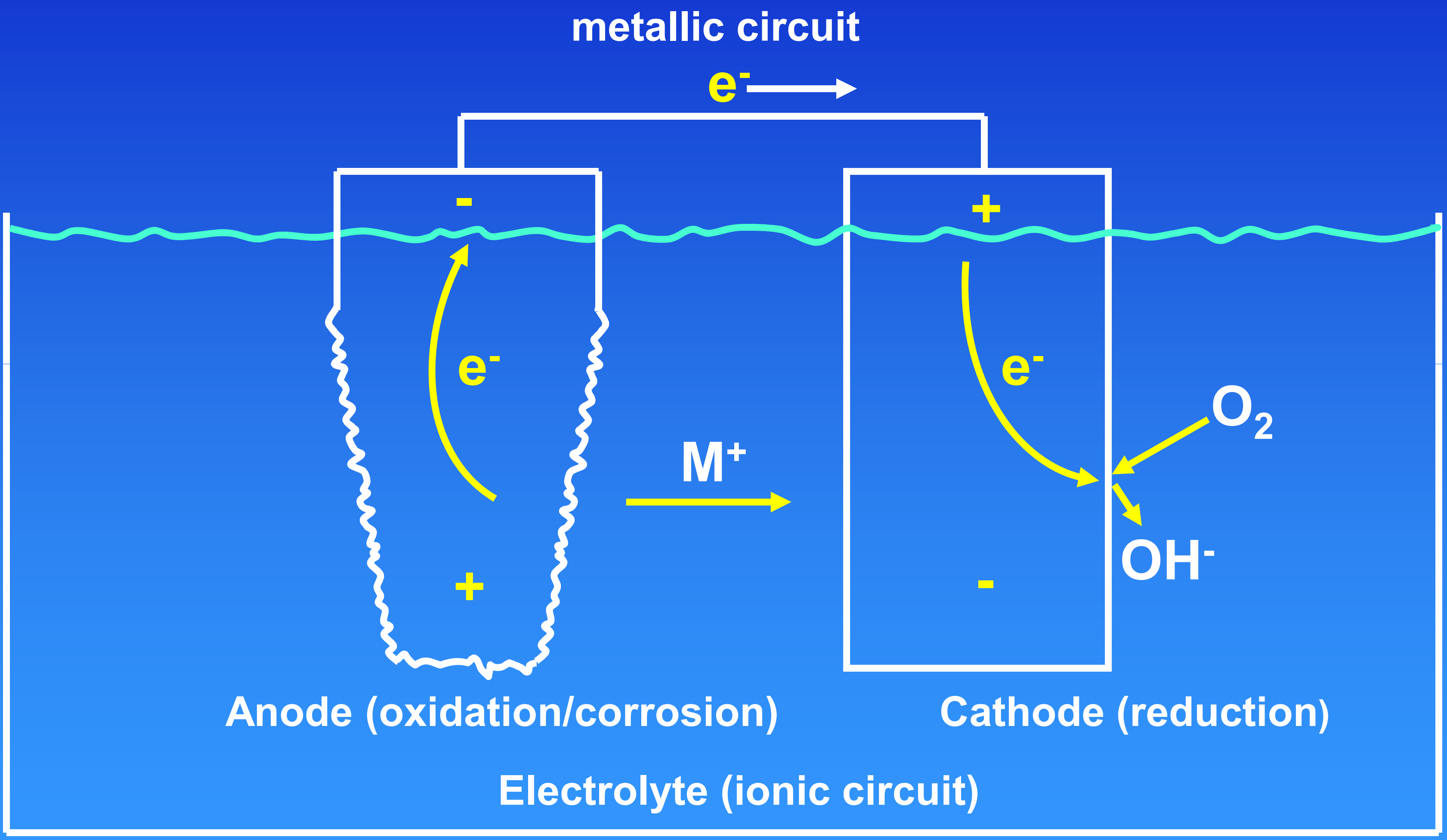
- PWR primary water chemistry (varies with time)
  - 260–338°C (500–640°F) ~26 (BOC) → ~6 (EOC) µS/cm "high purity" water
  - BOC - H_3BO_3 (1200-1900 ppm B) + LiOH (up to 6 ppm Li)
  - EOC - H_3BO_3 (0 - 100 ppm B) + LiOH (0.7 ppm Li)
  - pH ~7 at temperature (pH ~6 at RT due to H_3BO_3)
  - 1800 - 5400 ppb dissolved H_2
  - Alloy 600 corrosion potential -750 mV(SHE)
- PWR secondary water chemistry
  - 270°C (520°F) 0.3 µS/cm high "purity" water
  - Ammonia/morpholine or ethanolamine w/hydrazine
  - pH 6 at temperature (pH ~9 at RT)
  - Alloy 600 corrosion potential <-450 mV(SHE)

Metallic Circuit

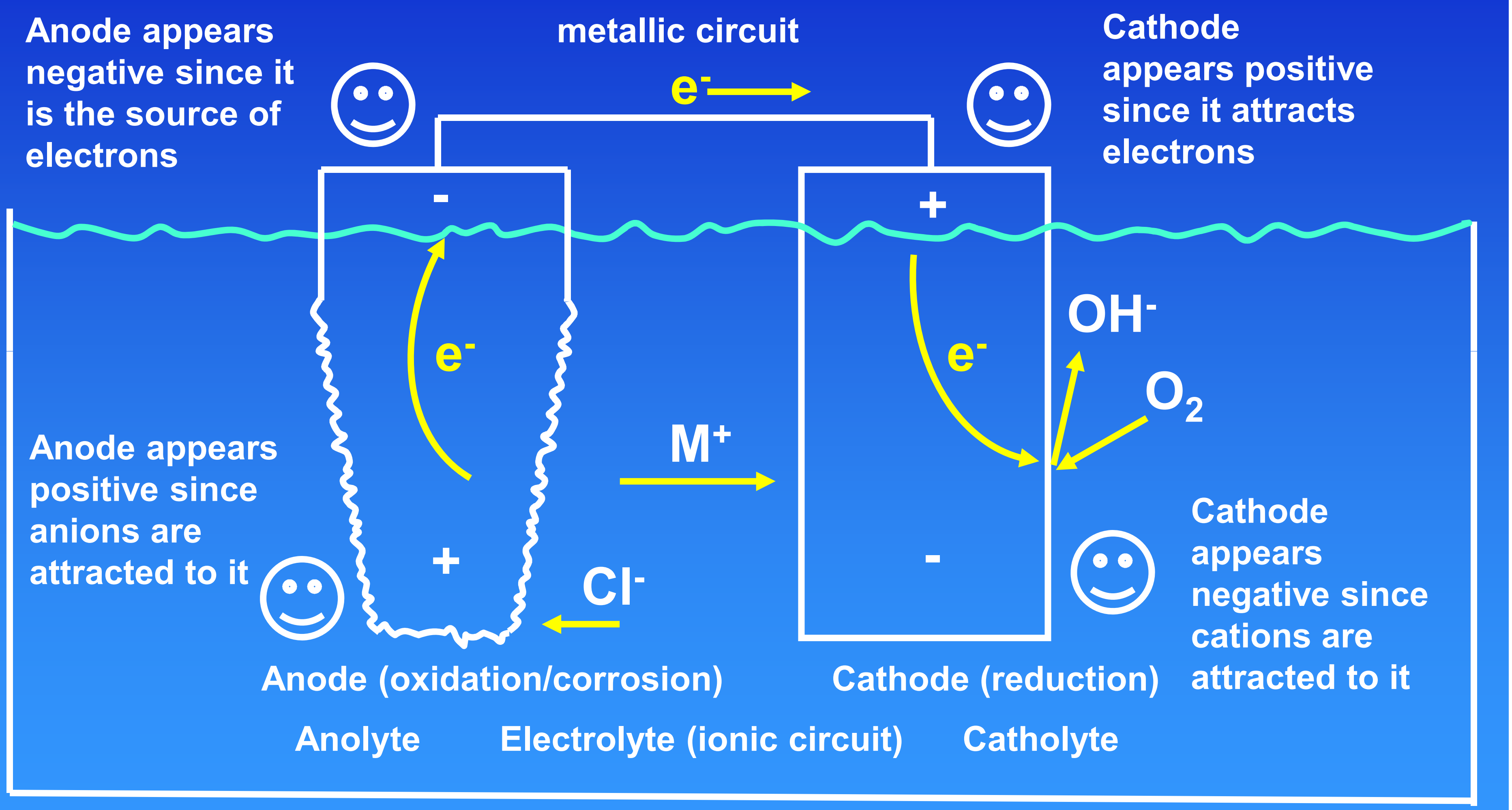
- When metallic circuit is closed, the electrons generated by corrosion of the anode flow to the cathode
- Electrons can't "swim"*
- Metallic circuit, anode and cathode are usually located on the same surface!

*except in irradiated environments, i.e., aqueous electrons, e_{aq}^{-}

Basic Corrosion Cell



Details of Basic Corrosion Cell



Anode appears negative since it is the source of electrons

Cathode appears positive since it attracts electrons

Anode appears positive since anions are attracted to it

Cathode appears negative since cations are attracted to it

U. R. Evans

- Ulick Richardson Evans (1889 – 1980)
  - “Father of Corrosion Science”
  - 1923 – “Metals and Metallic Compounds” was published in four volumes
  - 1924 – wrote “Corrosion of Metals” – 1st corrosion book!
  - 1926 – anodes and cathodes experiment
  - 1937 – “Metallic Corrosion Passivity and Protection”
  - 1948 – “An Introduction to Metallic Corrosion”

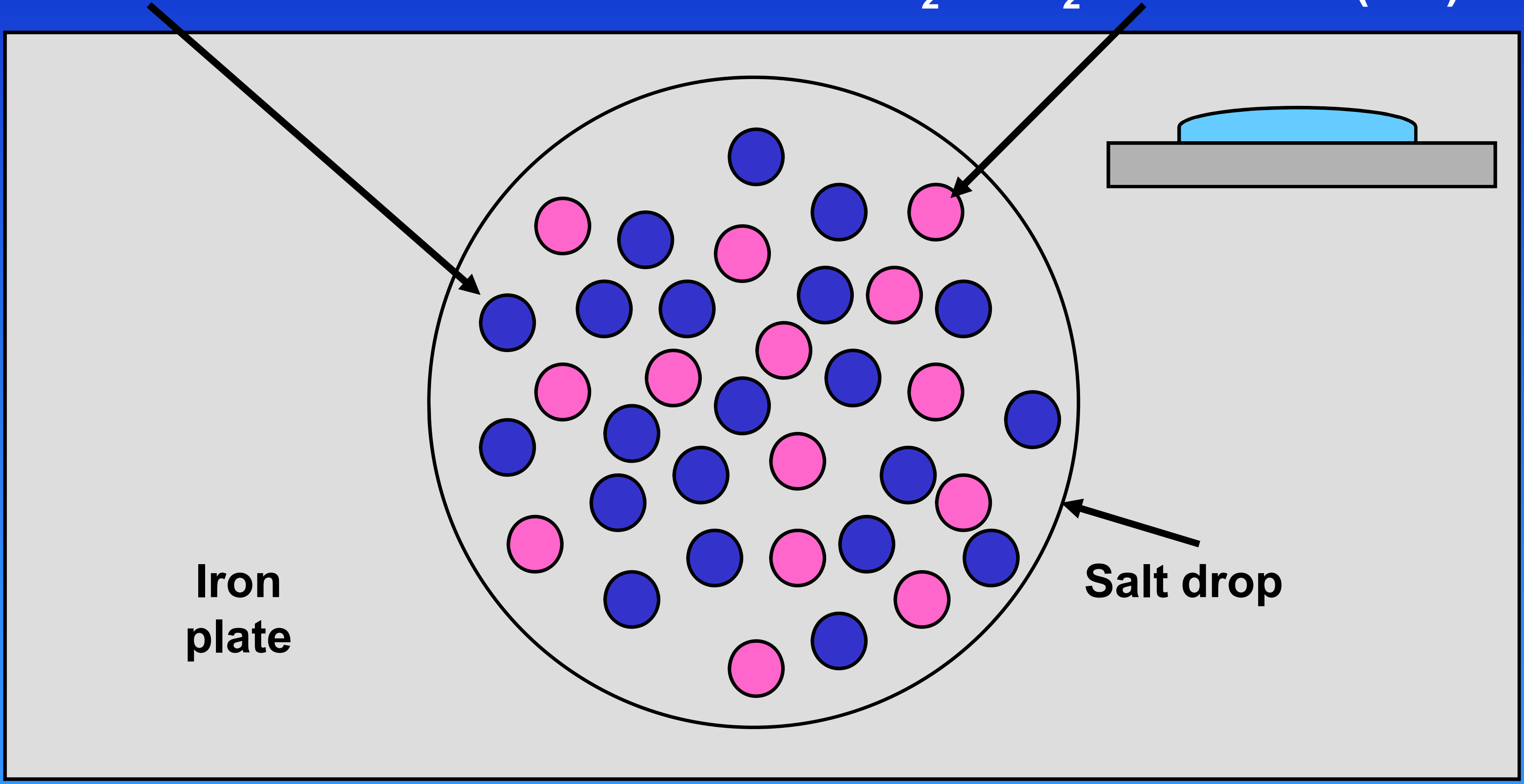
“Corrosion is largely an electrochemical phenomenon, [which] may be defined as destruction by electrochemical or chemical agencies...”

Salt Drop Experiment

- Drop of 3% NaCl solution on finely abraded iron
  - Why did he add NaCl?
  - Why 3%?
- Potassium ferricyanide ($K_4Fe[CN]_6•H_2O$) - turns blue with ferrous ions (Fe^{2+})
- Phenolphthalein ($C_{20}O_4H_{14}$) - turns pink with hydroxyl (OH^-) when the pH > 8.5
- What did U. R. Evans see before his eyes?

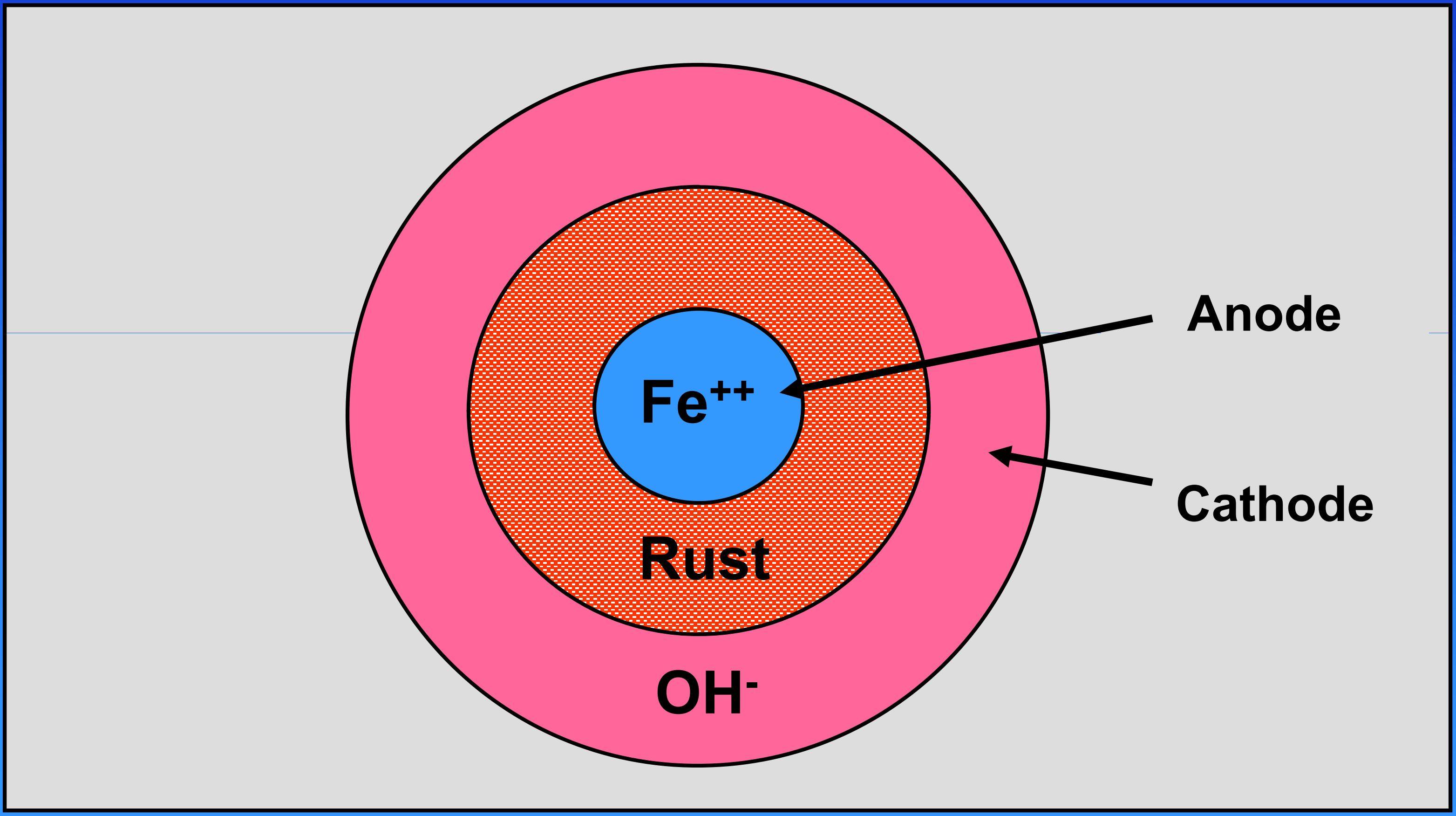
Salt Drop Experiment – Early Stages

Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$

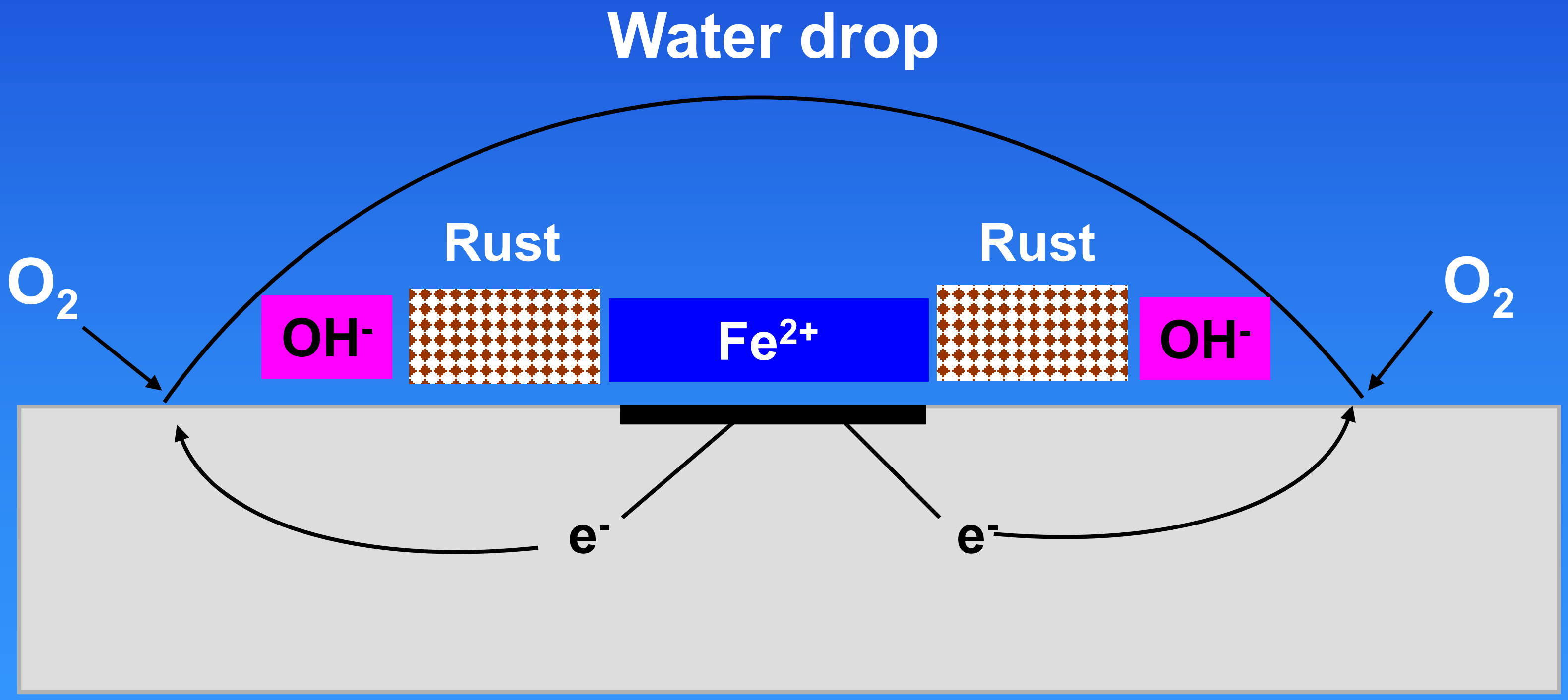


NaCl is not involved in the corrosion reaction! What was the role of NaCl?

Salt Drop Experiment – Later Stages



Salt Drop Experiment – Cross Section



Painting with Phenolphthalein

Carbonated Concrete

Evans Differential Aeration Principal

“Any geometrical configuration that results in a higher concentration of dissolved oxygen at one part of a metal surface and a lower (or zero) concentration at another will result in the former becoming a cathode and the latter the anode.”

This is the essence of IGSCC in BWRs!

This is the essence of HWC in BWRs!

This is the essence of NMCA in BWRs!

But this in <u>not</u> the essence of PWSCC in PWRs!

Electromotive Series Background

- “Galvanic action” or “galvanic effects”
- One metal will corrode more rapidly when coupled to another
- Which metal is more active in a metal couple?
- Is it OK to connect copper pipe to galvanized pipe in your home?
- Is it OK to have an aluminum head bolted with low alloy steel bolts to a cast iron engine block?
- It is necessary to determine which metals are affected by others, i.e., need a ranking system in the environment of concern

Potential and Current Analogies

Water Pressure

↓

Electron Pressure

↓

Potential

Water Flow Rate

↓

Electron flow

↓

Current

What is Potential E?

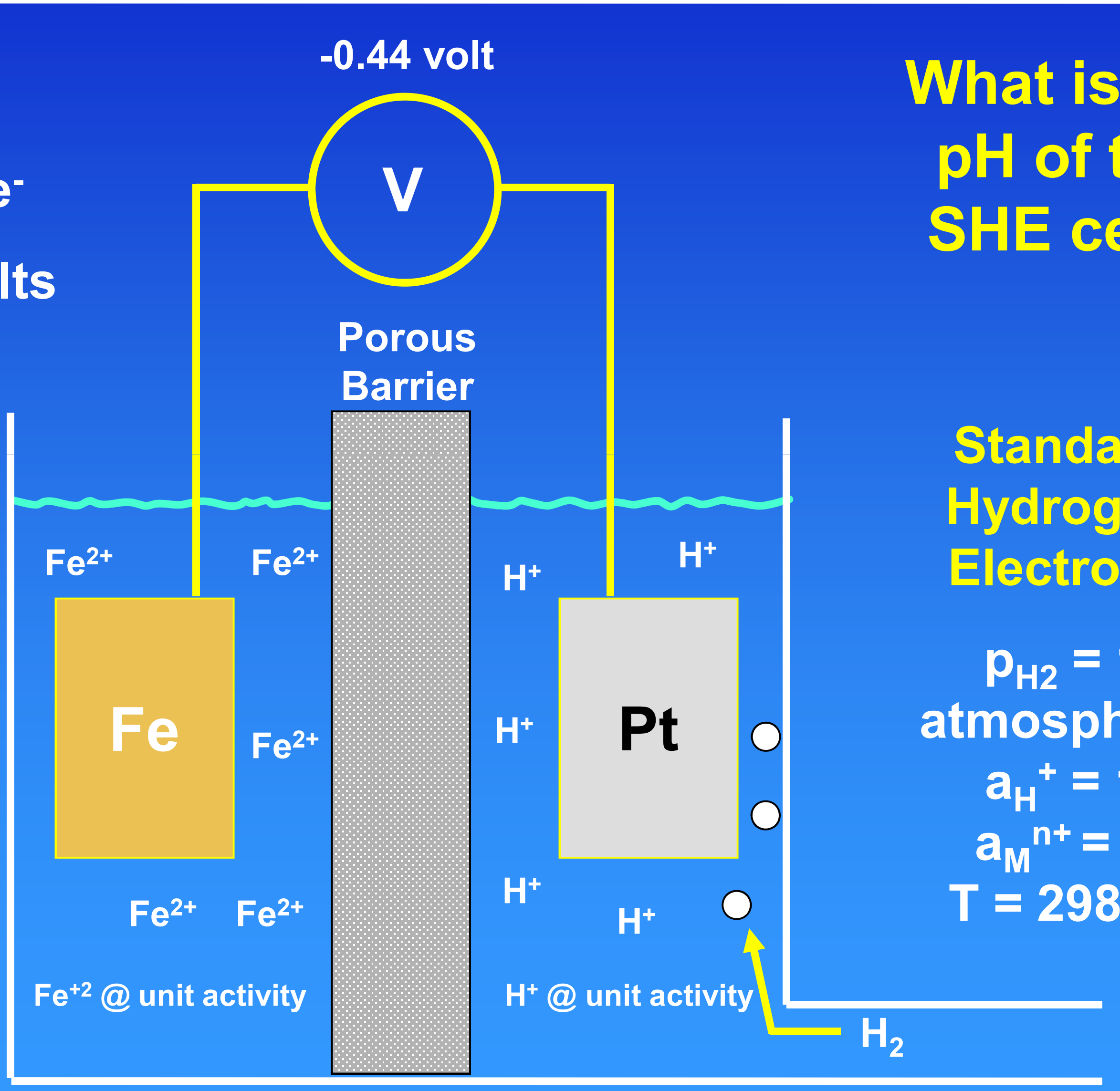
- Unit: Volt
- E is a measurement of the force required to remove electrons from atoms and form soluble ions
- E is related to free energy, i.e., E = $\Delta G/nF$
- E is always measured versus a reference electrode defined relative to the H_2O/H_2 equilibrium half cell
- 0 volts is <u>not zero, i.e., not nothing</u>!
- There is <u>no relationship</u> between E and the kinetics of a corrosion reaction!!!

Standard Measurement of E Standard Hydrogen Electrode (SHE)

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

$E^{0}_{SHE} = -0.44$ volts

Pure Fe electrode at standard state



What is the pH of the SHE cell?

Standard Hydrogen Electrode

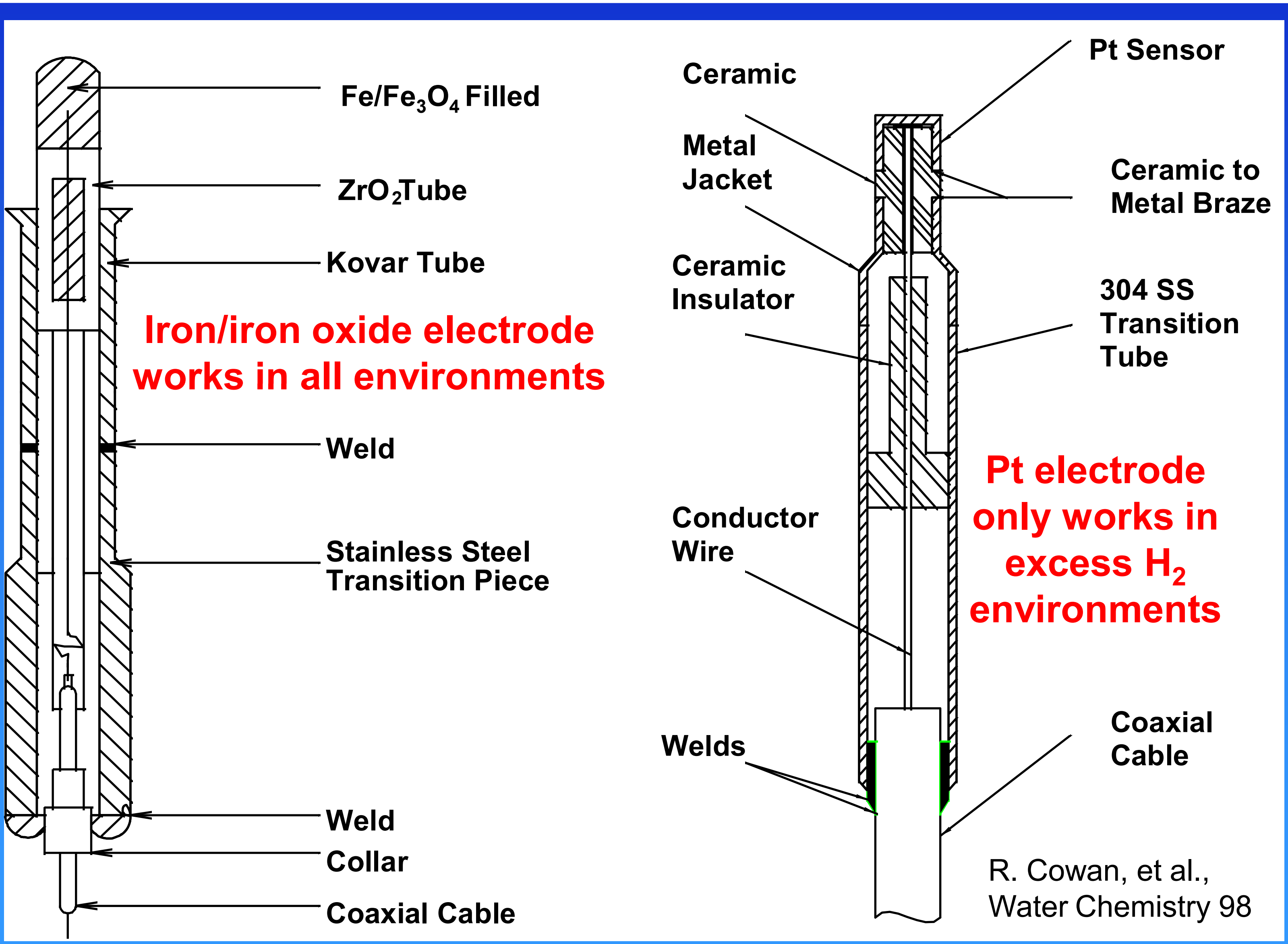
$p_{H2} = 1$ atmosphere

$a_{H}{}^{+} = 1$

$a_{M}{}^{n+} = 1$

T = 298°K

High Temperature Reference Electrodes

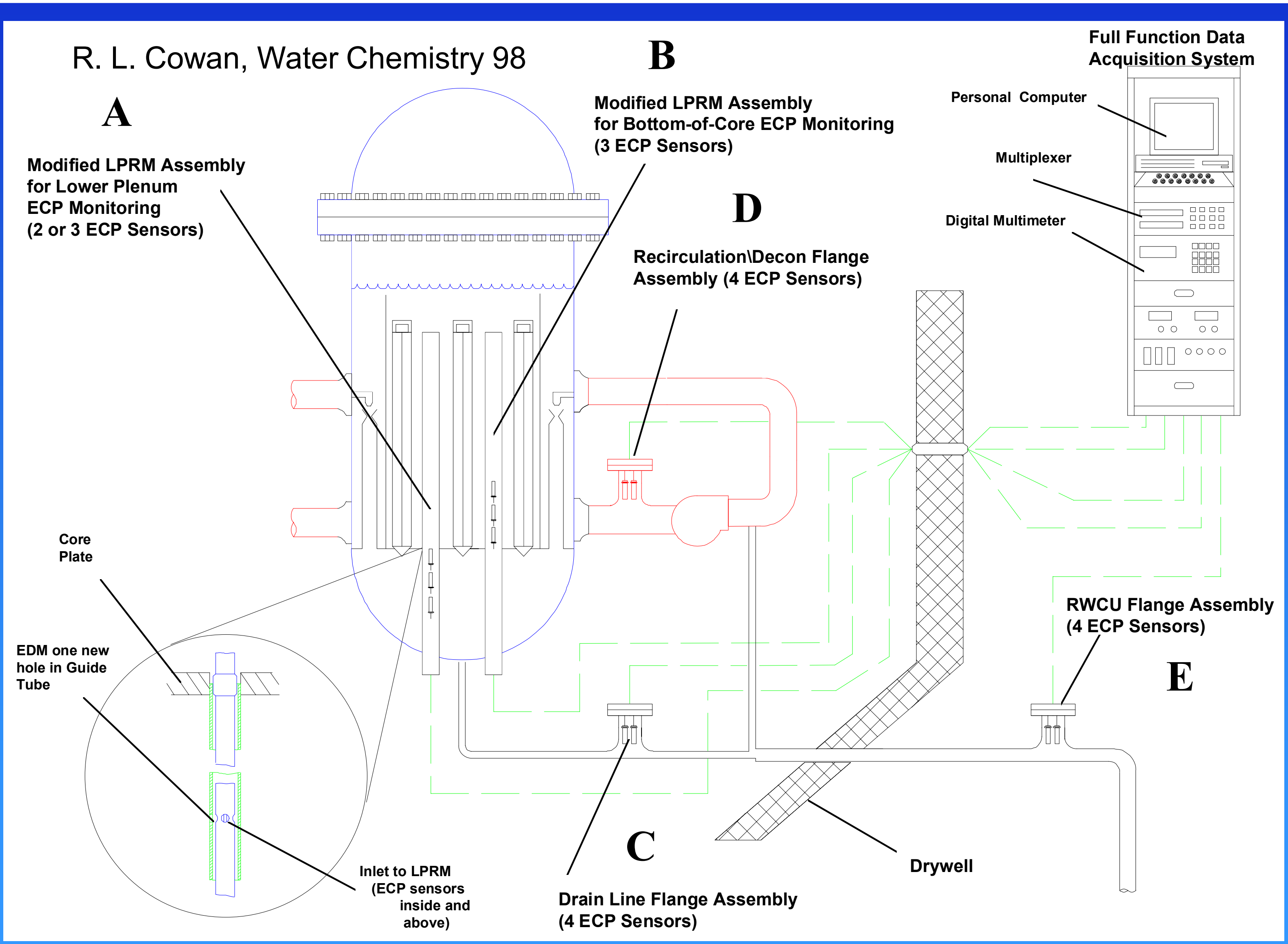


Iron/iron oxide electrode works in all environments

Pt electrode only works in excess H_2 environments

R. Cowan, et al., Water Chemistry 98

Potential Locations for Corrosion Potential Measurements in the BWR

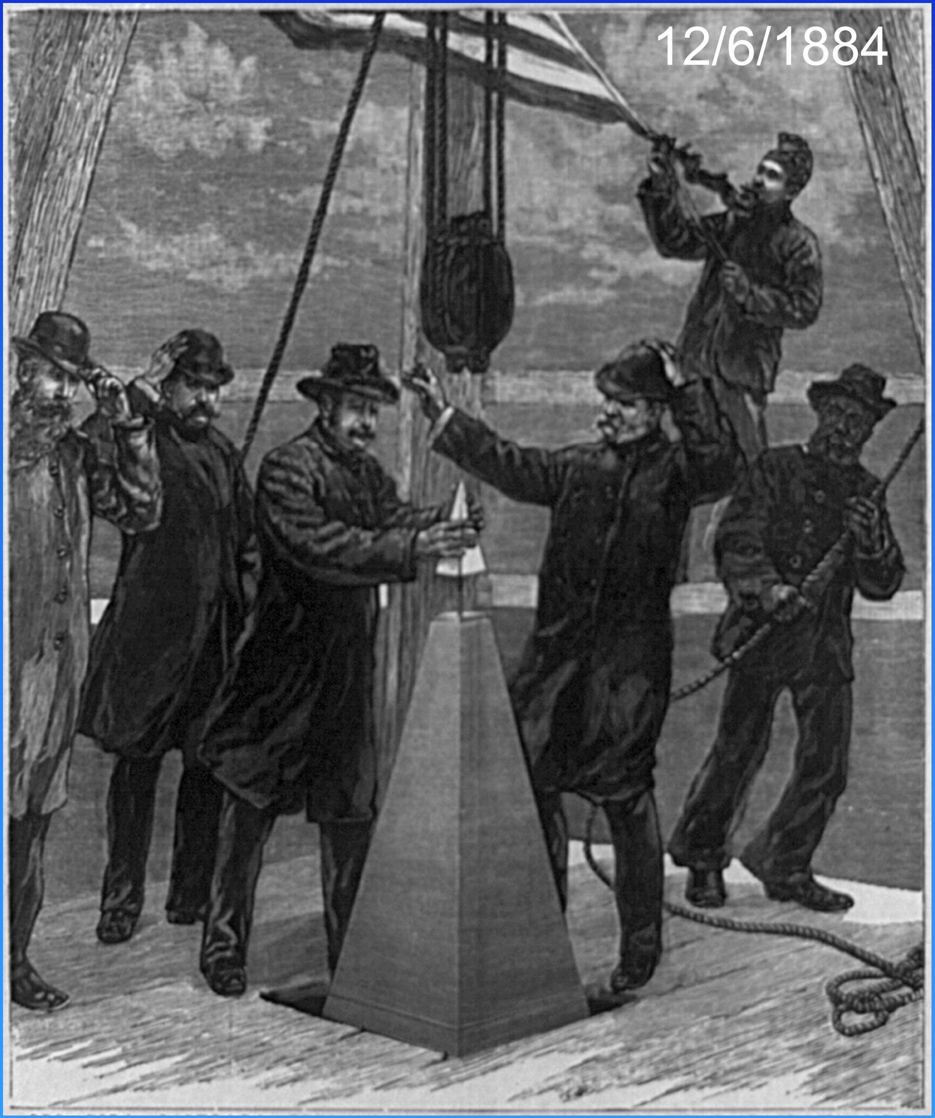


The Electromotive Series (SHE)

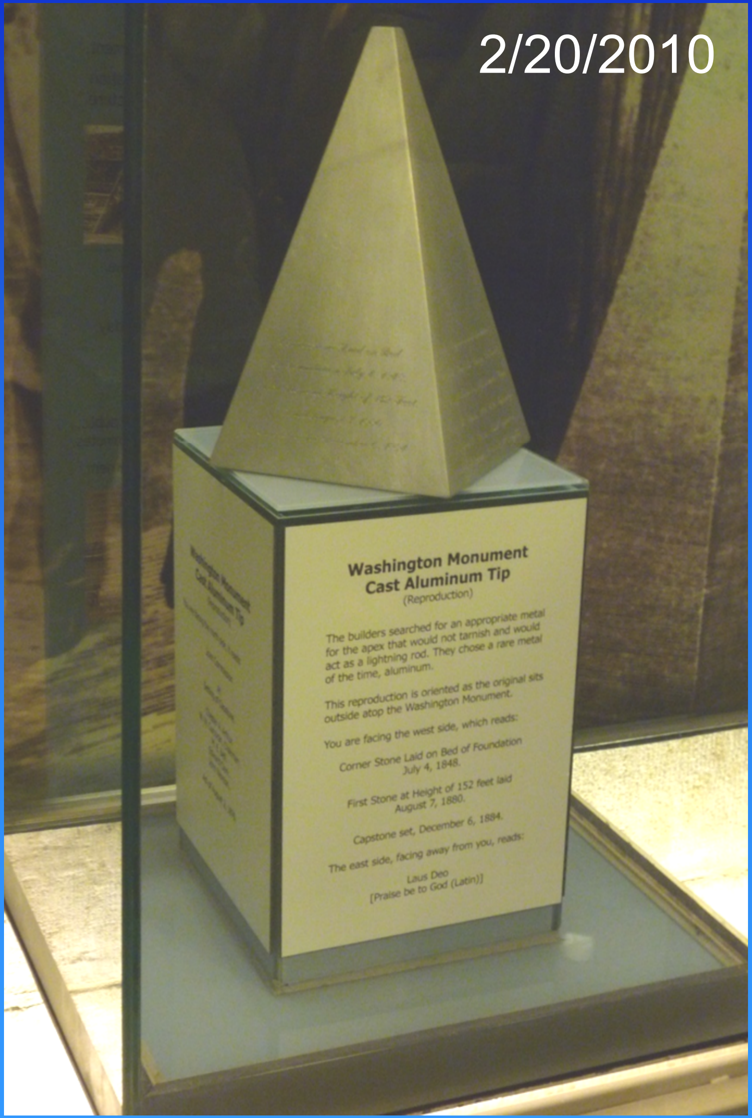
Metal System	E^0, V(SHE)	
Au/Au^{3+}	1.50	More noble
Pd/Pd^{2+}	0.99	
Cu/Cu^{+}	0.52	
Cu/Cu^{2+}	0.34	
H/H^{+}	0.00	by definition
Mo/Mo^{3+}	-0.20	
Ni/Ni^{2+}	-0.25	
Co/Co^{2+}	-0.28	
Fe/Fe^{2+}	-0.44	
Cr/Cr^{2+}	-0.74	
Zn/Zn^{2+}	-0.76	
Zr/Zr^{4+}	-1.53	
Al/Al^{3+}	-1.66	More active

Note that these values are thermodynamic calculations

Washington Monument Capstone



12/6/1884



2/20/2010

Washington Monument
Cast Aluminum Tip
(Reproduction)

The builders searched for an appropriate metal for the apex that would not tarnish and would act as a lightning rod. They chose a rare metal of the time, aluminum.

This reproduction is oriented as the original sits outside atop the Washington Monument.

You are facing the west side, which reads:

Corner Stone Laid on Bed of Foundation
July 4, 1848.

First Stone at Height of 152 feet laid
August 7, 1880.

Capstone set, December 6, 1884.

The east side, facing away from you, reads:

Laus Deo
[Praise be to God (Latin)]

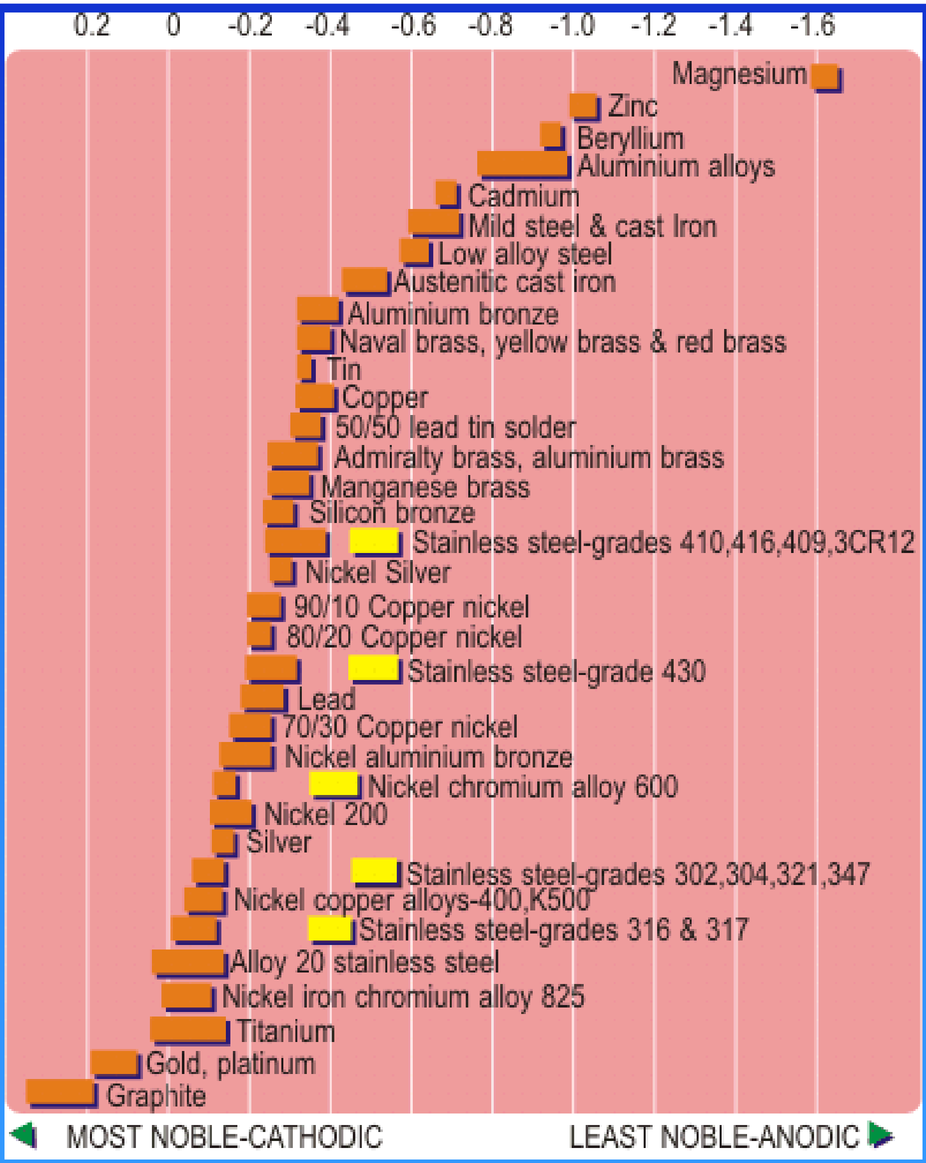
Electromotive Series in Seawater

Most Active (Most Negative Potential)

Magnesium
Zinc
Aluminum and Aluminum Alloys
Iron or steel
Type 304 stainless steel (active)
Type 316 stainless steel (active)
Aluminum bronze
Muntz metal or naval brass
Admiralty brass
90/10 copper-nickel
70/30 copper-nickel
Type 304 stainless steel (passive)
Type 316 stainless steel (passive)
Titanium
Graphite

Most Noble (Most Positive Potential)

Electromotive Series in Flowing Sea Water



Note that these values are based on measurements

2.4 to 4.0 m/s at 10-27°C (50-81°F)

0 VSCE = + 0.241 VSHE

Electromotive Series Tendencies

Generally, the following tendencies can be derived from such a series:

- Position on table thermodynamically determines the corrosion behavior, the more negative, the more reactive
- Any metal can displace one above it in the series (e.g., Fe displaces Cu^{2+} from $CuSO_4$. Fe would dissolve and Cu would plate out on the Fe.)
- Metals below H/H^+ can dissolve producing H_2. Noble metals (above H/H^+) will not dissolve in non-oxidizing acids
- The greater the separation between two metals in the series, the more violent the dissolution of the more negative (active) metal

Electromotive Series Caveats

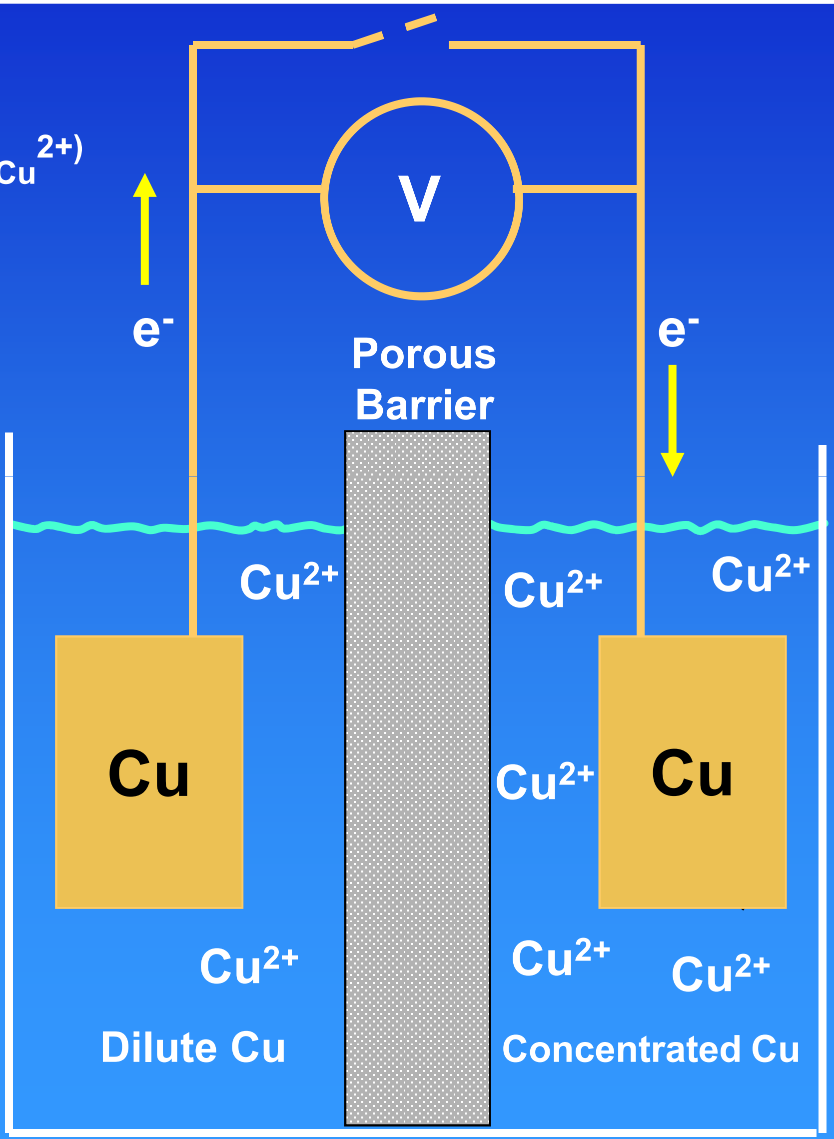
There are numerous caveats with electromotive series:

- Ranking depends on everything that affects E!
- Position is only a guide to relative corrosion resistance. If Cr is more active than Fe, then why does the addition of Cr to Fe (e.g., stainless steel), have a higher corrosion resistance than Fe?
- Formation of protective films are not considered. Al is a very active metal, yet its corrosion rate is very low due to the formation a protective oxide.
- The series reveals nothing concerning kinetics. E^0 of Zn/Zn^{2+} is -0.76 V, yet is corrosion rate is 1/3 of Fe with an E^0 of -0.44 V. List reflects thermodynamics only!

Concentration Cell

Nernst Equation

$$E = E^0 + \frac{0.059}{2} \log(A_{Cu^{2+}})$$



V

e^-

e^-

Porous Barrier

Cu

Cu

Cu^{2+}

Cu^{2+}

Cu^{2+}

Cu^{2+}

Cu^{2+}

Cu^{2+}

Cu^{2+}

Dilute Cu

Concentrated Cu

Anode

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

Cathode

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

Corrosion Thermodynamics
a.k.a, the “Driving Force”

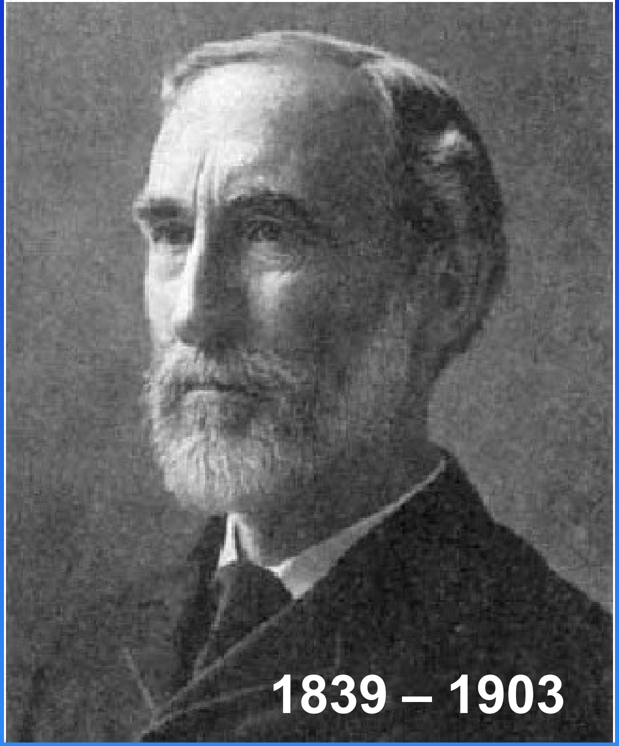
Corrosion Thermodynamics

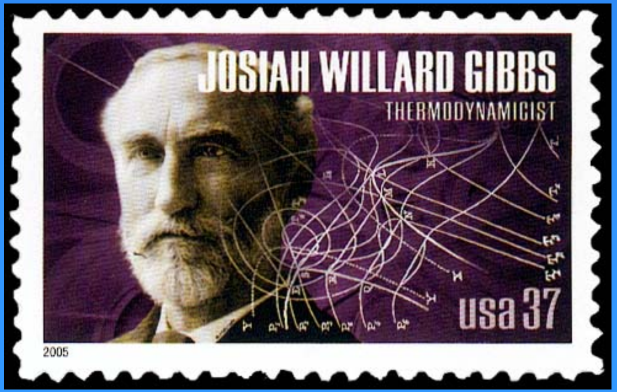
- Corrosion is thermodynamically driven to lower the overall energy of the system
  - Involves electron/charge transfer
  - Controls the spontaneous direction for corrosion
- Thermodynamics provides an understanding of the energy changes involved in corrosion
  - Thermodynamics show how conditions may be adjusted to prevent corrosion, i.e., $\Delta G>0$
  - Thermodynamics can indicate corrosion is possible, i.e., $\Delta G<0$, but <u>thermodynamics cannot predict the rate</u>
- Change in E or the electron activity or availability at a metal surface has a profound effect on corrosion rate

Gibbs Free Energy

- In the late 19th century Josiah Willard Gibbs formulated a theory to predict whether a chemical reaction is spontaneous based on the free energy $\Delta G = \Delta G^0 + RT \ln Q$

  ΔG = change in Gibbs free energy
  T = absolute temperature
  R = gas constant, Q = reaction quotient
- Gibbs' key contribution was to formalize the understanding of the effect of reactant concentration on spontaneity
  - Warranted a US 37¢ stamp!


1839 – 1903



Nernst Equation

- E of an electrochemical cell requires standard conditions for all of the reactants
- When reactant concentrations differ from standard (unit activity) conditions, the cell E will deviate from the standard potential, E°
- In the 20th century, German chemist Walther Nernst proposed a mathematical model to determine the effect of reactant concentration on E

1864 - 1941

More on the Nernst Equation

- Nernst equation describes the fundamental relationship between the potential applied to an electrode and the concentration of the species at the electrode surface
- If an electrode is at equilibrium with the solution in which it is immersed, the electrode will have a potential, invariant with time, which is thermodynamically related to the composition of the solution

ΔG and E

- Relationship between chemical free energy change that occurs for a reaction and electrode potential

$$x + y \text{ (reactants)} \rightarrow c + d \text{ (products)}$$

Gibbs $$\Delta G = \Delta G^0 + RT \ln \frac{(a_{\text{products}})}{(a_{\text{reactants}})}$$

a = activity

$$\Delta G = nFE \quad E = \Delta G/nF \text{ (ΔG and E same sign)}$$

Nernst $$E = E^0 + \frac{RT}{nF} \ln \frac{(a_{\text{products}})}{(a_{\text{reactants}})}$$

R = gas constant
F = Faraday's constant
n = # electrons involved in reaction

Nernst Equation

- Nernst extended the Gibbs' theory to include the contribution from electric potential on charged species
- 1920 Nobel Prize

1

$M \rightarrow M^{n+} + ne^-$

$$E_M = E^0_M + RT/nF \times \ln\frac{[a_M{}^{n}+][a_{e-}]^n}{[a_M]}$$

1

At 298°K (25°C) 2.3RT/F = 0.059:

$$E_M = E^0_M + 0.059/n \times (\log[a_M{}^{n}+])$$

R = 1.987 cal/ºK/mole

F = 23,060 cal/volt/mole

Nernst Equation Calculation Example

Given $E^0_{Al/Al^{3+}}$ = -1.66 volts, calculate the single electrode potentials (or redox potential or half cell potential) for 10^{-3} and 10^{-6} M activities of this ion at 25°C

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

$E_M = E^0_M + 0.059/n \times (\log[a_M{}^n+])$ What is n?

$E_{Al/Al^{3+}} = E^0_{Al/Al^{3+}} + 0.059/3 \times (\log[a_M{}^n+])$

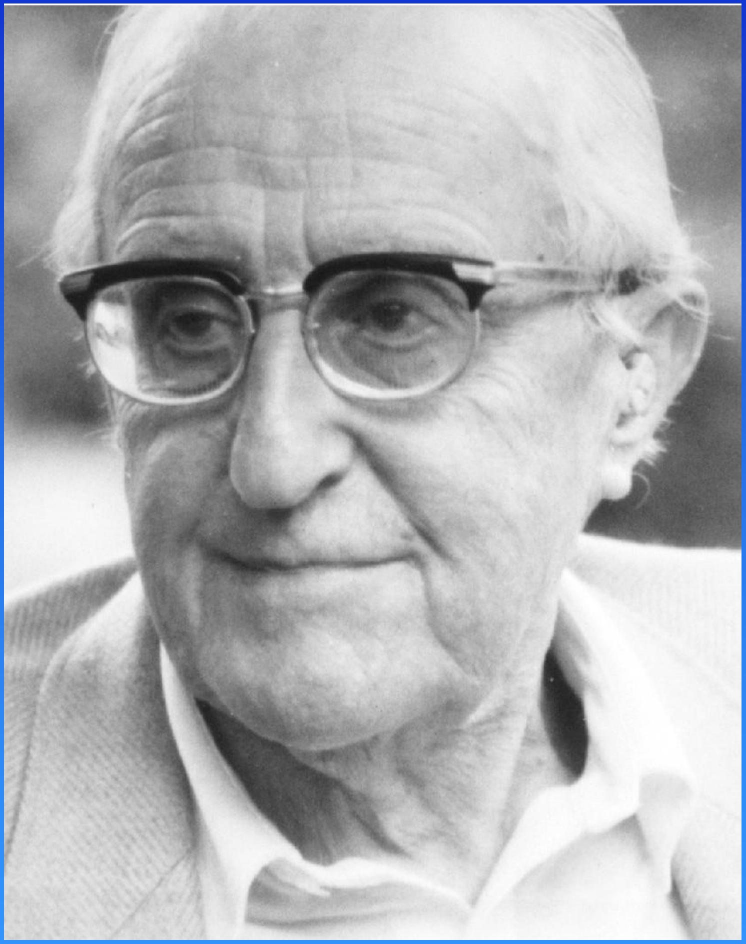
For 10^{-3} M $E_{Al/Al^{3+}} = -1.66 + 0.059/3 \times -3 = -1.72v$

For 10^{-6} M $E_{Al/Al^{3+}} = -1.66 + 0.059/3 \times -6 = -1.78v$

Makes sense! The more dilute the solution, the greater the thermodynamic tendency for corrosion, i.e., the lower the E

Po-Boy vs. Pourbaix

Fried Oyster Po-Boy



Marcel Pourbaix
1904 - 1988

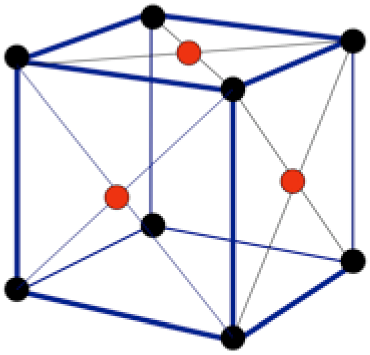
Pourbaix Diagrams

- Delayed 1945 Ph. D. thesis of Marcel Pourbaix (Belgium)
- Used of thermodynamic theory (Nernst equation) to create potential – pH diagrams
- Analogous to the composition – temperature diagrams (phase diagrams) for alloy systems
- Both diagrams are “maps”

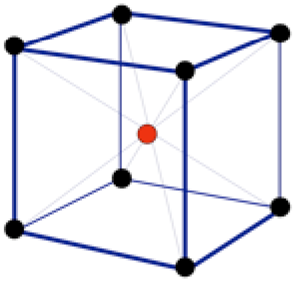
Pourbaix Diagrams for LWRs

- Provides criteria for roles of O_2 and H_2
- Provides bases for minimizing release and deposition of corrosion products at low solubility locations
- Connects reactor water chemistry with stability of materials
  - ♦ Provides bases for selecting LWR corrosion resistant materials
  - ♦ Provide bases for expected reactions of metals with their respective LWR environments

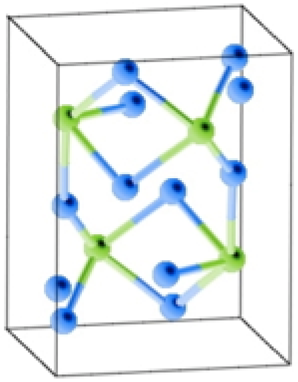
Iron-Carbon Phase Diagram



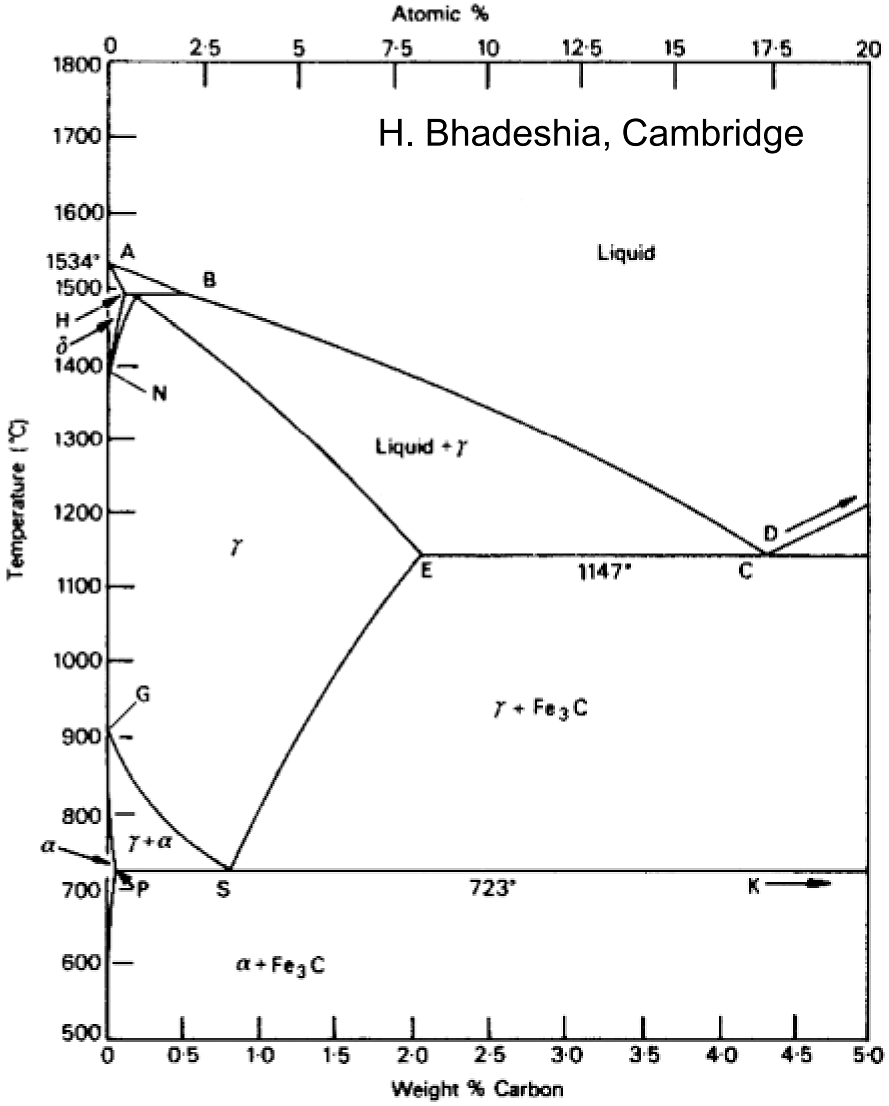
austenite



ferrite



cementite



H. Bhadeshia, Cambridge

Pourbaix Diagram Domains

Diagrams have three domains:

- ***Immunity*** **– region of thermodynamic stability of the pure metal. Corrosion is thermodynamically impossible.**
- ***Corrosion*** **- region of thermodynamic stability of the metal ion and dissolution will occur**
- ***Passivity*** **- region of thermodynamic stability of the metal oxide. Corrosion is mitigated by the formation of a "passive" protective oxide.**

Pourbaix Diagram Reactions

Four types of reactions:

- Independent of H^+ ions (pH) and E (electrons):

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

- pH dependent and E independent:

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$$

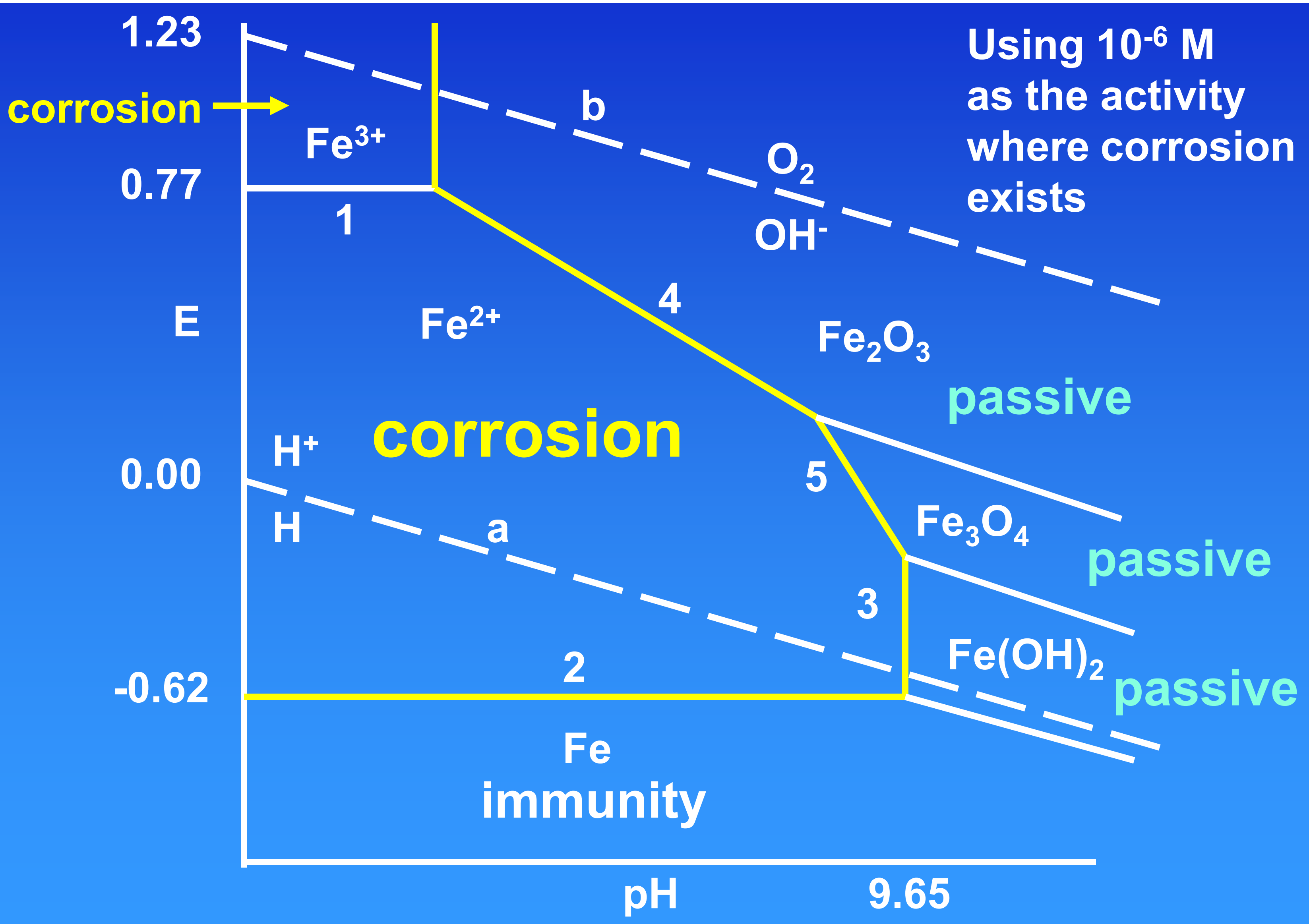
- E dependent and pH independent:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

- E and pH dependent

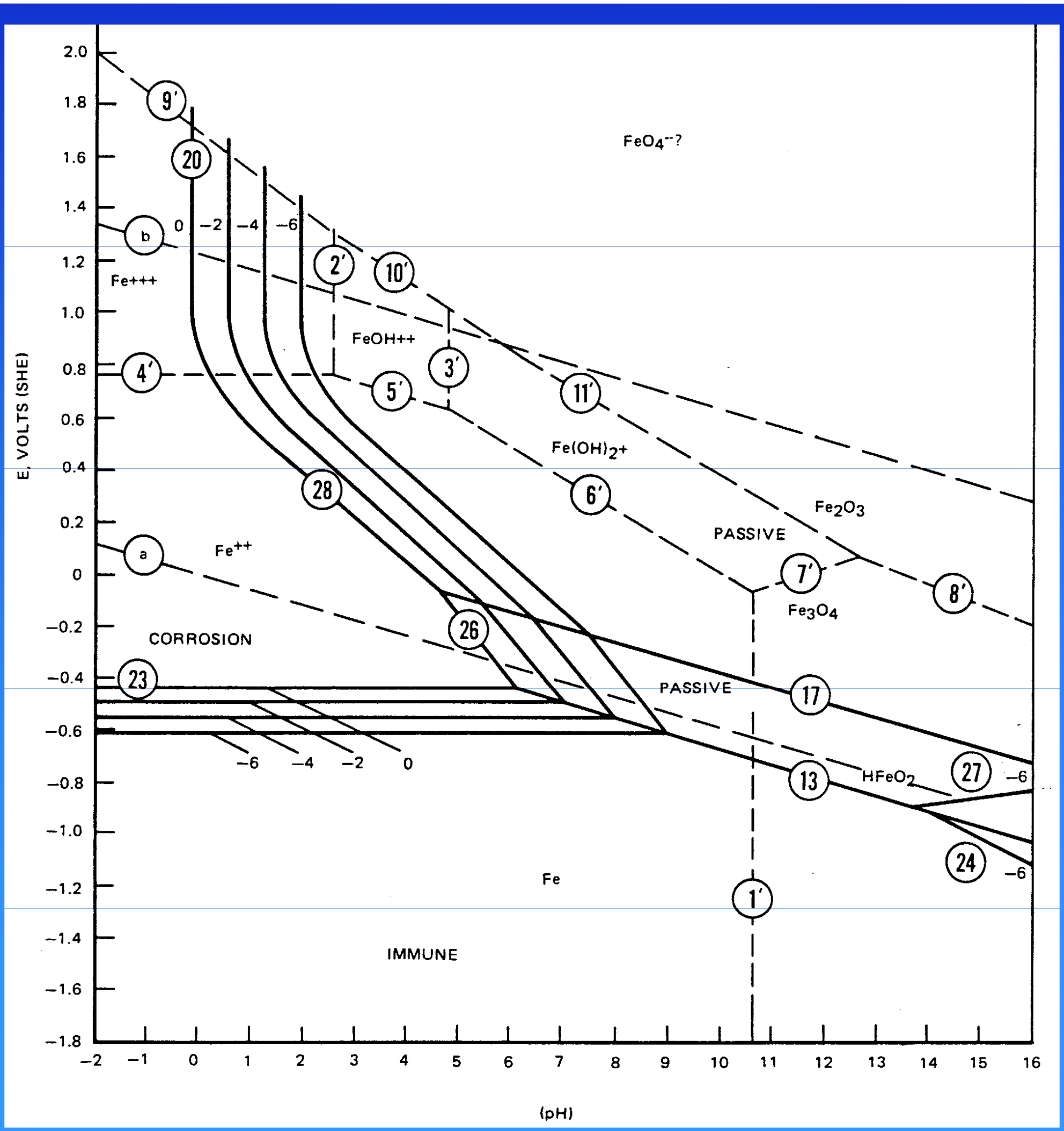
$$2Fe^{2+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 2e^-$$

Pourbaix Diagram for Fe-H_2O at 25 °C



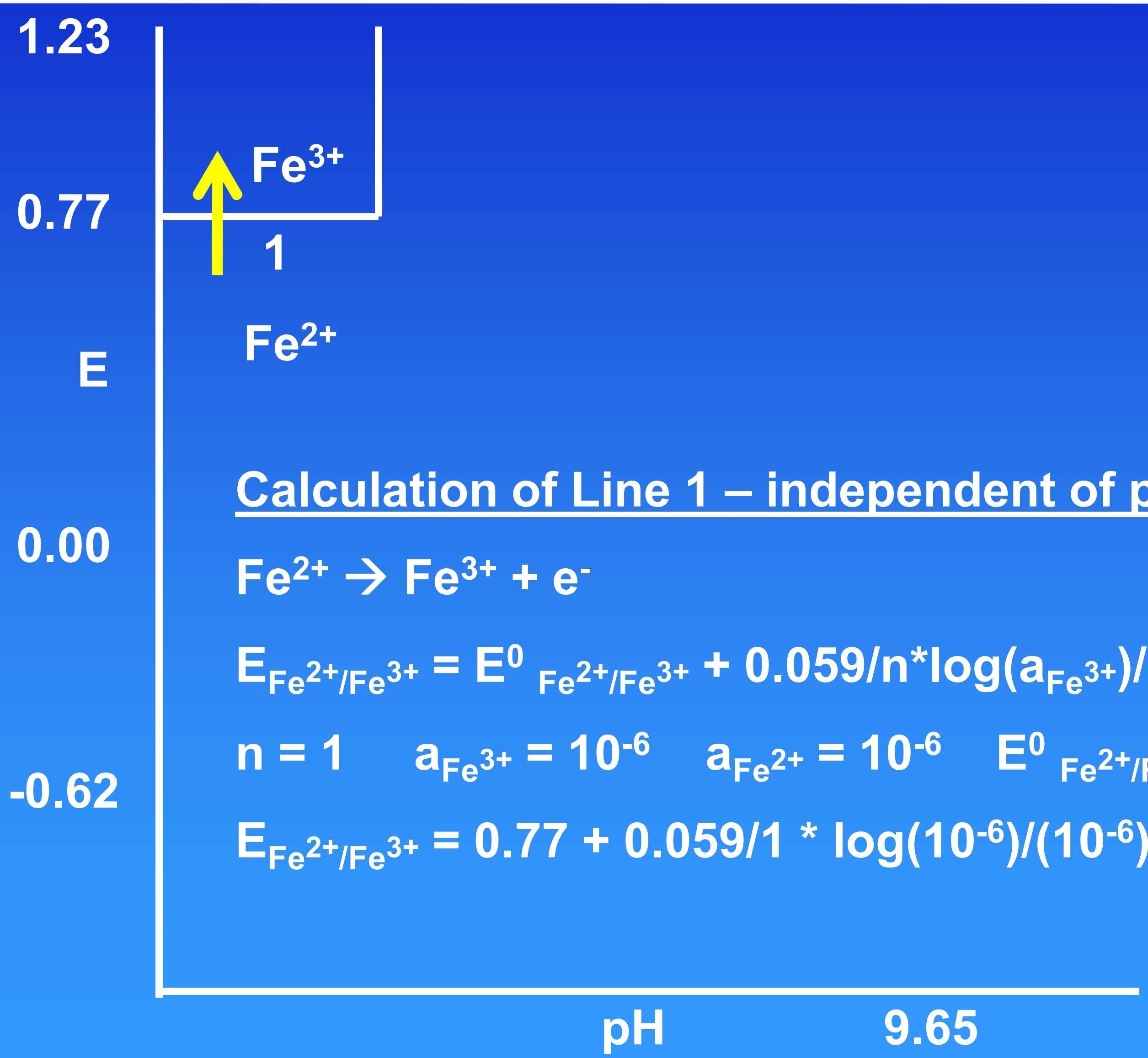
Using 10^{-6} M as the activity where corrosion exists

Pourbaix Diagram for Fe-H_2O at 25 °C



M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, 1974

Pourbaix Diagram for Fe-H_2O at 25 °C
Line 1



Calculation of Line 1 – independent of pH

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$E_{Fe^{2+}/Fe^{3+}} = E^0{}_{Fe^{2+}/Fe^{3+}} + 0.059/n * \log(a_{Fe^{3+}})/(a_{Fe^{2+}})$

$n = 1 \quad a_{Fe^{3+}} = 10^{-6} \quad a_{Fe^{2+}} = 10^{-6} \quad E^0{}_{Fe^{2+}/Fe^{3+}} = 0.77$

$E_{Fe^{2+}/Fe^{3+}} = 0.77 + 0.059/1 * \log(10^{-6})/(10^{-6}) = 0.77$

Pourbaix Diagram for Fe-H_2O at 25 °C
Line 2

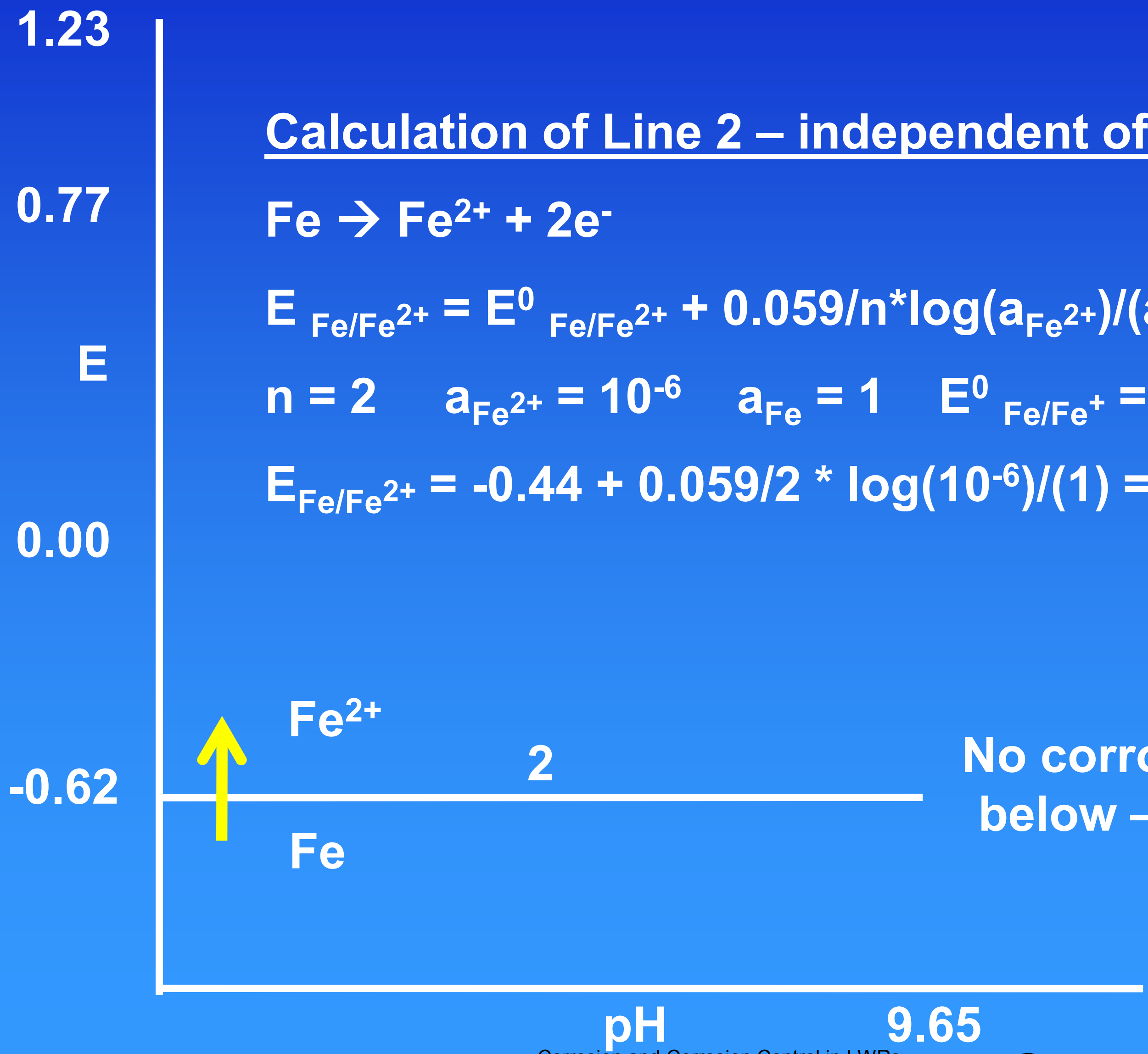
Calculation of Line 2 – independent of pH

Fe → $Fe^{2+} + 2e^-$

$E_{Fe/Fe^{2+}} = E^0_{Fe/Fe^{2+}} + 0.059/n*\log(a_{Fe^{2+}})/(a_{Fe})$

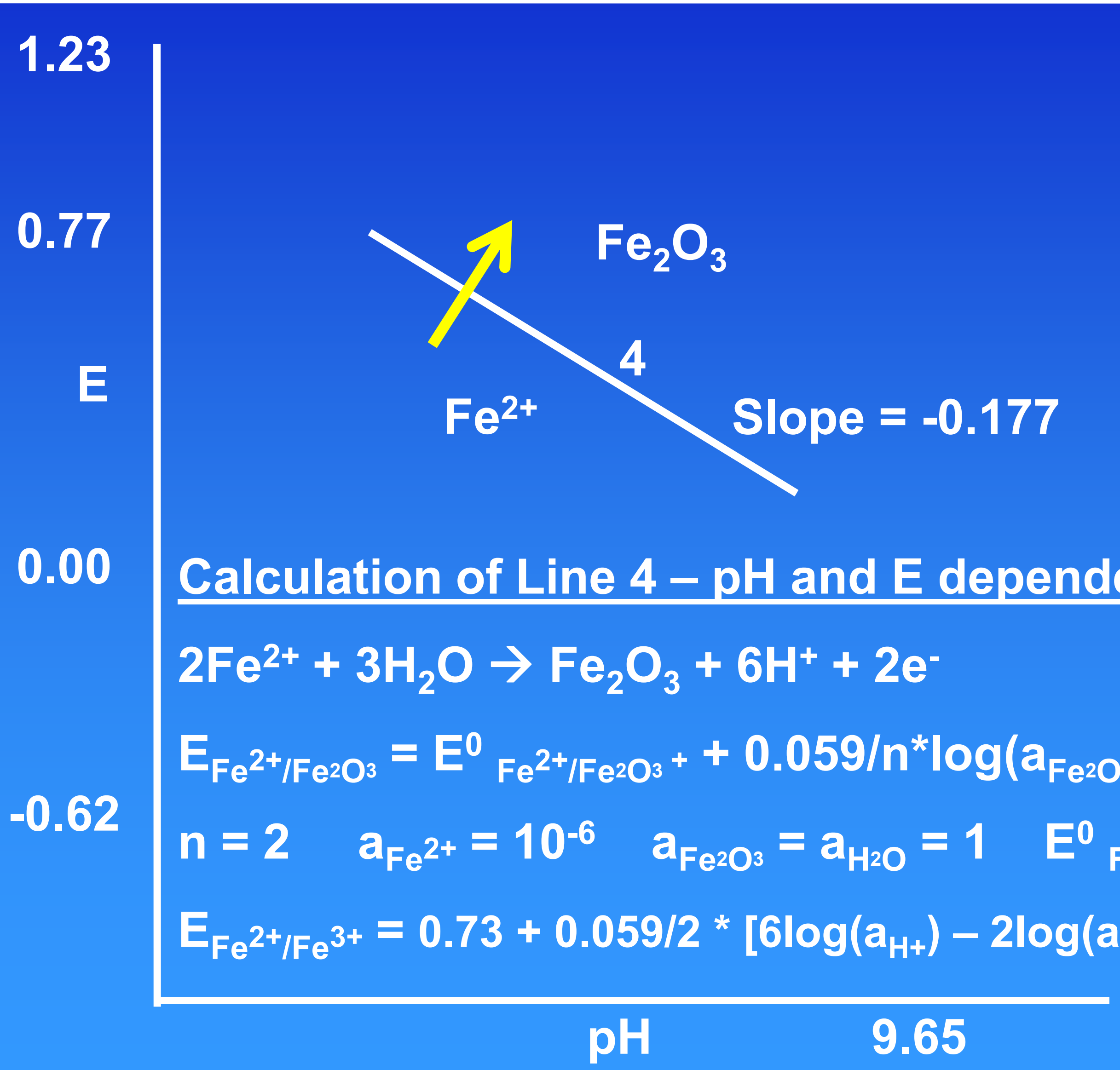
$n = 2 \quad a_{Fe^{2+}} = 10^{-6} \quad a_{Fe} = 1 \quad E^0_{Fe/Fe^+} = -0.44$

$E_{Fe/Fe^{2+}} = -0.44 + 0.059/2 * \log(10^{-6})/(1) = -0.62$



No corrosion of Fe below –0.62 volts

Pourbaix Diagram for Fe-H_2O at 25 °C
Line 4



Calculation of Line 4 – pH and E dependent

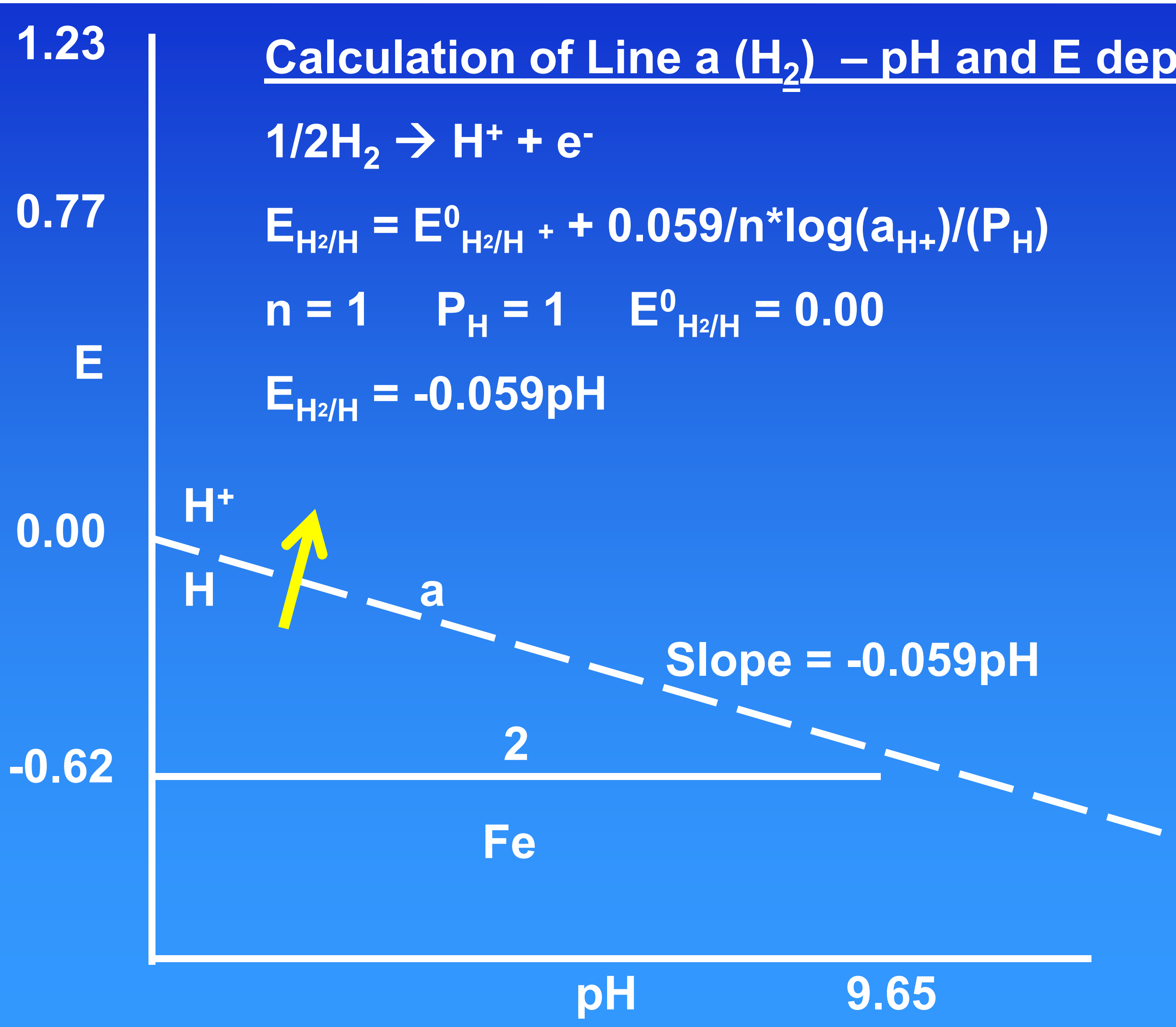
$2Fe^{2+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 2e^-$

$E_{Fe^{2+}/Fe_2O_3} = E^0_{Fe^{2+}/Fe_2O_3} + 0.059/n * \log(a_{Fe_2O_3})(a_{H+})^6/(a_{H_2O})^3(a_{Fe^{2+}})^2$

$n = 2 \quad a_{Fe^{2+}} = 10^{-6} \quad a_{Fe_2O_3} = a_{H_2O} = 1 \quad E^0_{Fe^{2+}/Fe_2O_3} = 0.73$

$E_{Fe^{2+}/Fe^{3+}} = 0.73 + 0.059/2 * [6\log(a_{H+}) - 2\log(a_{Fe}2+)] = 1.084 - 0.177pH$

Pourbaix Diagram for Fe-H_2O at 25 °C
Line a - Hydrogen



Calculation of Line a (H_2) – pH and E dependent

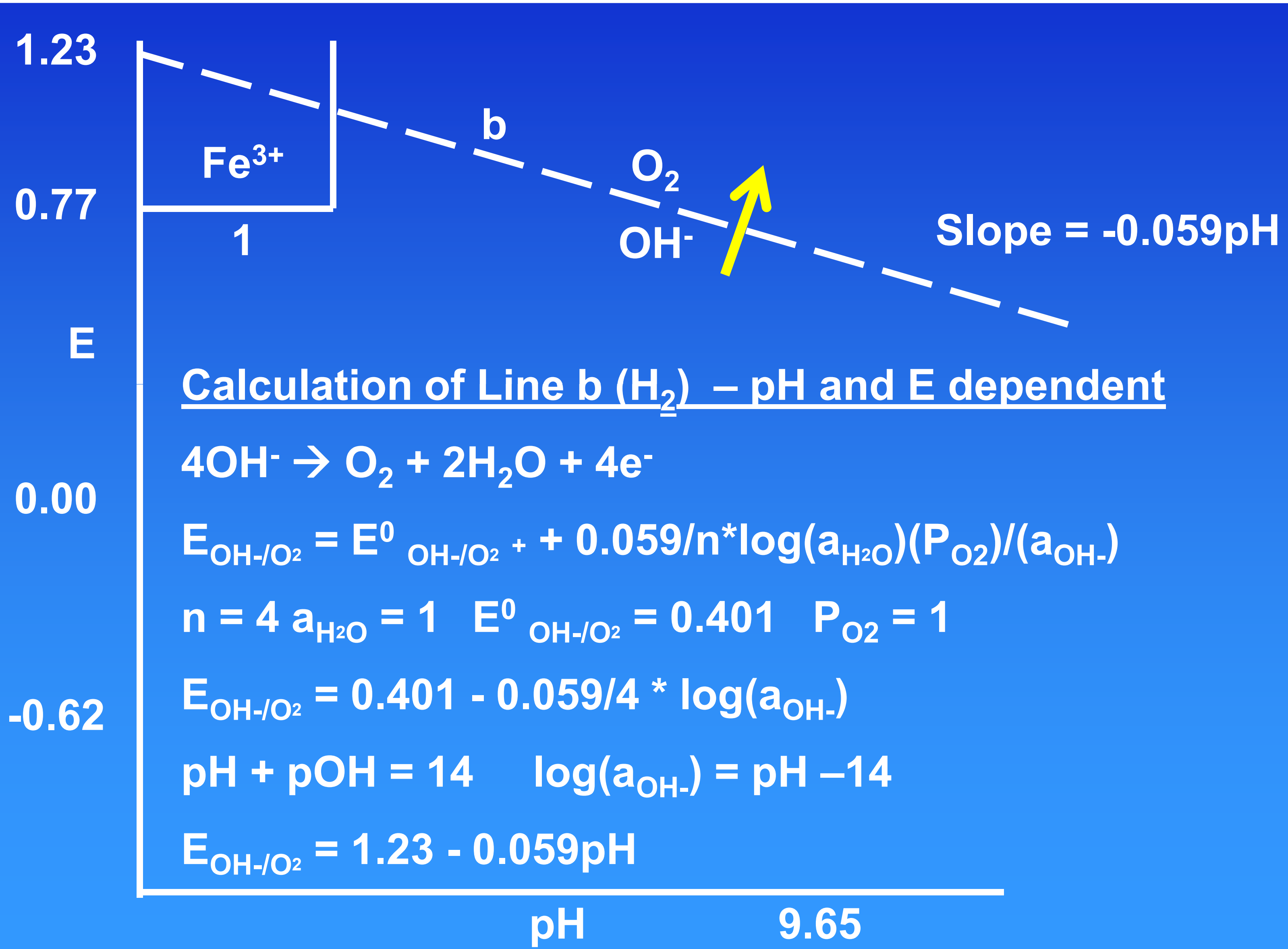
$1/2H_2 \rightarrow H^+ + e^-$

$E_{H2/H} = E^0_{H2/H^+} + 0.059/n*\log(a_{H+})/(P_H)$

$n = 1 \quad P_H = 1 \quad E^0_{H2/H} = 0.00$

$E_{H2/H} = -0.059pH$

Pourbaix Diagram for Fe-H_2O at 25 °C
Line b - Oxygen



Calculation of Line b (H_2) – pH and E dependent

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

$E_{OH-/O_2} = E^0_{OH-/O_2\,+} + 0.059/n*\log(a_{H_2O})(P_{O2})/(a_{OH-})$

$n = 4$ $a_{H_2O} = 1$ $E^0_{OH-/O_2} = 0.401$ $P_{O2} = 1$

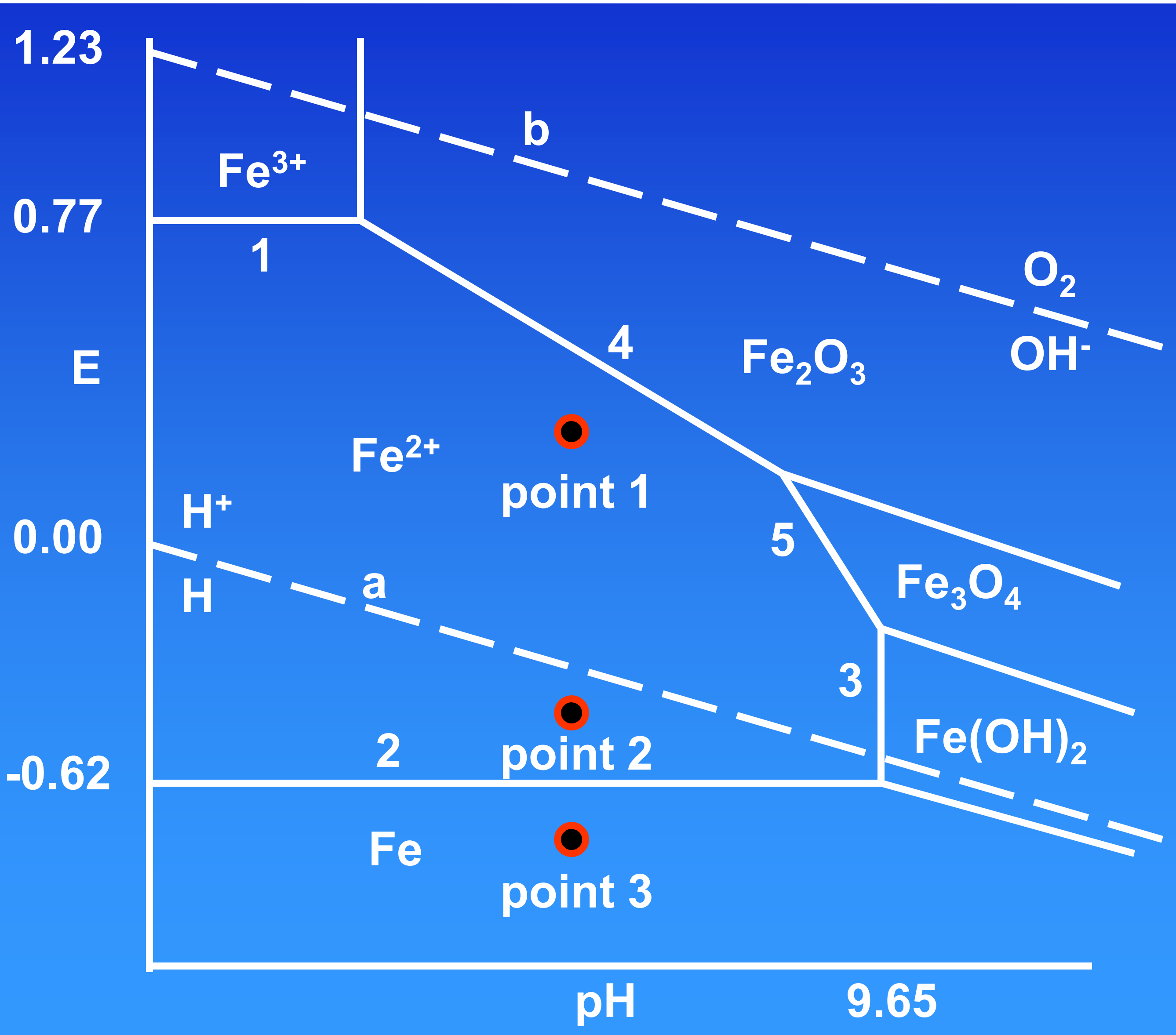
$E_{OH-/O_2} = 0.401 - 0.059/4 * \log(a_{OH-})$

$pH + pOH = 14$ $\log(a_{OH-}) = pH - 14$

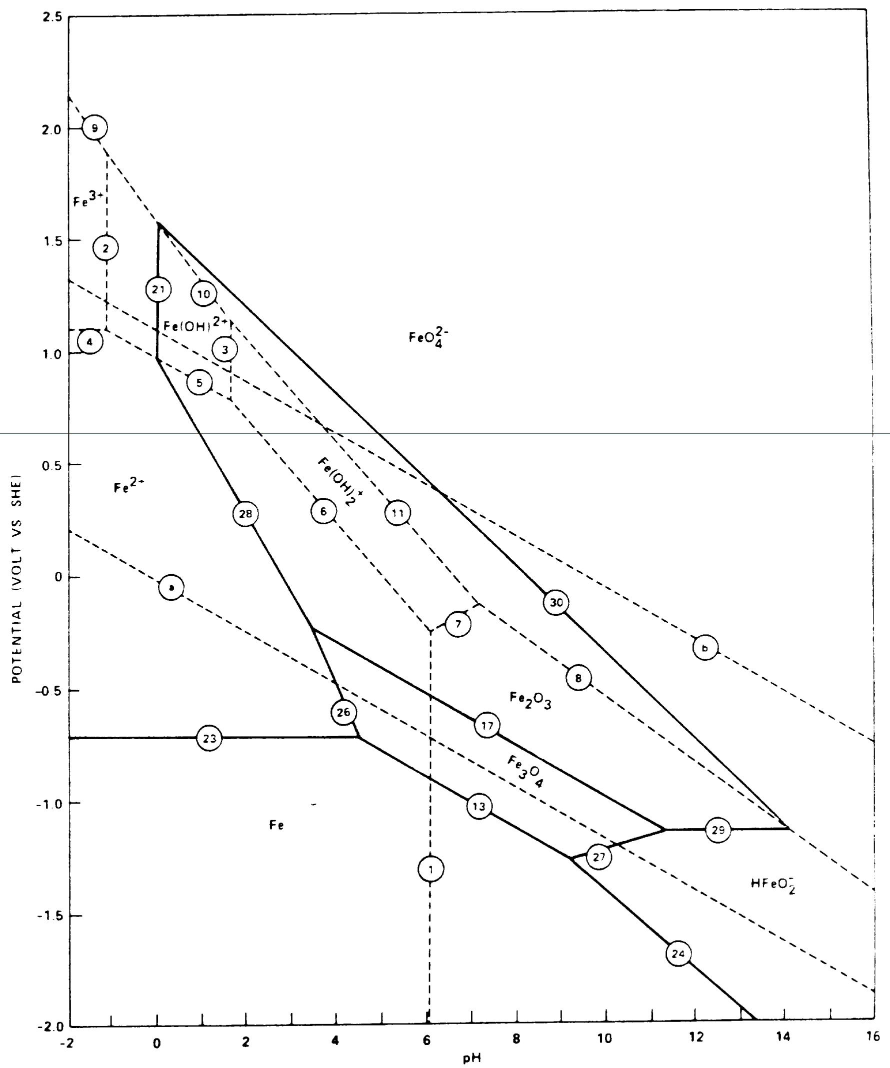
$E_{OH-/O_2} = 1.23 - 0.059pH$

Pourbaix Diagram Example

Is there a problem? What can you do?



Pourbaix Diagram for Fe-H_2O at 300°C

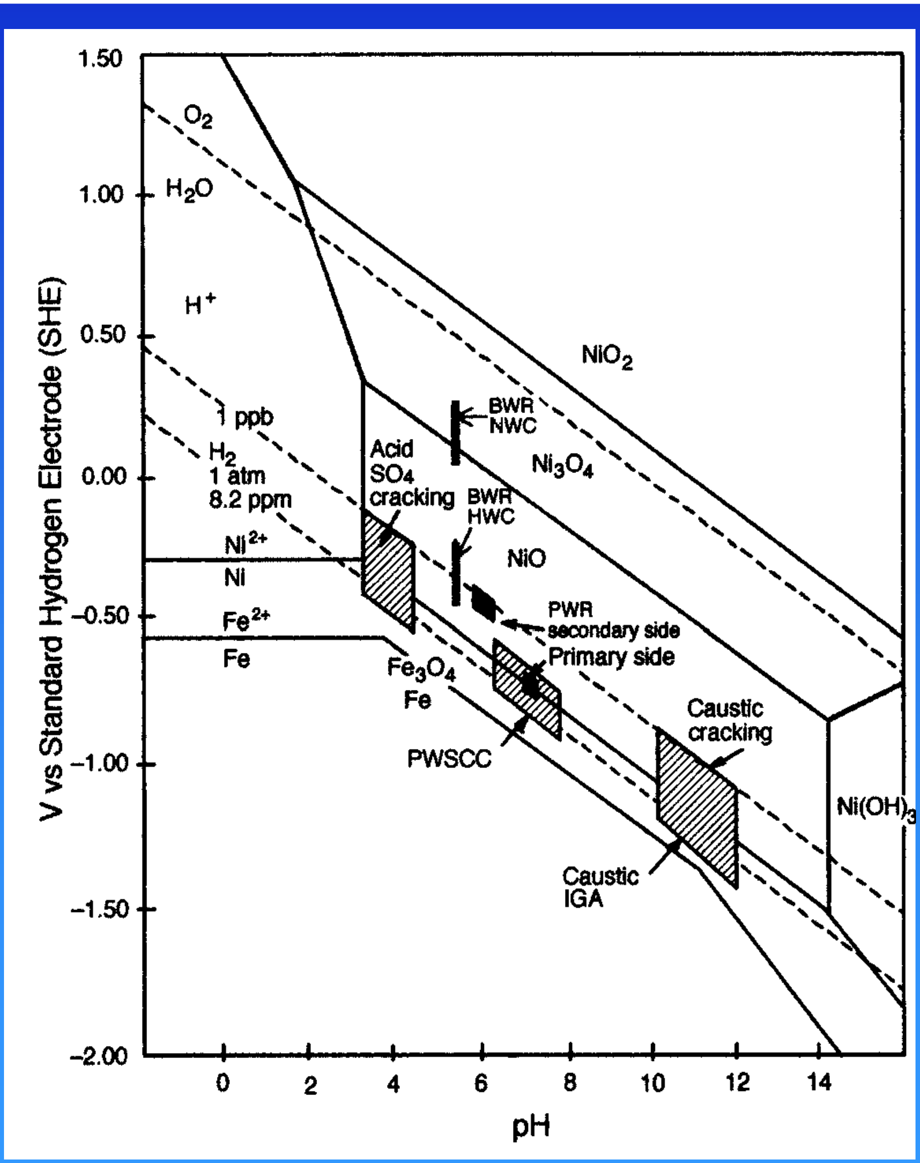


300°C

$A_{Fe} = 10^{-6}$
$A_{gas} = 1$
$A_{solid} = 1$

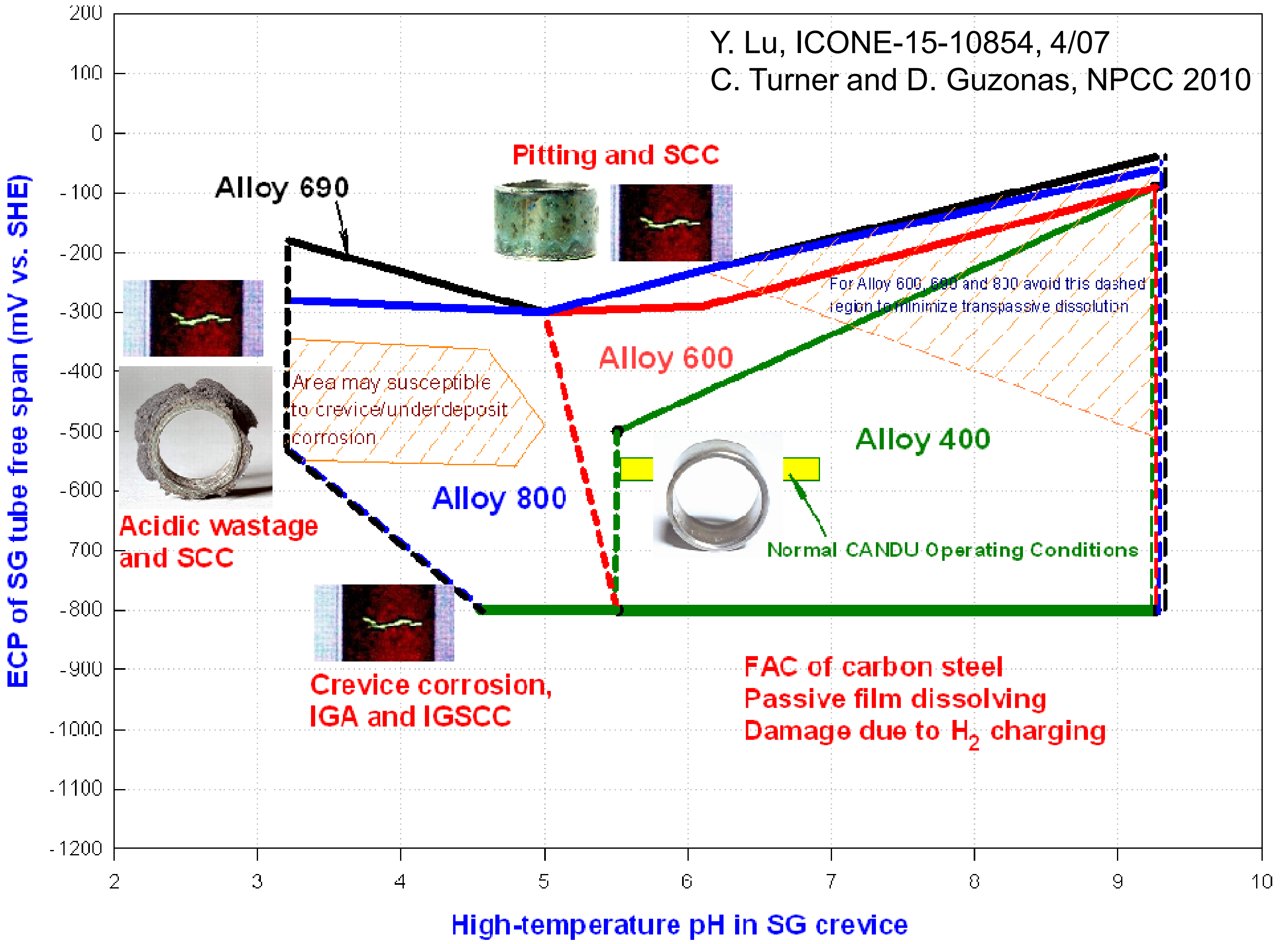
P. Andresen, 93CRD215, 10/93

Pourbaix Diagram for Ni Alloys in LWRs



P. Scott, Corrosion, Vol. 56, No. 8, 2000

ECP-pH Zones to Minimize Degradation Risk of CANDU® SG Alloys at 300ºC



Y. Lu, ICONE-15-10854, 4/07
C. Turner and D. Guzonas, NPCC 2010

Pourbaix Diagram Limitations

- M-H_2O diagrams present equilibria among metal, metal ions and solid oxides in systems where only metal, water, H^+ and OH^- exist. This is not the real world!
- Diagram is based on <u>pure</u> metals, not alloys
- These equilibrium thermodynamic diagrams reveal nothing concerning corrosion kinetics
- Criteria for passivity is a concern (e.g., Fe_2O_3 [rust] is considered passive!)
- Bulk chemistries are different than chemistries inside a crevice, pit or crack, i.e., the local environment must be considered

Corrosion Kinetics

Thermodynamics vs. Kinetics

- Thermodynamics
  - Equilibrium between metals and their environments
  - Corrosion tendency of metals
  - Qualitative picture of what can happen at a given pH and potential (Pourbaix Diagram)
- However:
  - Considerations of equilibrium are irrelevant to the study of corrosion rates
  - Some metals with pronounced tendency to react (e.g., Al) react so slowly that they meet the requirements of a structural metal

Kinetics of Corrosion

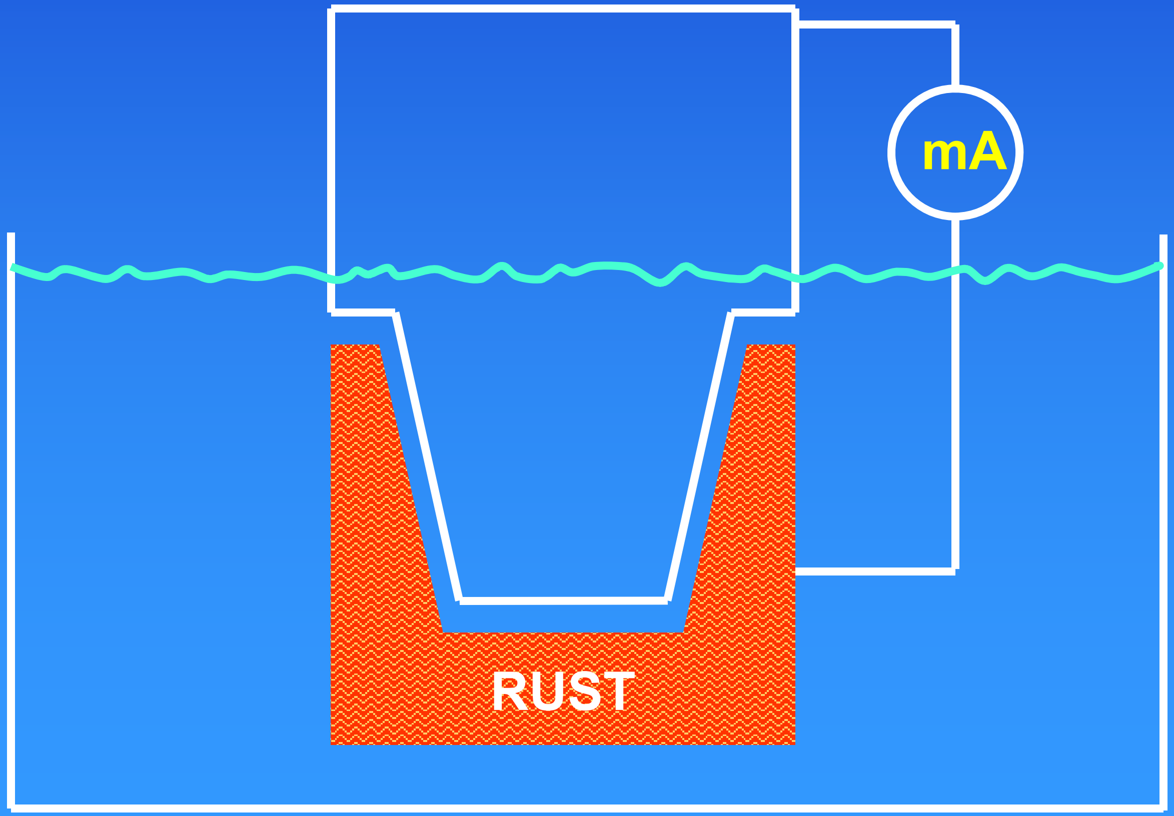
- Corrosion is thermodynamically possible for most environmental conditions
- Kinetics is the study of the rates of corrosion reactions
- Electrode kinetics are studied to predict the corrosion rates for the actual conditions
- An understanding of the fundamental laws of electrochemical reaction kinetics is essential to develop more corrosion-resistant alloys and techniques for corrosion mitigation

What is Current i?

- Unit: ampere (mA, µA, nA)
- Electron flow is the result of a corrosion reaction
- Current is a measure of the <u>rate</u> of the corrosion reaction (electrons per second)
- 0 current <u>is nothing</u>! If i = 0, then no corrosion!
- Anodic (oxidation) and cathodic (reduction) have different polarity
- Current may be expressed as amps, I, or current density, i/cm^2
- Current density ≠ today's stupidity

Another Salt Solution Experiment

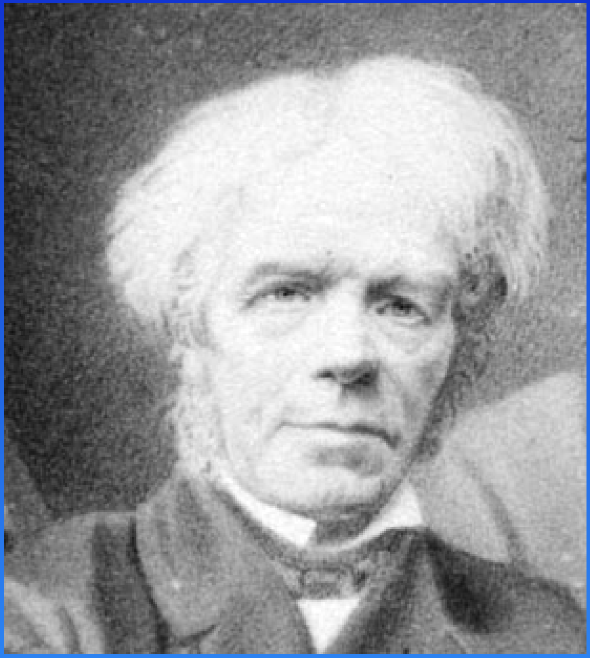
- U. R. Evans and Thomas Percy Hoar (a.k.a. T. P. Hoar or Sam Hoar) (1907 – 1978)
- Experiment in 1932 using 3% KCl
- Corrosion was directly proportional to the current



T. P. Hoar

Current Density and Faraday's Law

- Current density (A/cm^2) was found to be electrochemically equivalent to the weight loss of the rusted section
- Current, I (amps), measured during a corrosion reaction is the rate of charge transfer
- 1 Amp = 1 coulomb/s = 1 C/s
- Charge on an electron = 1.602 x 10^{-19} C
- Mole = 6.0235 x 10^{23} atoms (Avogadro's number)



1 Faraday
1791-1867

Total charge on a mole of monovalent metal ions = 1.602 x 10^{-19} C x 6.0235 x 10^{23} = 96,469 C/mole or 23,060 cal/volt/mole = 1 Faraday

Faraday's Law and Corrosion Rates

- In the more general instance of anodic dissolution of a species by charge transfer, nF coulombs, where n equals the number of electrons involved in one act of the reaction, will be required for 1 mole of atoms
- Example: $Fe \rightarrow Fe^{2+} + 2e^{-}$ $n = 2$
- Corrosion rates can be expressed several ways:

$\frac{i}{nF}$ for moles/cm^2/s

$\frac{iM}{nF}$ for gms/cm^2/s where M = atomic weight (used for wall thinning rates)

$\frac{iM}{nF\rho}$ for cm/s where ρ = density (used for crack growth rate calculations)

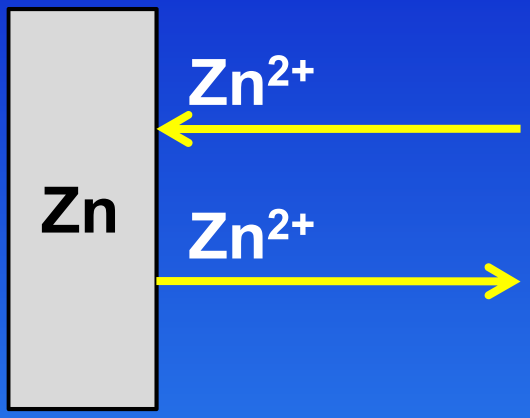
Determination of Corrosion Rates

- Corrosion rates can be measured by applying a potential to produce a polarization curve (the degree of potential change as a function of the amount of potential applied) for the metal surface
- When the potential of the metal surface is polarized by the application of the potential in a positive direction, it is said to be anodically polarized; a negative direction signifies that it is cathodically polarized

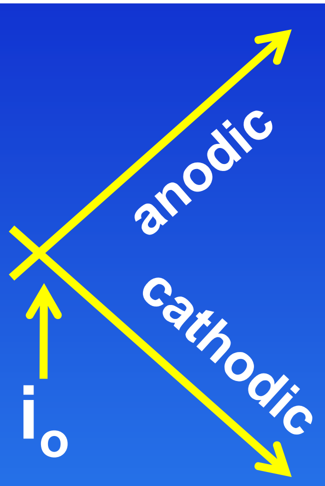
Determination of Corrosion Rates

- Degree of polarization is a measure of how the rates of the anodic and the cathodic reactions are affected by:
    - Surface processes (adsorption, film formation, ease of release of electrons, etc.) factors - activation polarization
    - Concentration of metal ions, dissolved oxygen, etc. in solution - concentration polarization
- Variation of i as a function of E (polarization curves/Evans diagrams) allows the evaluation of the effect of concentration and activation processes on the rate of corrosion

Exchange Current Density



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



- Reduction and oxidation reaction occur at the same rate at the equilibrium potential of a reaction
- For a Zn electrode, Zn ions are released from the metal and discharged on the metal at the same rate
- Reaction rate in each direction can also be expressed by the transport rate of electric charges, i.e., by exchange current density, i_o
- Net reaction rate and net current density are zero

Exchange Current Density

- ECD is a measure of the reversibility of a reaction such as $2H^+ + 2e^- \rightarrow H_2$
- At the standard half-cell (redox E), $E^0_{H^+/H2}$, of this reaction is in equilibrium where the forward rate (left to right), r_f, is equal to the reverse rate (right to left), r_r

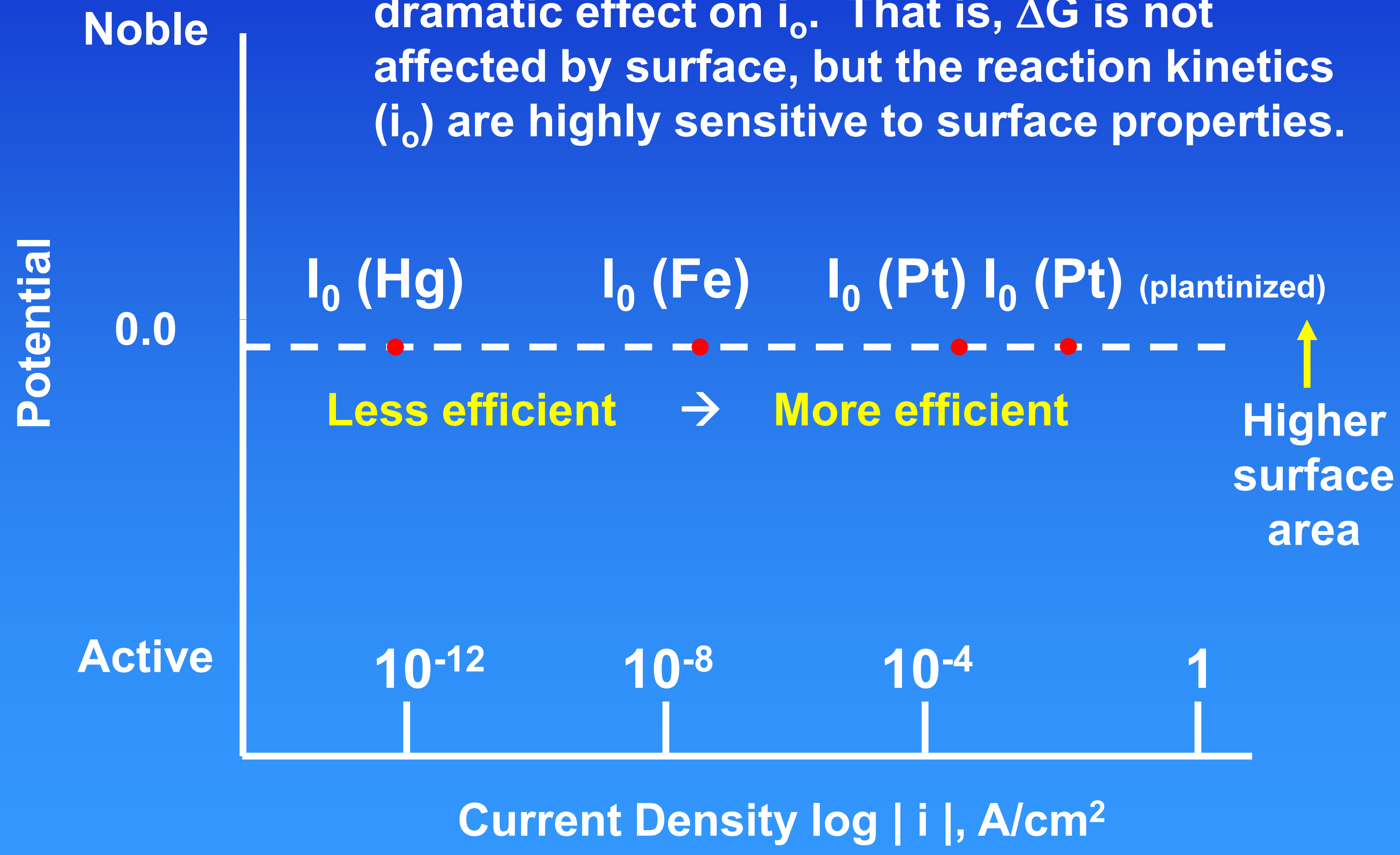
$$r_f = r_r = \frac{i_0 M}{nF}$$

where i_0 = ECD, a fundamental thermodynamic parameter that must be measured

- ECD is <u>affected</u> by the nature of the surface
- E is <u>not</u> affected by the nature of the surface
- Evans Diagrams!

Exchange Current Density

While the surface has no effect on E, it has a dramatic effect on i_o. That is, ΔG is not affected by surface, but the reaction kinetics (i_o) are highly sensitive to surface properties.



Polarization and Overpotential

- Electrode reactions are assumed to induce deviations from equilibrium due to the passage of an electrical current through an electrochemical cell causing a change in the electrode potential. This is *polarization*.
- Deviation from equilibrium causes an electrical potential difference between the polarized and the equilibrium (unpolarized) electrode potential. This is *overpotential*.

Polarization is the potential shift away from the equilibrium/stabilized potential

Polarization and Overpotential

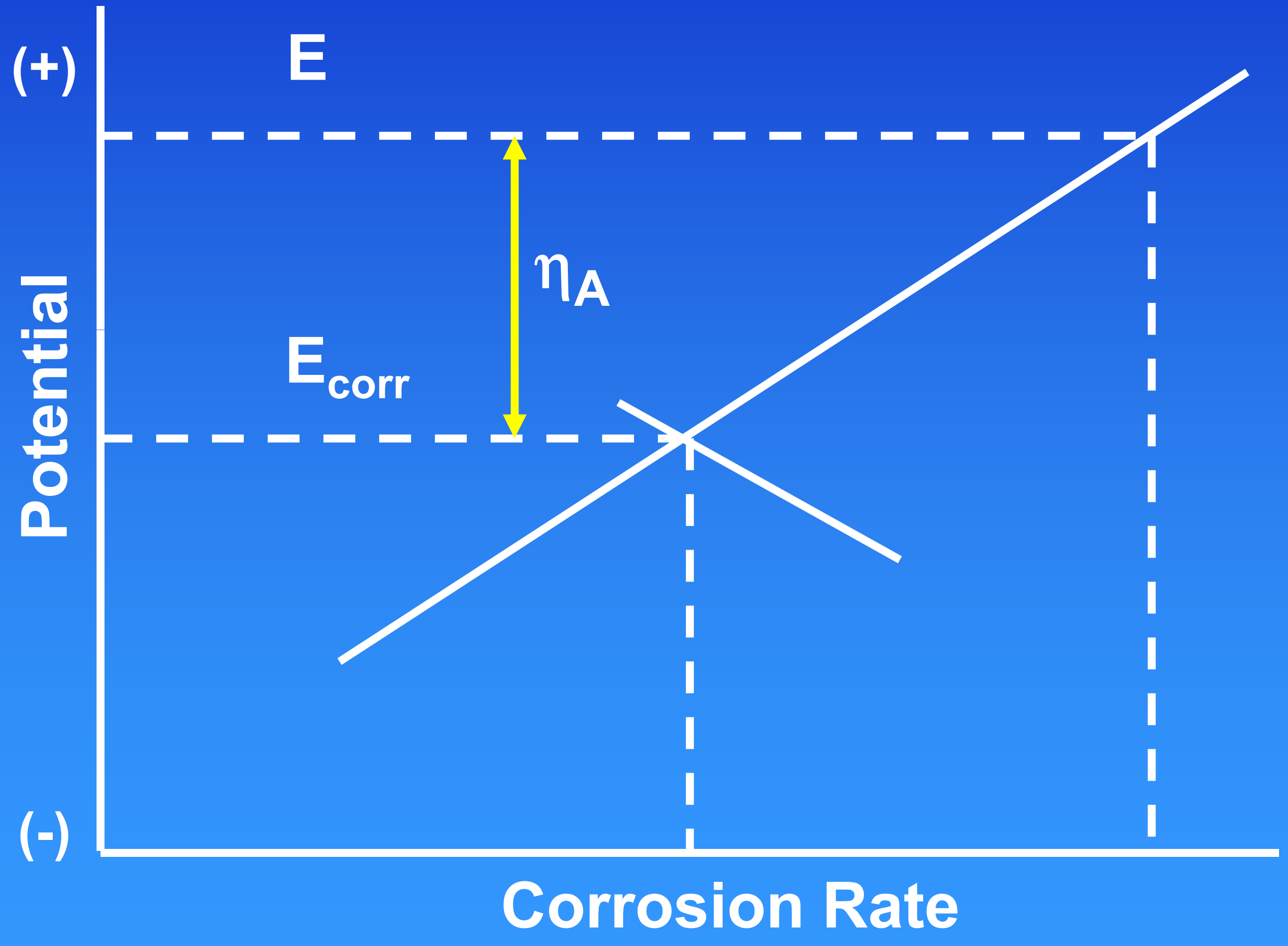
- Polarization, as measured by overpotential, η (eta), is the deviation of potential away from equilibrium
- Two basic types: anodic and cathodic
  - Anodic polarization – take the material to more positive potentials – anodic (corrosion) reaction increases
  - Cathodic polarization – take the material to more negative potentials – cathodic reaction increases
- What causes polarization?
  - Society: Politics, religion, economic status, etc.
  - Electrochemistry: electron supply or withdrawal

Polarization and Overpotential

- As electrons leave the anode, the anode potential becomes more positive
  - Positive potential change is anodic polarization
- As electrons enter the cathode, the cathode potential becomes more negative
  - Negative potential change is cathodic polarization
- The metal surface in an aqueous solution will reach a steady state potential, E_{corr}, that depends on the ability and rate at which electrons can be exchanged by the available cathodic and anodic reactions

Evans Diagram - Polarization

Anodic polarization: $\eta_A = E - E_{CORR}$



Activation Polarization

- When current flows through the anode and cathode, their shift in potential is partly due to activation polarization
- An electrochemical reaction may consist of several steps
- Slowest step determines the rate of the reaction that requires activation energy to proceed
- Subsequent shift in potential or polarization is termed activation polarization
- Most important example is that of hydrogen ion reduction at a cathode, $H^+ + e^- \rightarrow \frac{1}{2} H_2$, the polarization is termed as hydrogen overpotential

Hydrogen Activation Polarization

- H_2 gas evolution occurs in 3 major steps:

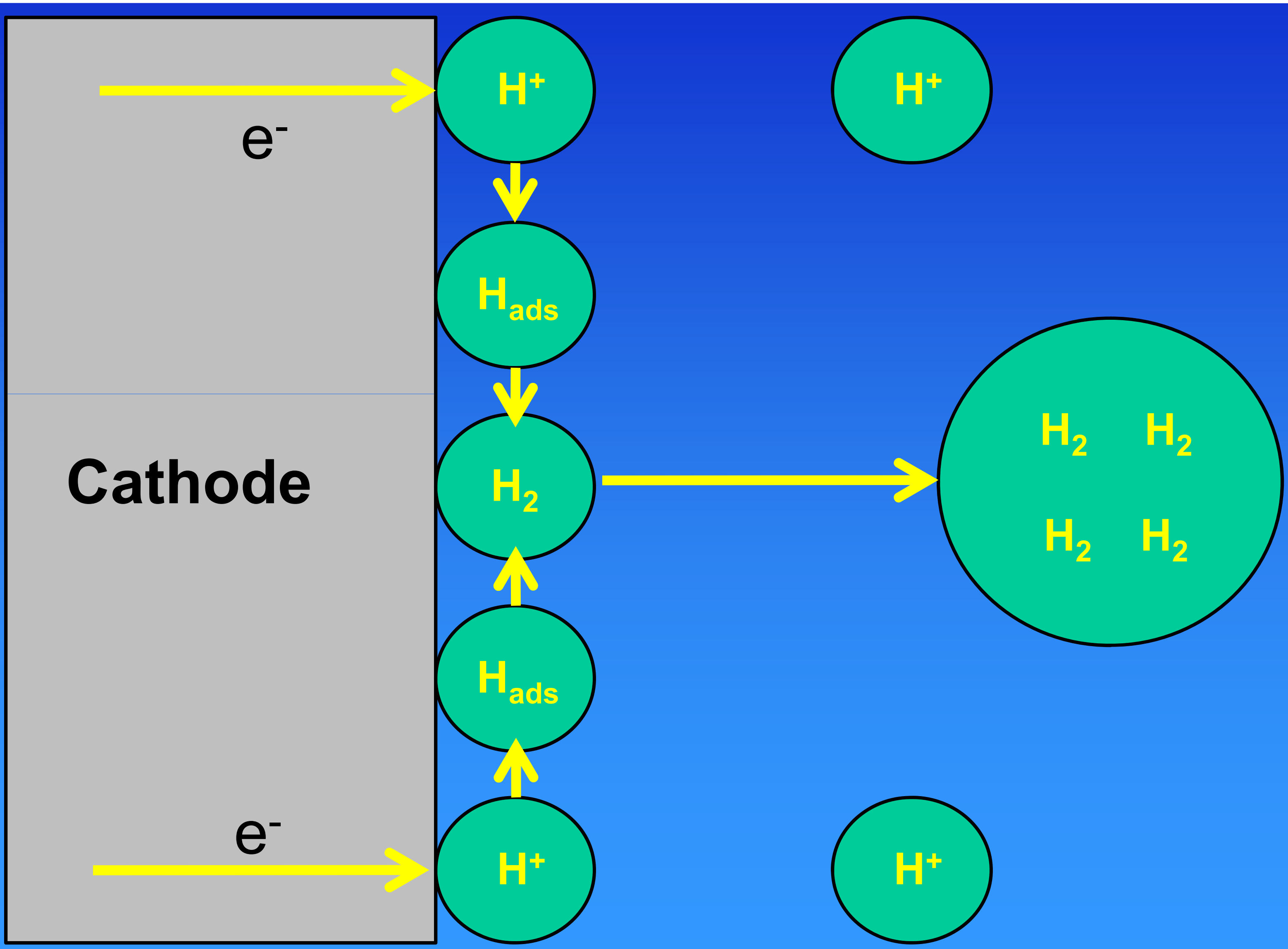
  1. $H^+ + e^- \rightarrow H_{ads}$

  2. $H_{ads} + H_{ads} \rightarrow H_2$

  3. Requires molecules to coalesce, nucleate and grow into H_2 bubbles on the surface

- Any one of the steps can be rate controlling and cause activation polarization

Rate of H^+ Reduction Reaction



Detail of Evans Diagram Near Corrosion Potential

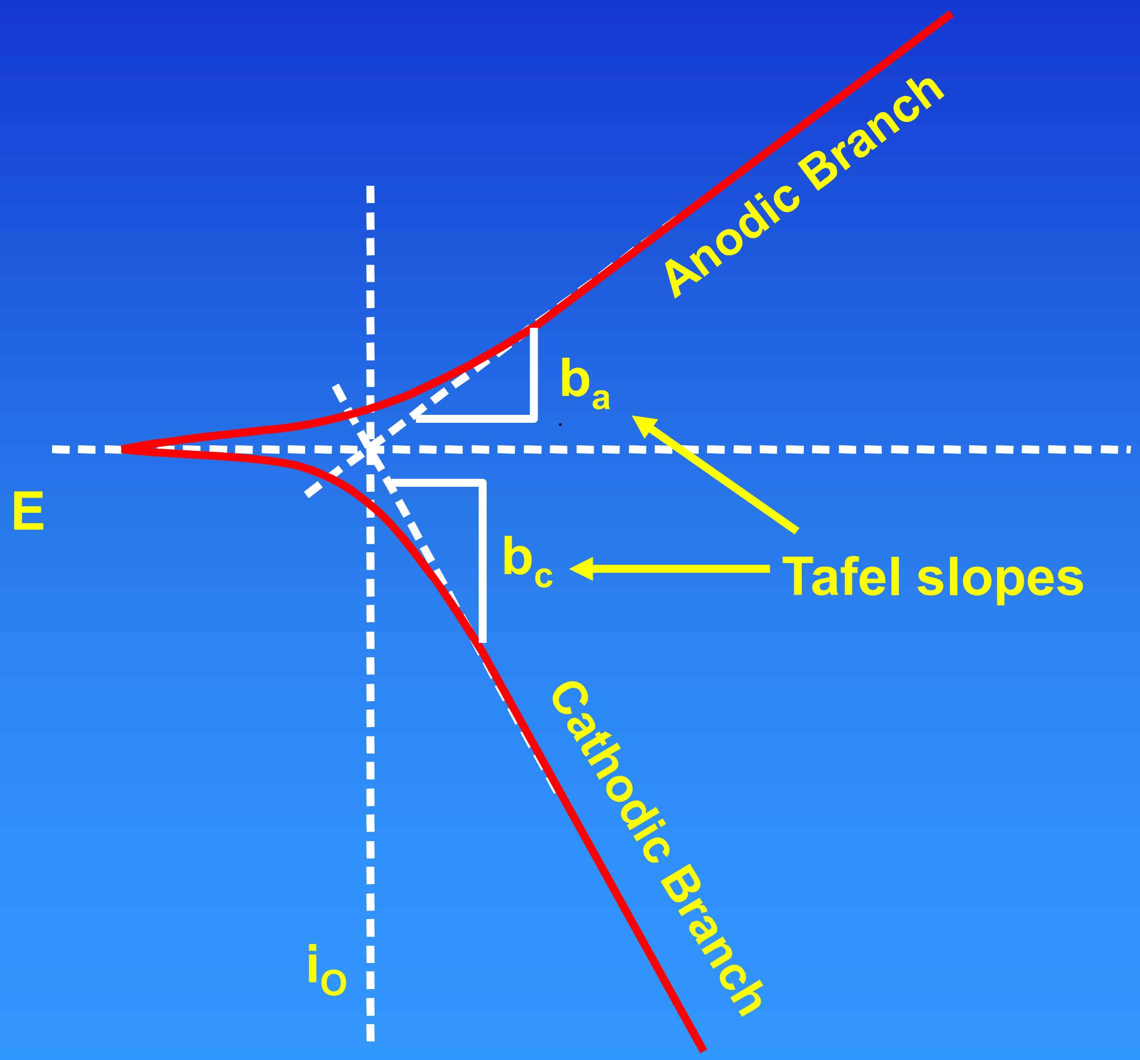
Julius Tafel (Swiss) mathematically described the relationship between E and i in 1905

1862- 1918

Activation polarization (*η*) increases with current density in accord with Tafel equation:

$$\eta = \pm\beta \log \frac{i}{i_o}$$

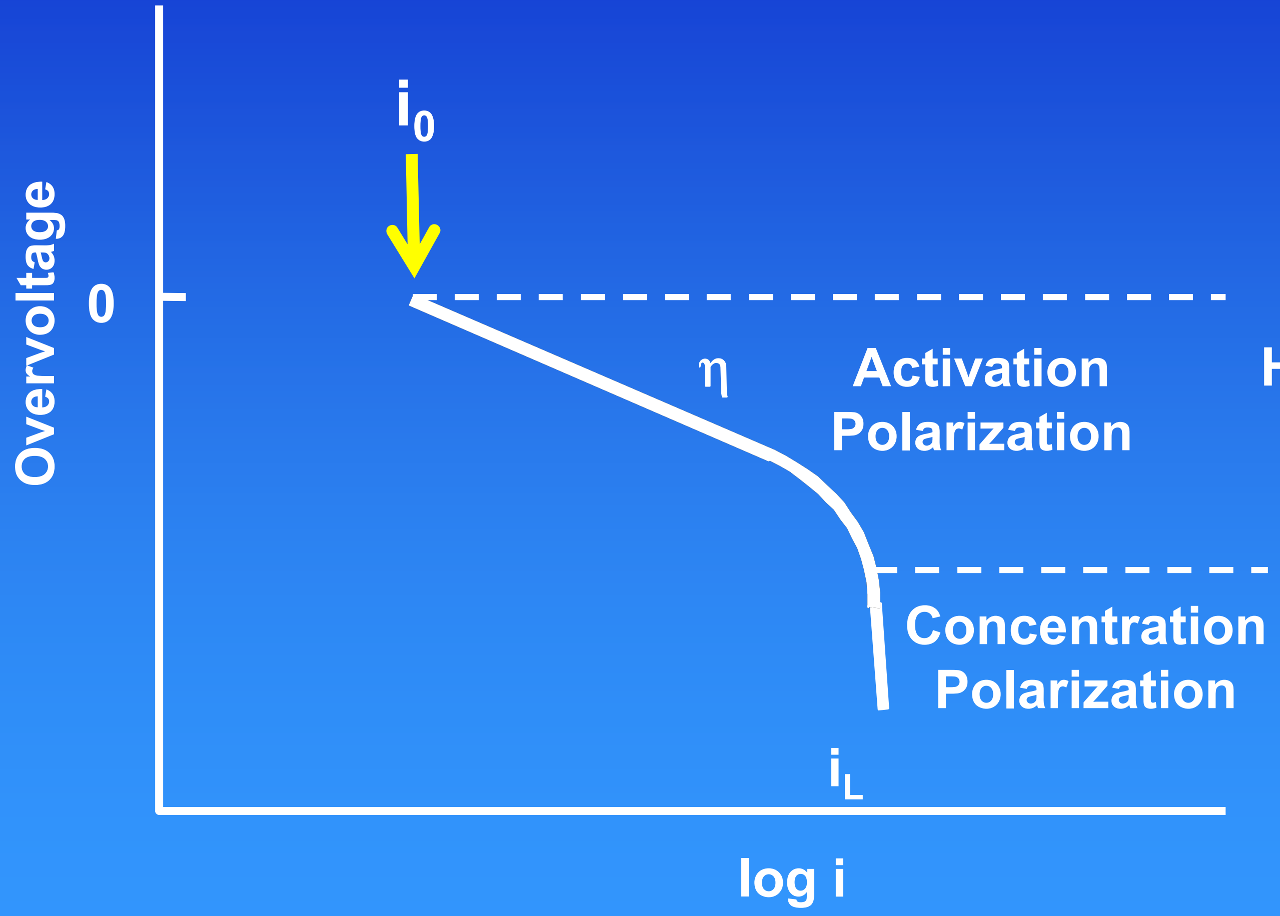
Detail of Evans Diagram Near ECD



Concentration Polarization

- Concentration polarization occurs when the mass transport within the solution is rate determining
- Concentration polarization implies either there is a shortage of reactants at the electrode or that an accumulation of reaction product occurs
    - ♦ Most typical concentration polarization due to a lack of reactants, i.e., most often for reduction reactions

Combined Polarization Curves - Activation and Concentration Polarization



How difficult is the reaction?

How much of the reactant is at the surface?

Mixed Potential Theory

- Tafel parameters, β_a and β_c plus exchange current density, i_0 , and limiting current density, i_L, can describe all electrochemical corrosion systems
- The principal of charge conservation is required to apply to all half-cell reactions occurring simultaneously on a conducting surface
- Total rate of oxidation = total rate of reduction
  - There is no accumulation of charge at the electrode

Mixed Potential Theory Example

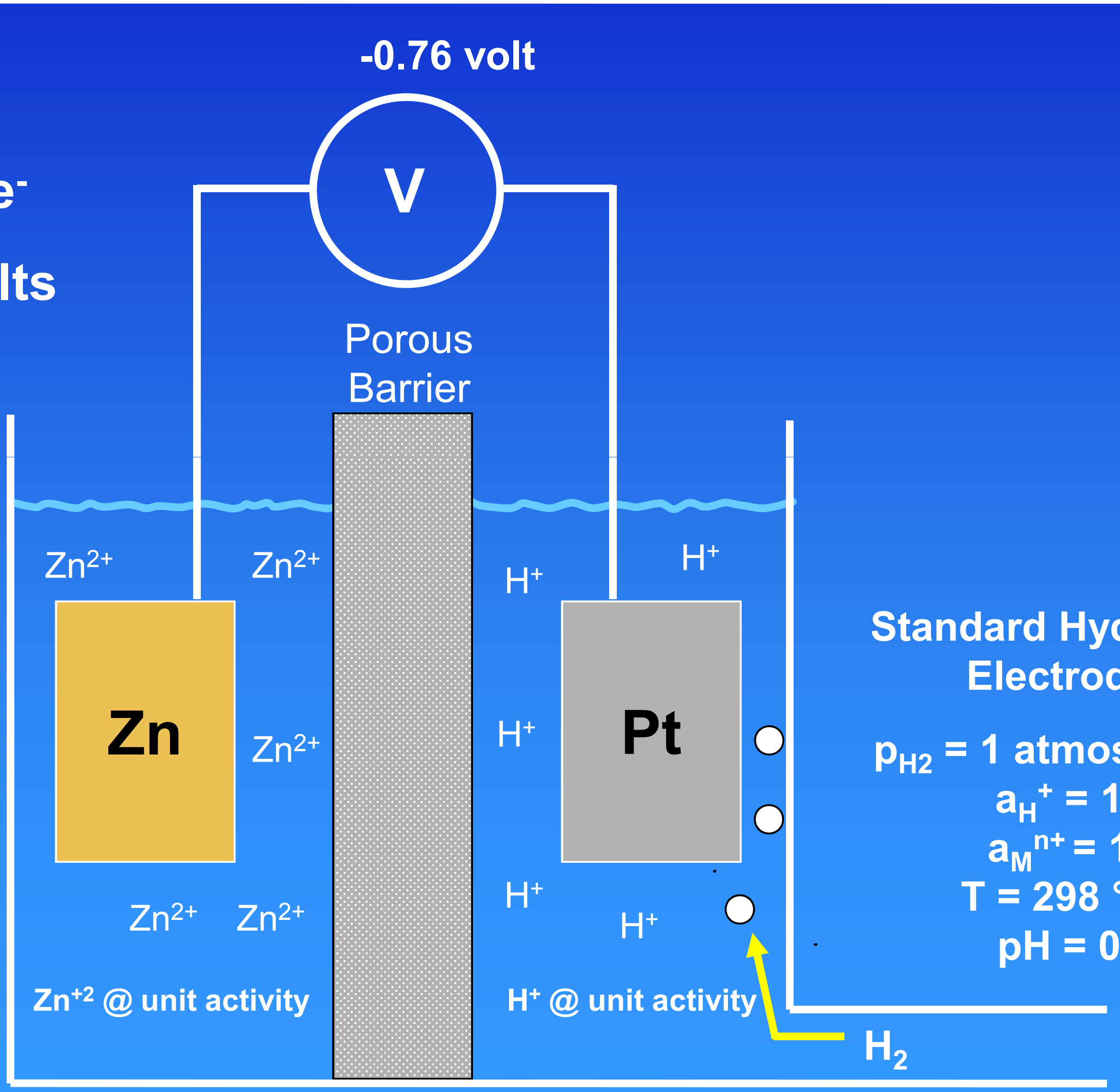
- Zn in acid
- $Zn \rightarrow Zn^{2+} + 2e^-$ Anode half-cell
- $2H^+ + 2e^- \rightarrow H_2$ Cathode half-cell
- Each half-cell has its own unique half-cell E and i_0
- However, the two half-cell Es cannot coexist separately on an electrically conductive surface
- Polarization of each reaction to some intermediate value, where anodic and cathodic reactions have equal and opposite rates, E_{corr} must occur
- This intermediate value, E_{corr}, is the corrosion potential or mixed potential

Zn Electrode and SHE

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

$E^0_{SHE} = -0.76$ volts

Zn electrode at standard state



Standard Hydrogen Electrode

p_{H2} = 1 atmosphere

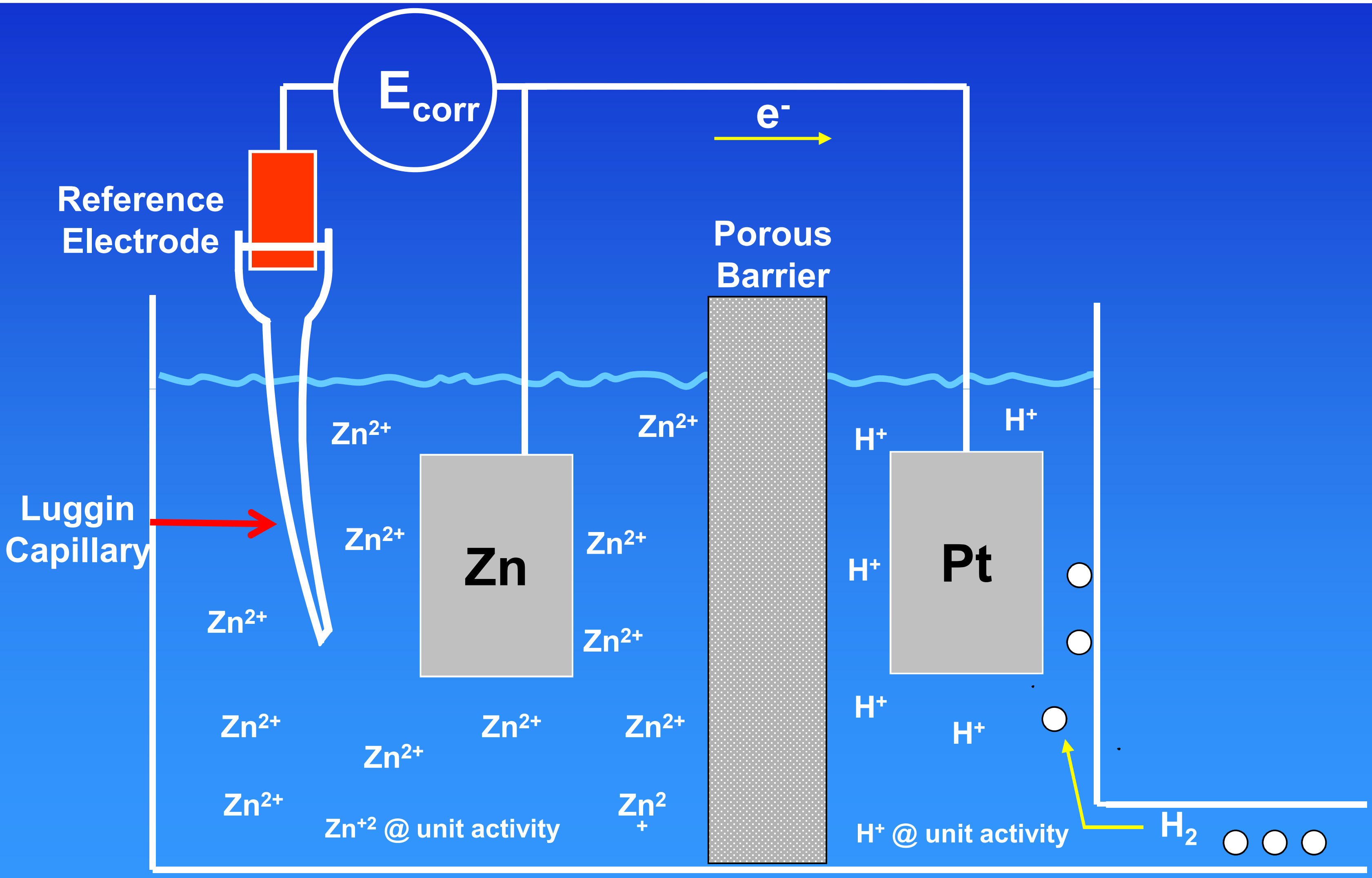
$a_H{}^+ = 1$

$a_M{}^{n+} = 1$

T = 298 °K

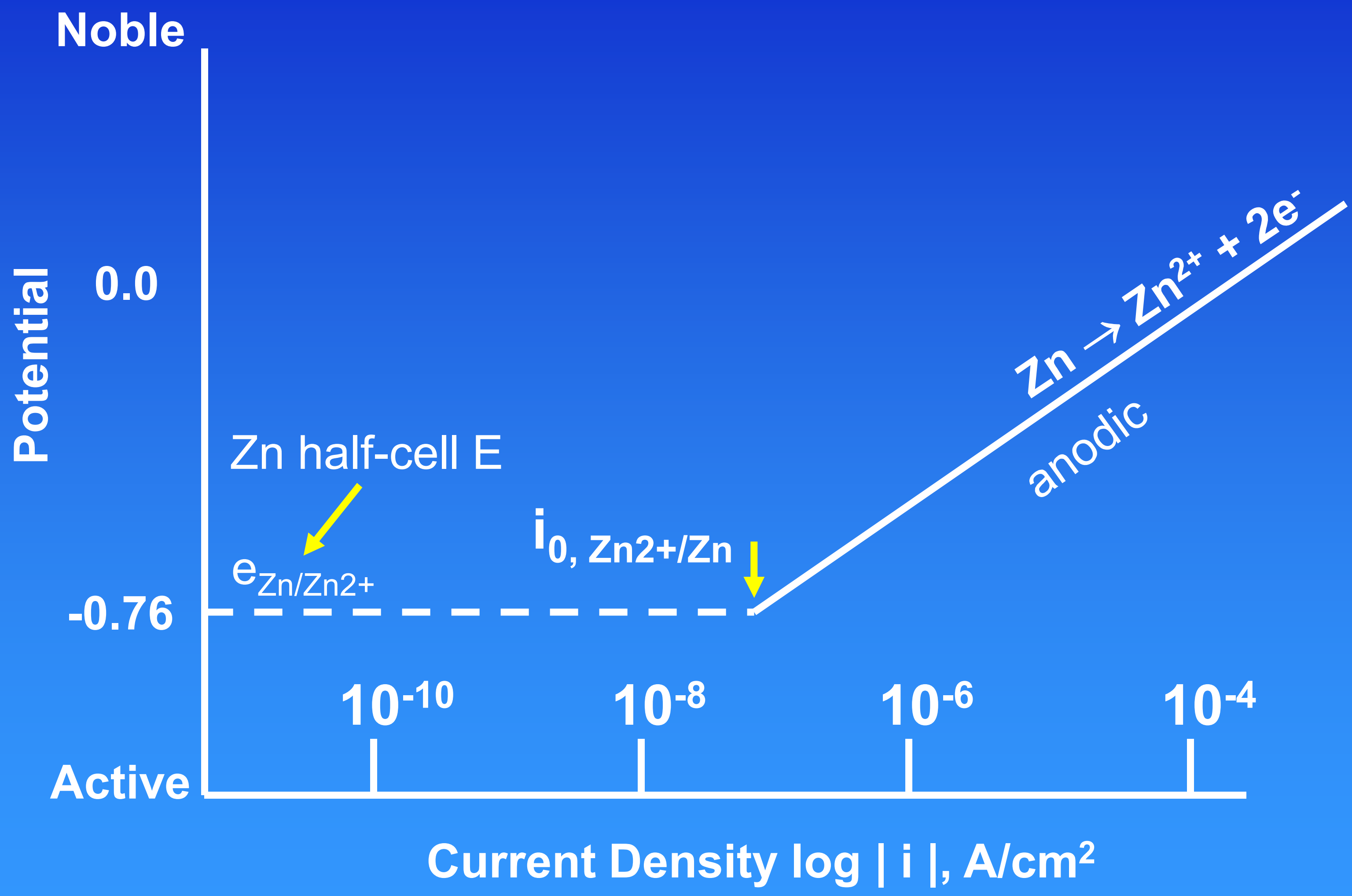
pH = 0

Measurement of E_{corr} of Zn

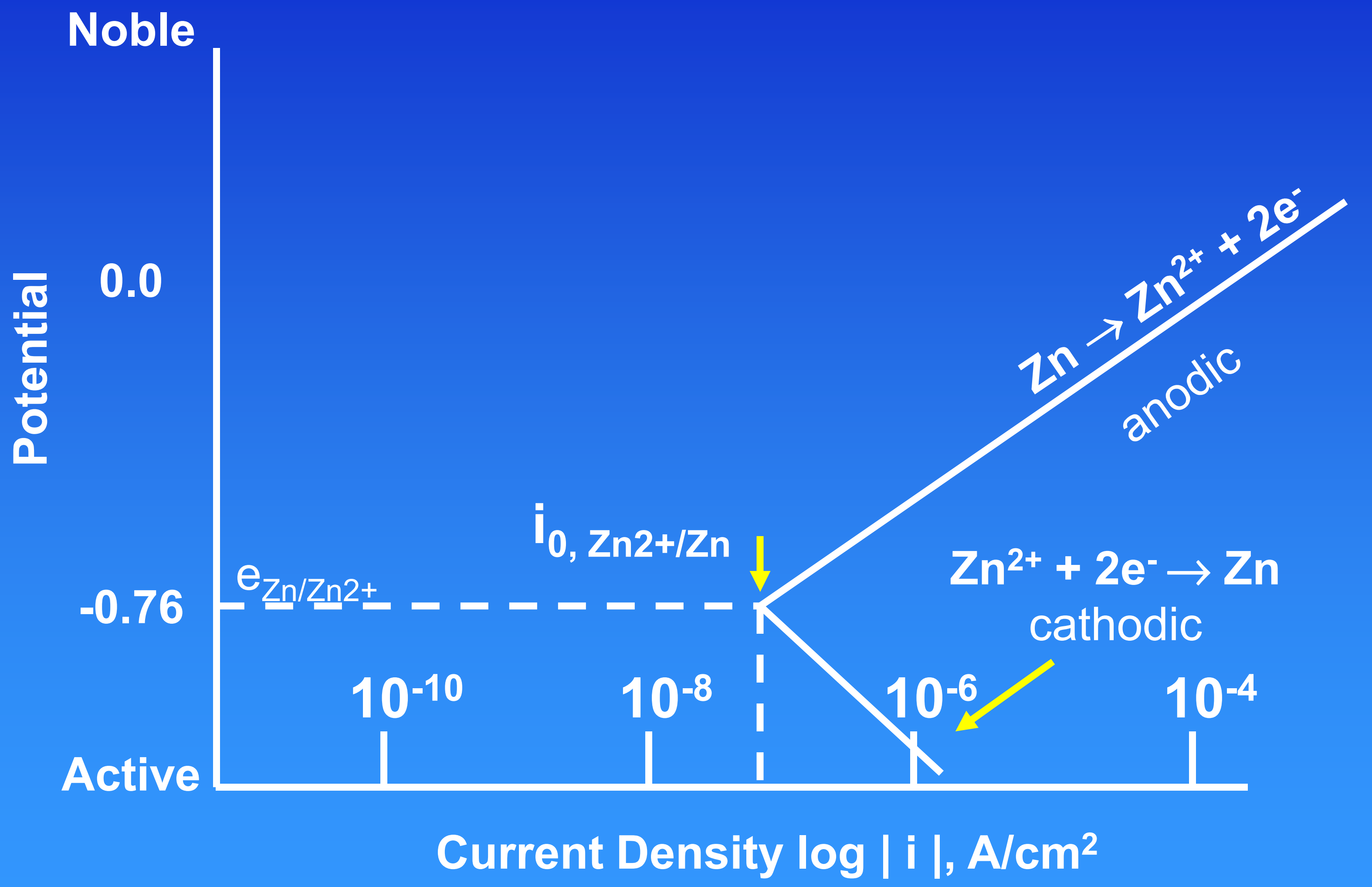


Corrosion and Corrosion Control in LWRs

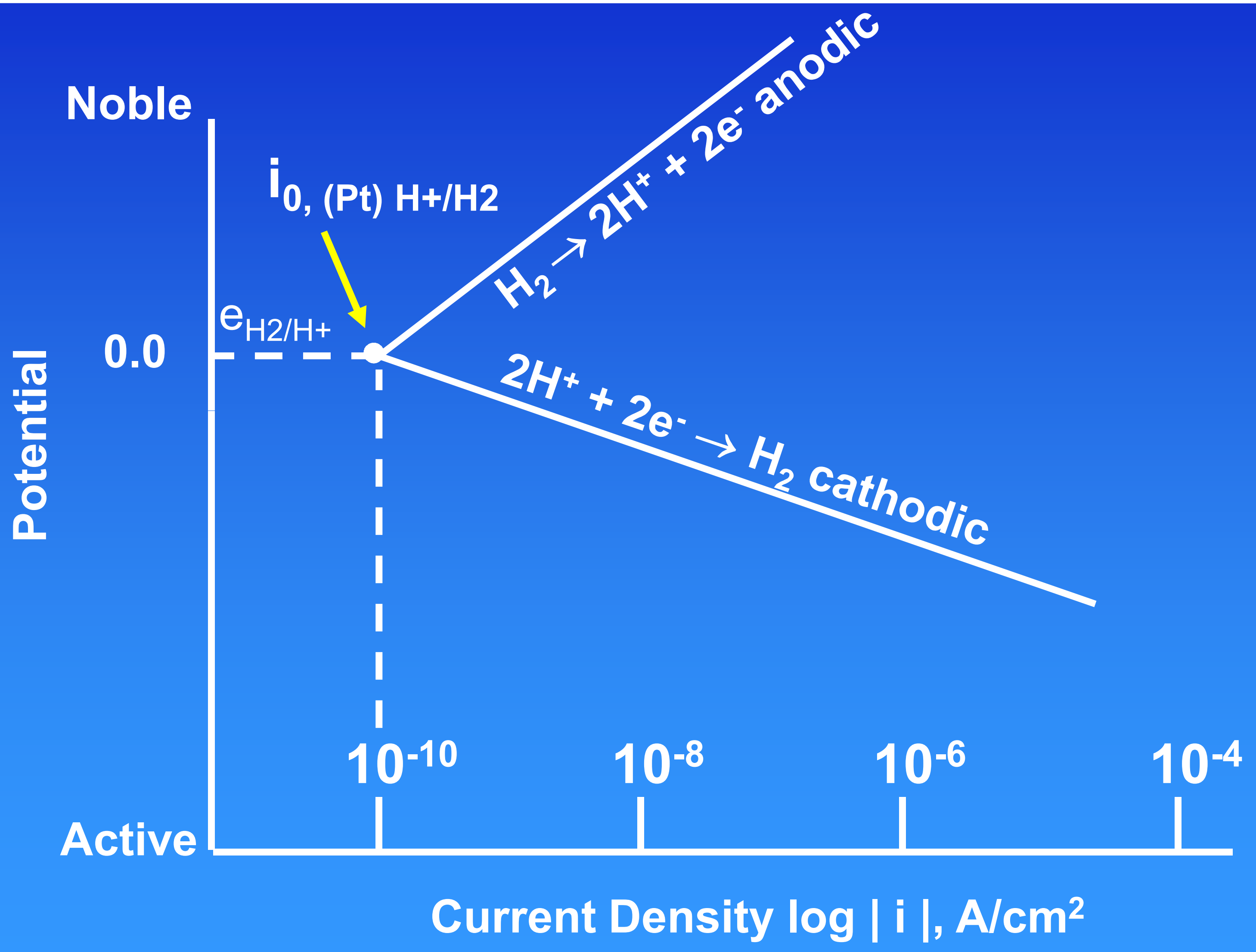
Mixed Potential Theory



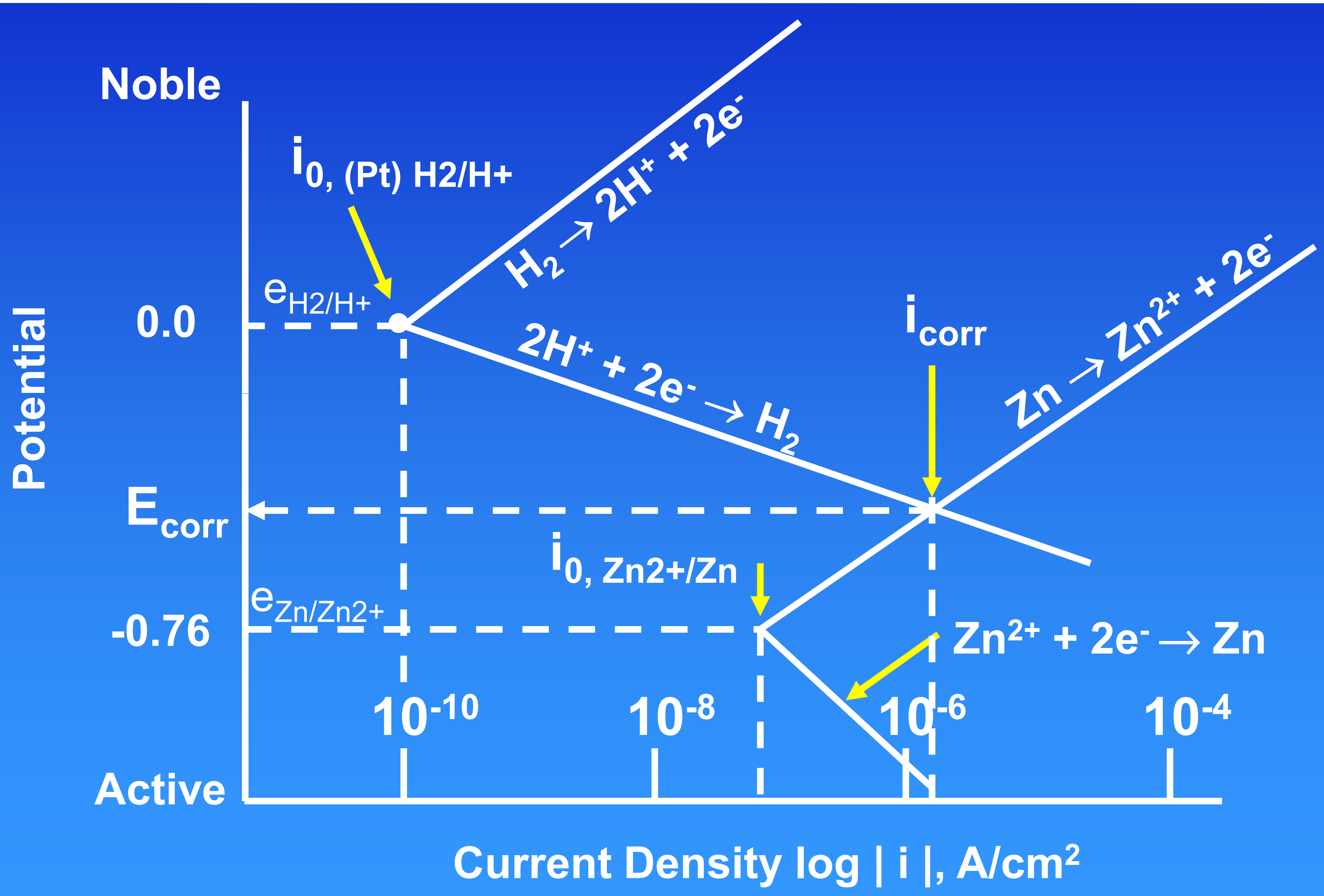
Mixed Potential Theory



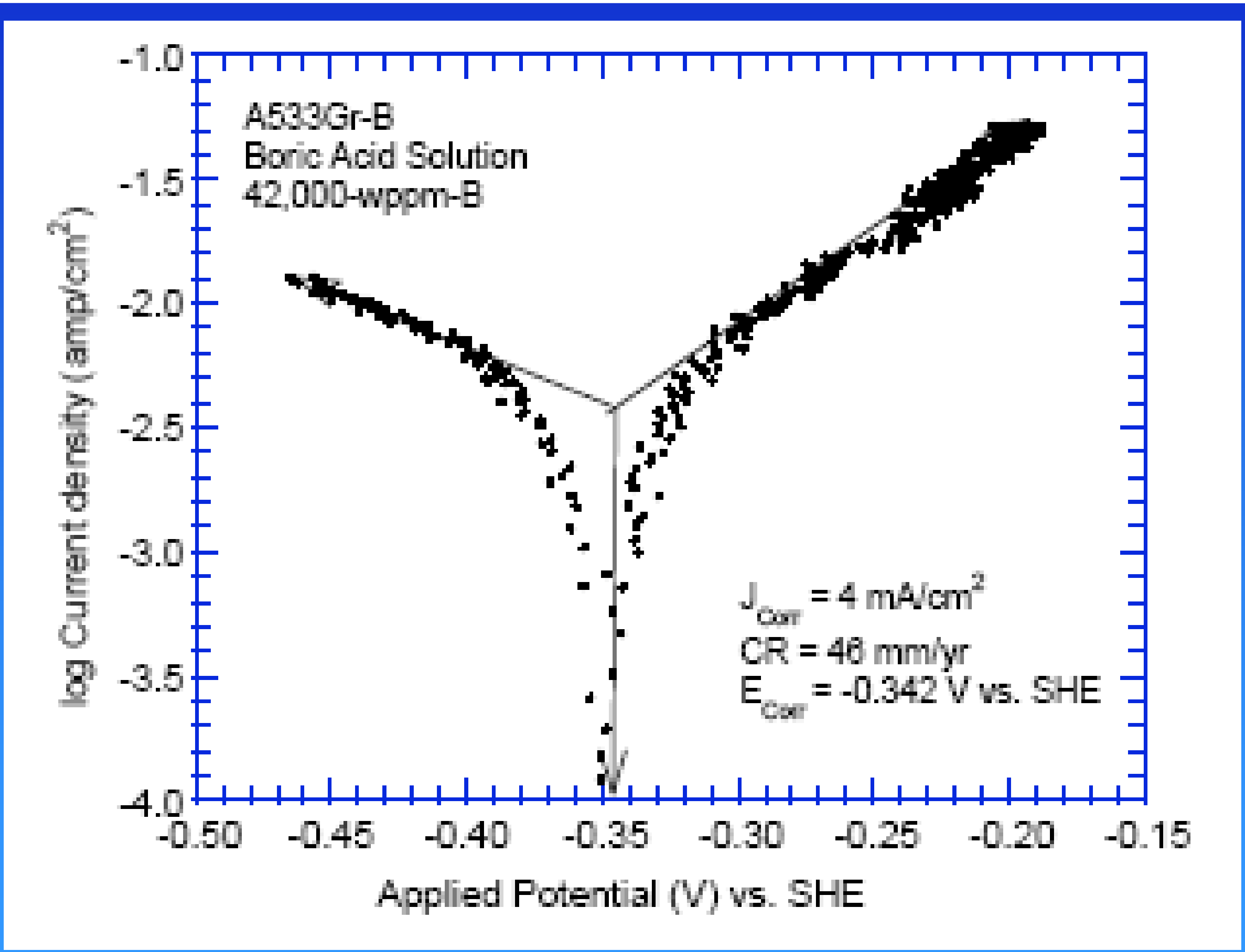
Mixed Potential Theory



Mixed Potential Theory



Example: A533 Gr. B in Boric Acid



Passivity

Passivity

- Condition of corrosion resistance due to formation of thin surface films under oxidizing conditions
- Many metals such as Fe, Ni, Cr, Zr, Co, etc. and their LWR alloys such as Type 304 SS, Alloys 600, 690 and X-750, zircaloy and Stellite™, demonstrate a decrease in corrosion rate above a critical E, E_p.
- Breakdown of passive films leads to localized corrosion such as pitting and environmentally-assisted cracking (EAC)

Passivity of SS and Ni-base Alloy Oxides

- Stainless steels and Ni alloys have low corrosion/oxidation rates in aqueous and gaseous environments due to the surface formation of passive chromia (Cr_2O_3) films at:
  - <100°C (212°F)
  - ~600°C (1110°F) gaseous environments
- At LWR temperatures (e.g.,200-350°C [392-662°F]) the spinel oxide, denoted as AB_2O_4, (A = Fe or Cr, B = Cr or Fe) is responsible for the low corrosion rates rather than Cr_2O_3

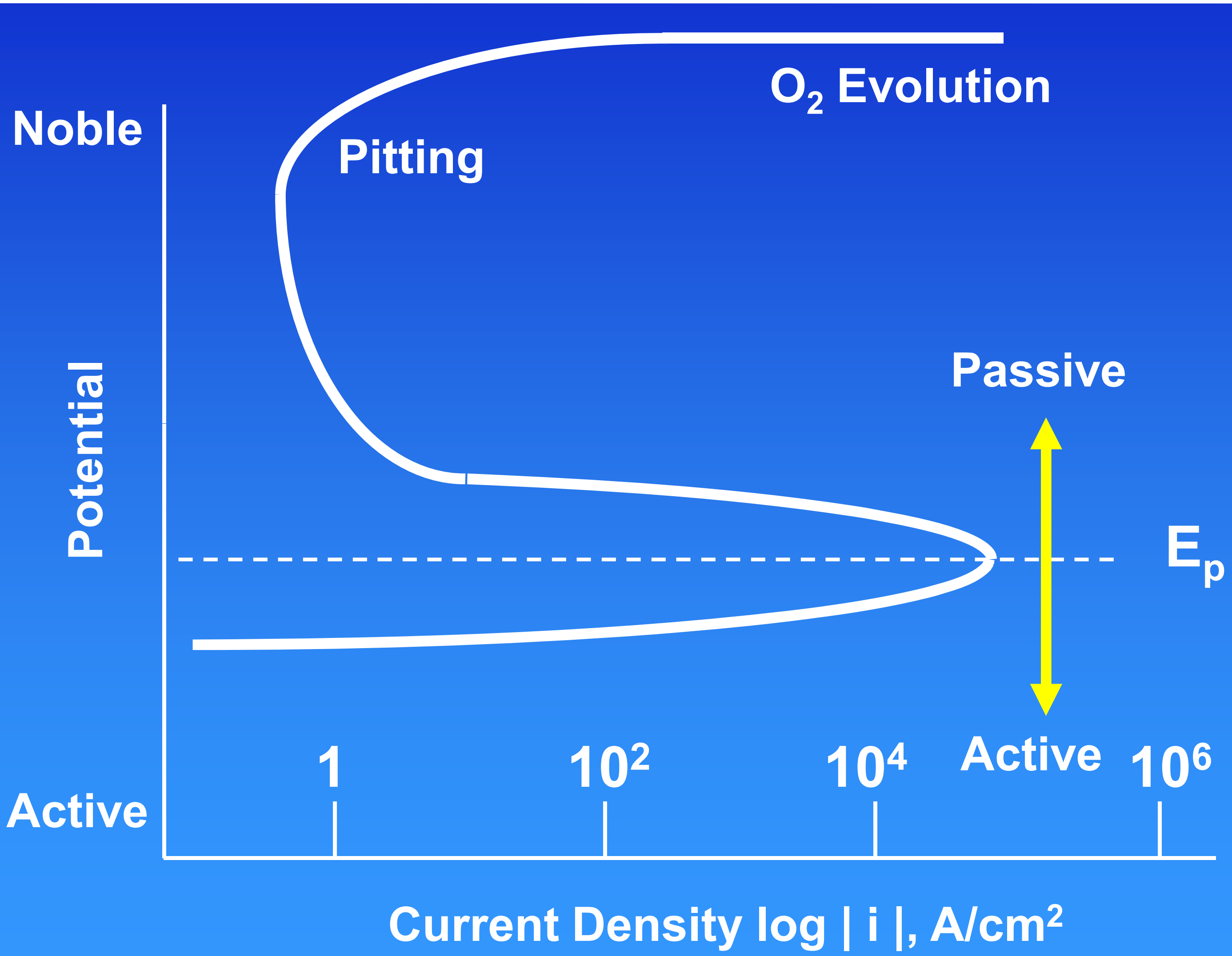
Duplex Oxides on Stainless Steels

- A duplex layered oxide is created by:
  - Inner layer widening by the in-situ oxidation of the metal following the ingress of water along oxide micropores
  - Outer layer growing by the outward diffusion of metal ions along oxide grain boundaries
- Outer oxide layer is typically released to solution, while the inner Cr spinel oxide layer is retained

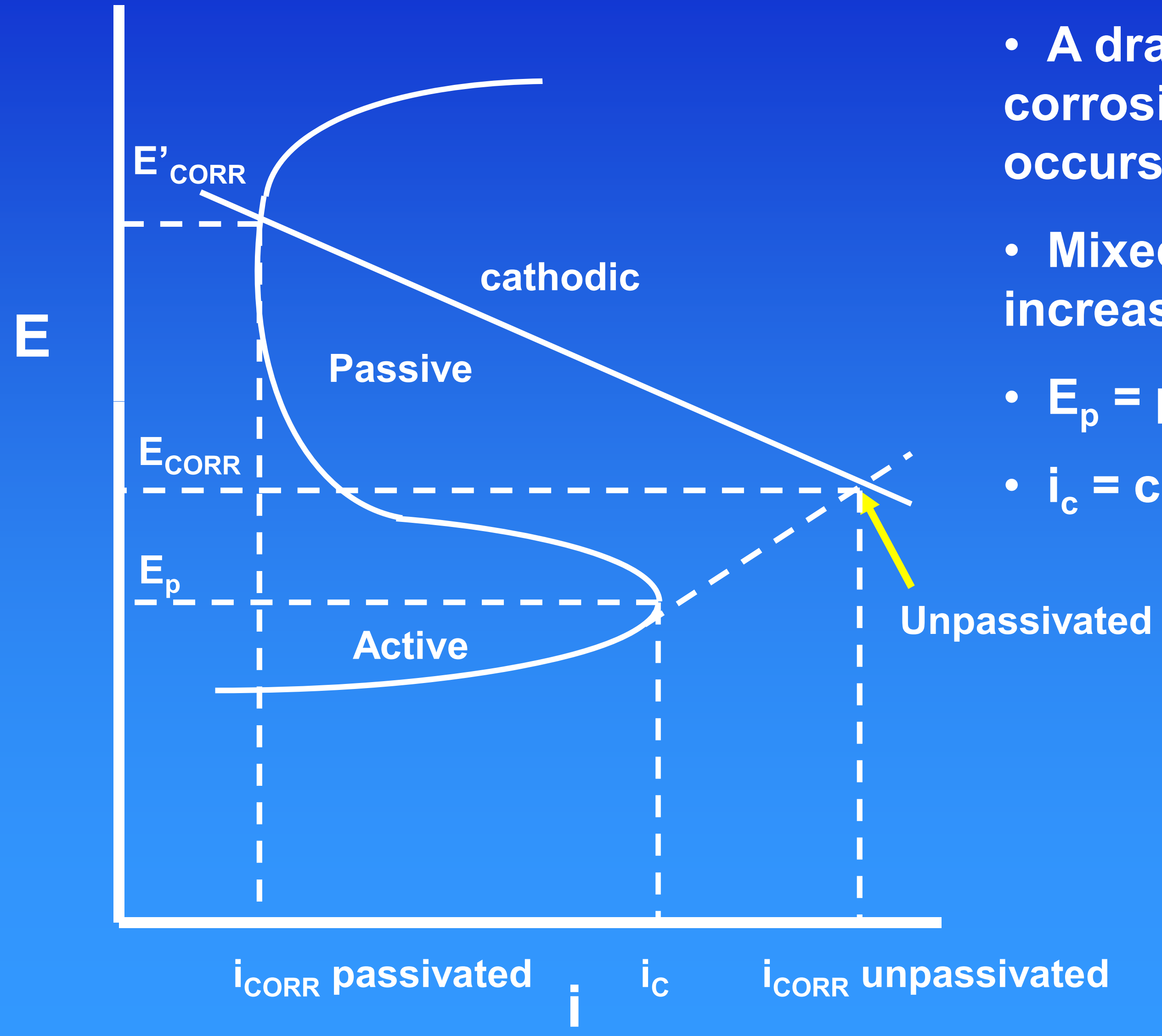
Duplex Oxides on Ni-based Alloys

- Due to their fixed valences, Ni and Cr can only form a spinel of a fixed composition of $NiCr_2O_4$, whereas the +2 and +3 valences of Fe allow it to form a continuous spectrum of spinels
- Alloy 600 (16% Cr)
  - Inner layer: ~48% $NiCr_2O_4$ + ~52% NiO
  - Outer layer: ~27% $NiCr_2O_4$ + ~73% NiO
- Alloy 690 (30% Cr)
  - Inner layer: ~90% $NiCr_2O_4$ + ~10% NiO
  - Outer layer: ~100% NiO

E vs. I Curve for Passive Alloys

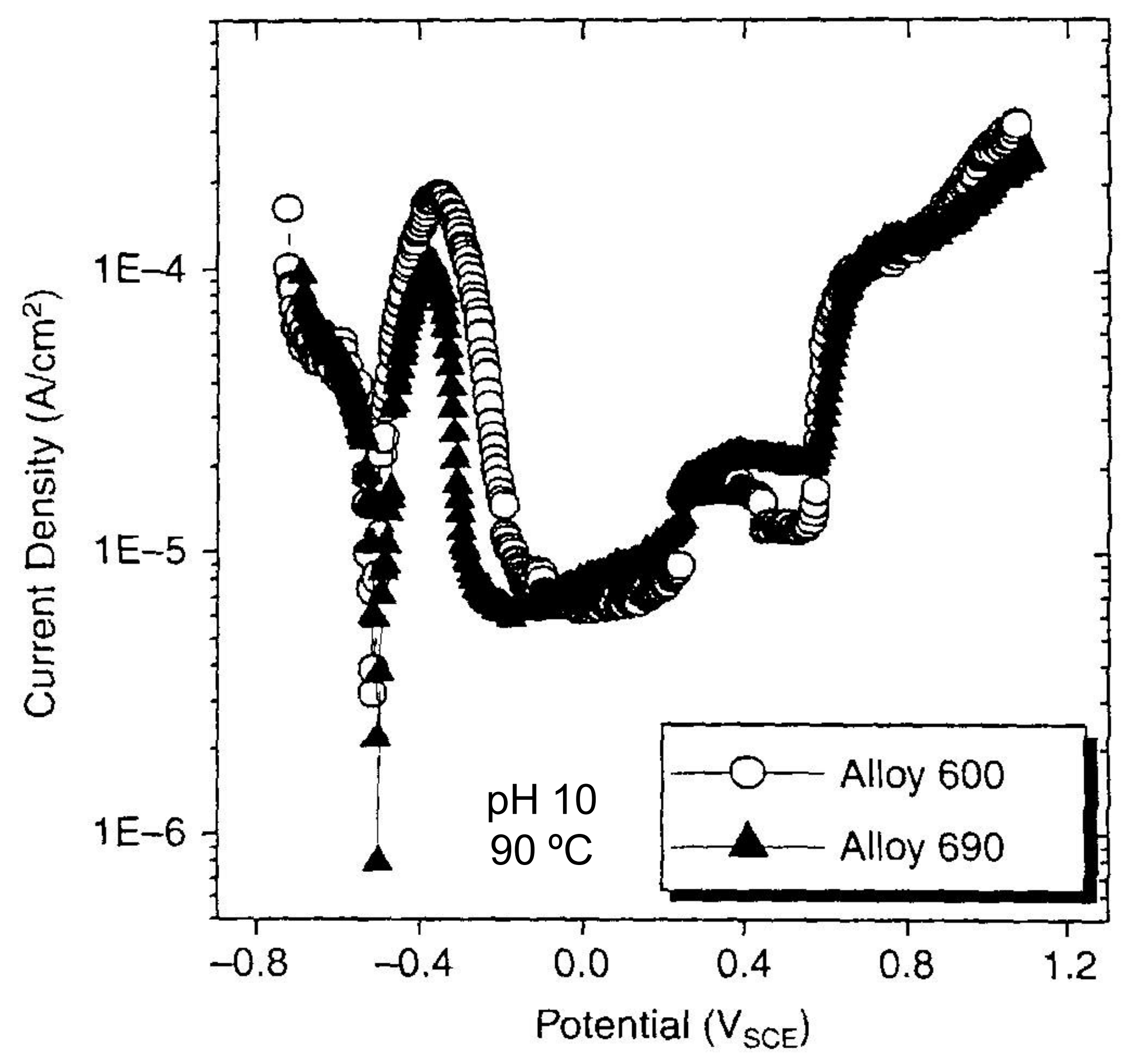


Anodic Polarization Plot for a Passive Alloy



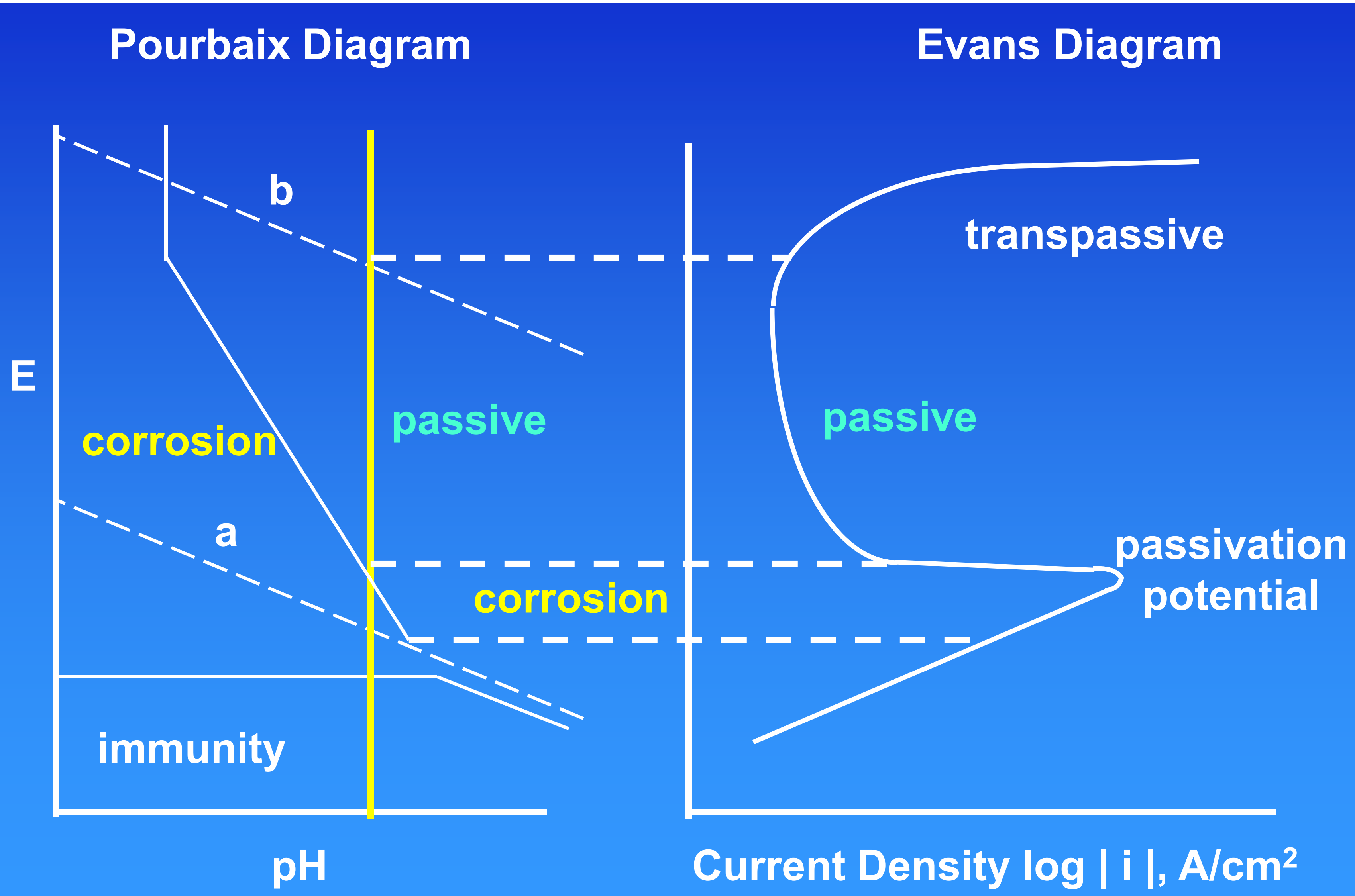
- A dramatic decrease in corrosion current density occurs upon passivation
- Mixed potential, E_{corr} increases to E'_{corr}
- E_p = passive potential
- i_c = critical current density

Alloy 600 and Alloy 690 Passivation Curves



S. Hwang and J. Kim, Corrosion, 5/02

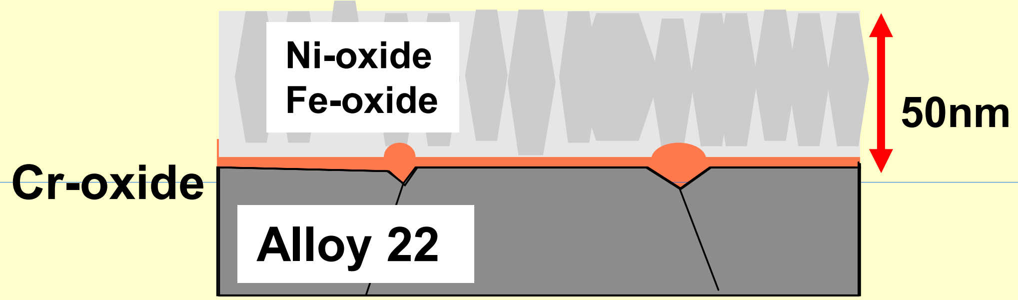
Relationship Between Pourbaix and Evans Diagrams

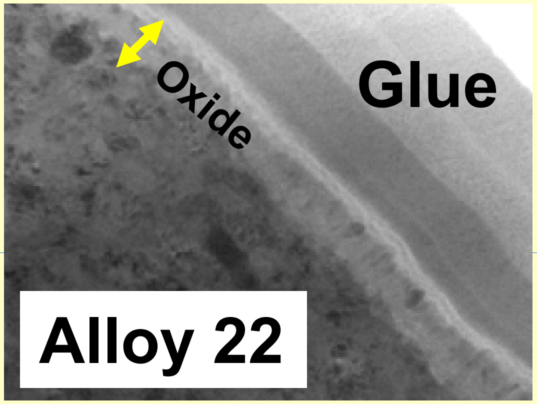


Anatomy of a Passive Oxide

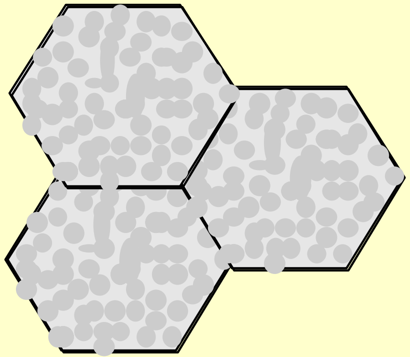
Passive oxides are *thin* layers that limit ionic transport between the metal and the environment

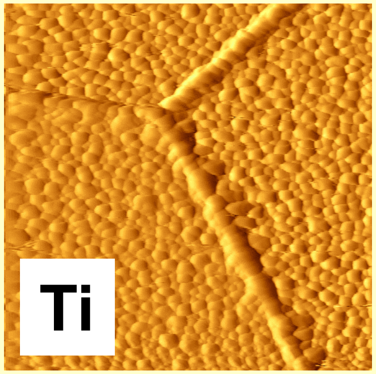
Side View:





Plan View:



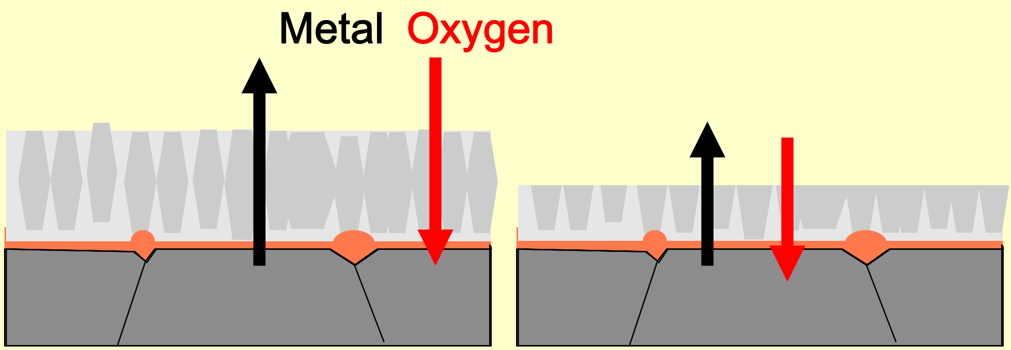


Alloy 22 = Ni + 0.015 C + 21 Cr + 13.5 Mo + 4 Fe + 3 W + 3 Co

C. Orme, LLNL 2002

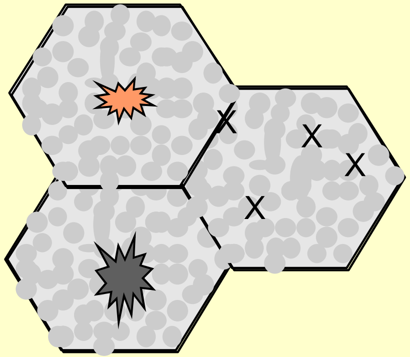
Passive Film Failure Modes

Side View



- **Oxide becomes porous**
- **Oxide thins**
- **Oxide converts to another form**

Plan View



- Local defects allow currents
- Oxide flakes off

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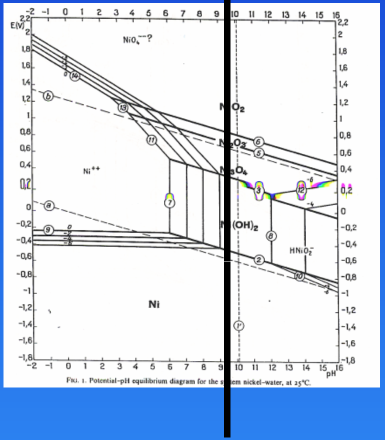
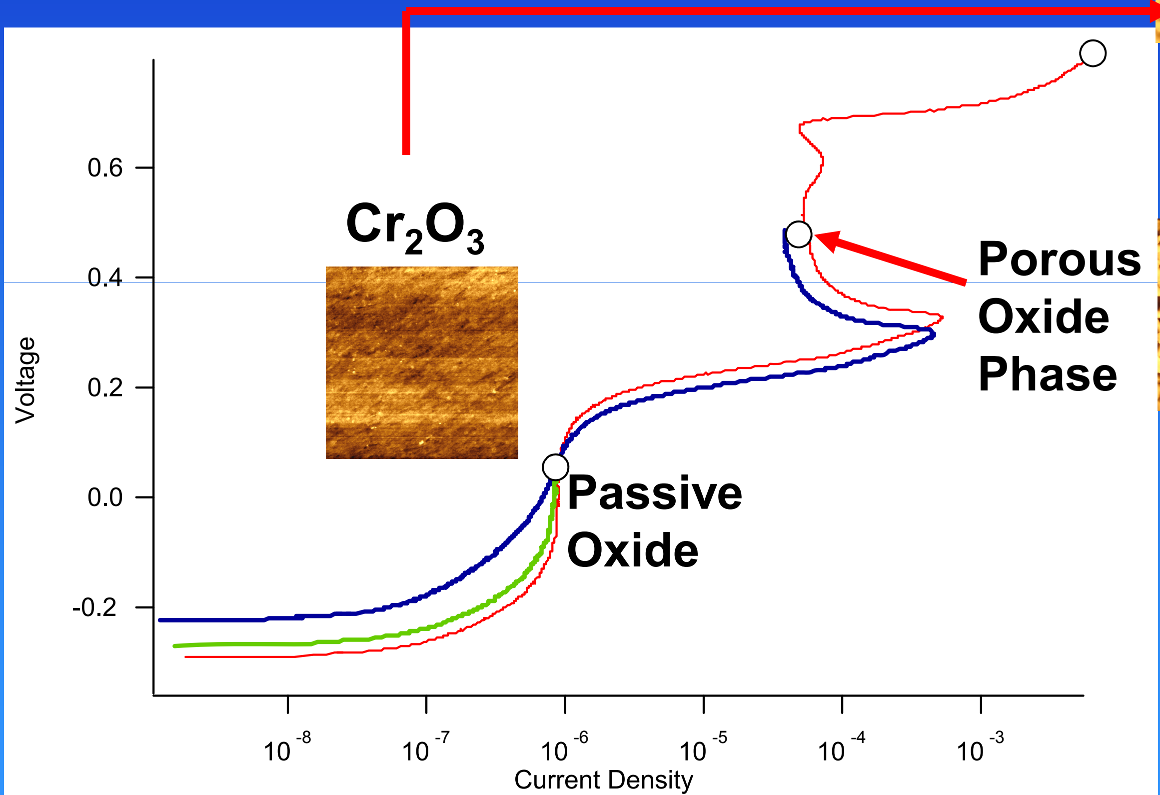
Passivity Curves for Alloy 22

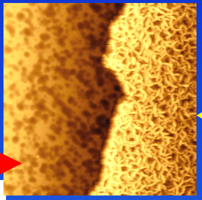
Simulated Concentrated Yucca Mountain Water, pH = 8, T = 90ºC

Pourbaix

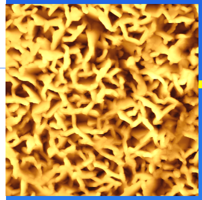


Atomic Force Microscopy





General Dissolution



NiO

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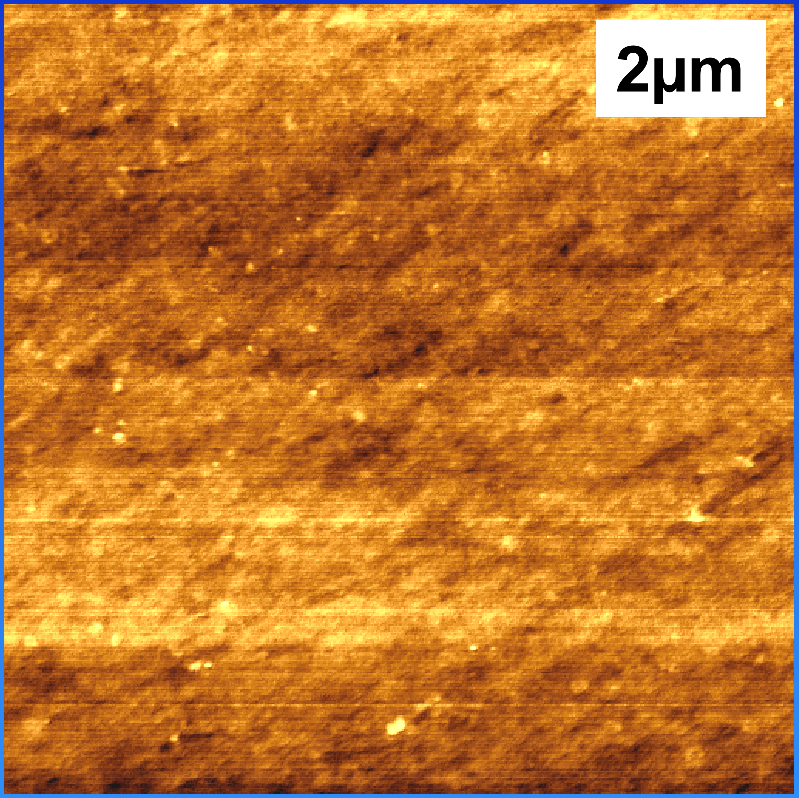
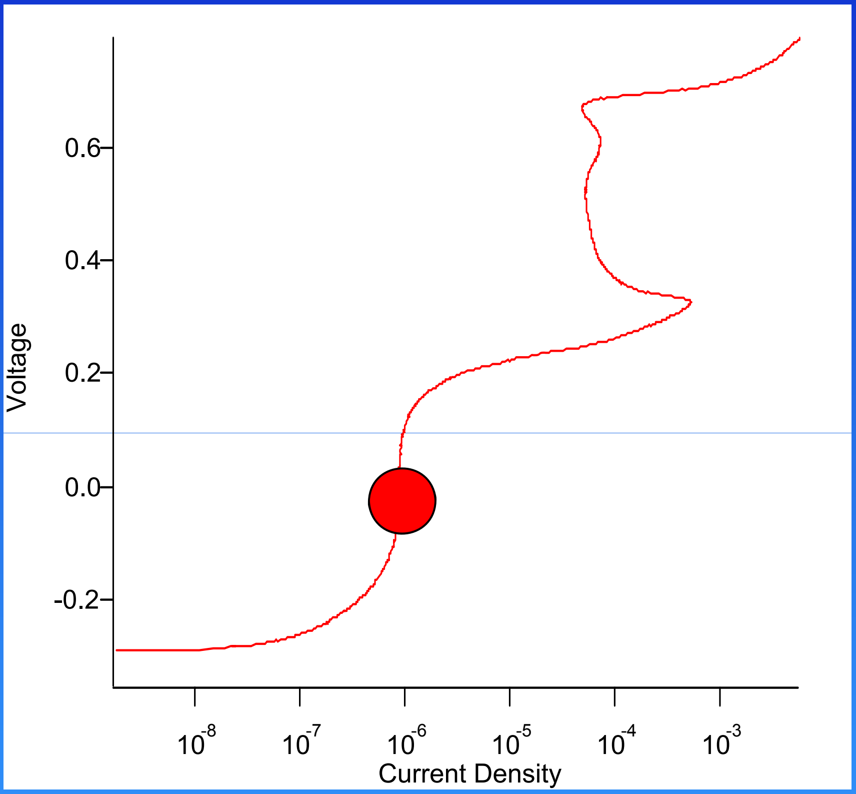
Alloy 22 Passive Oxide



Cr_2O_3



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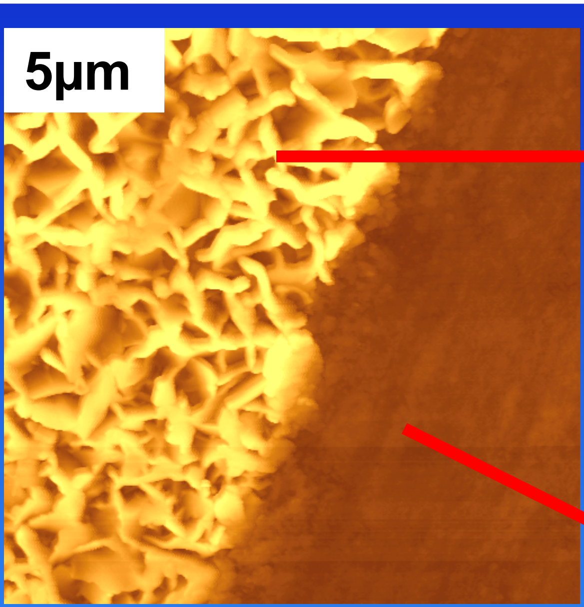
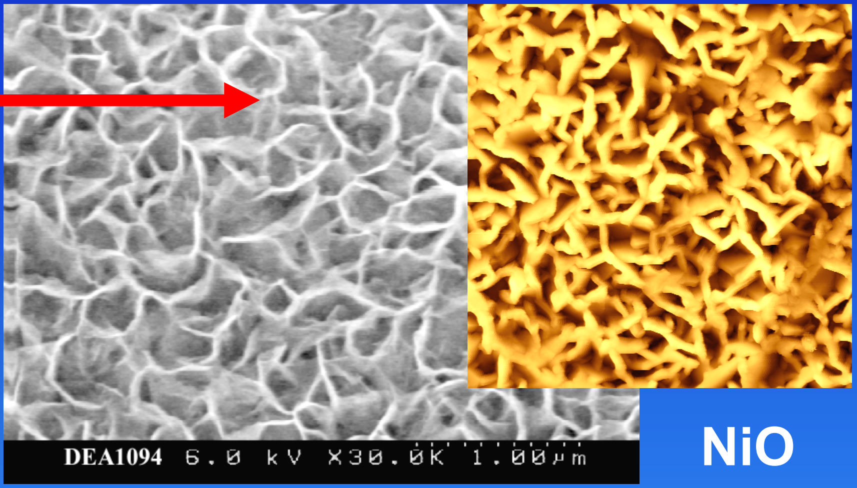
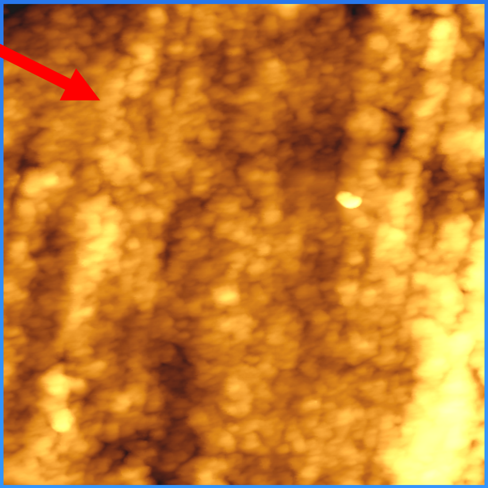
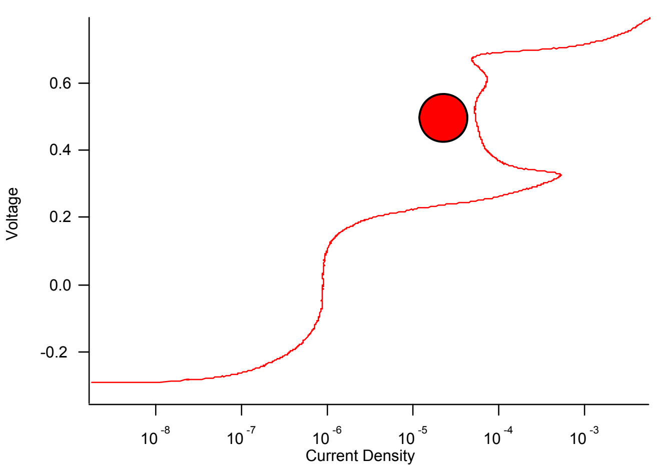
Alloy 22 Porous Oxide Passive Film





NiO





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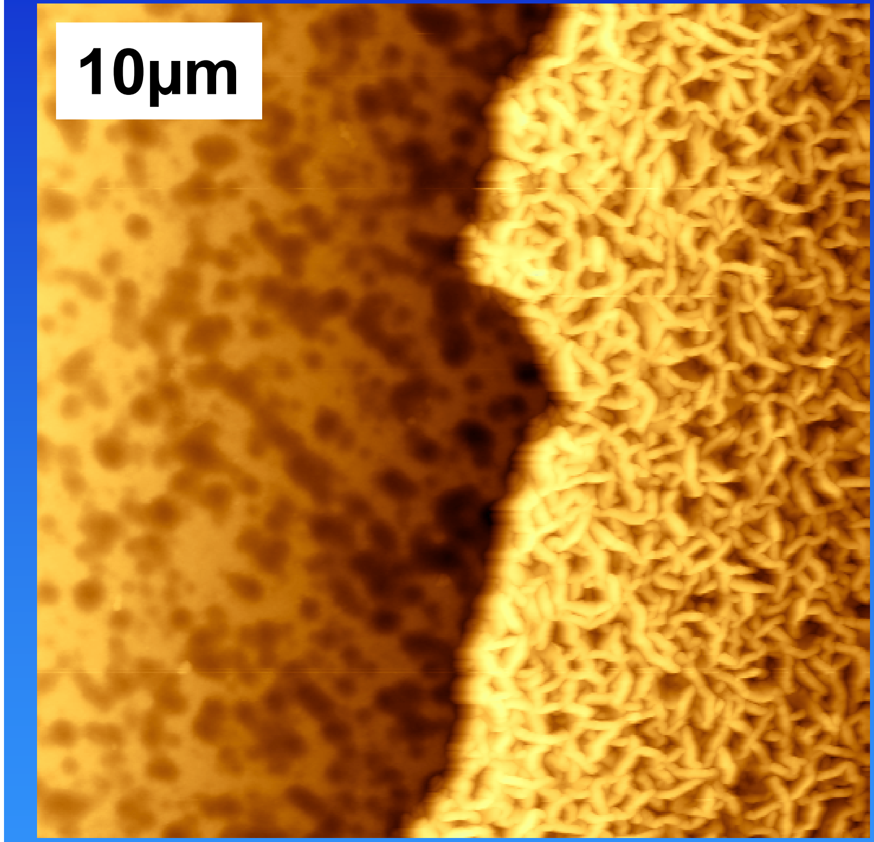
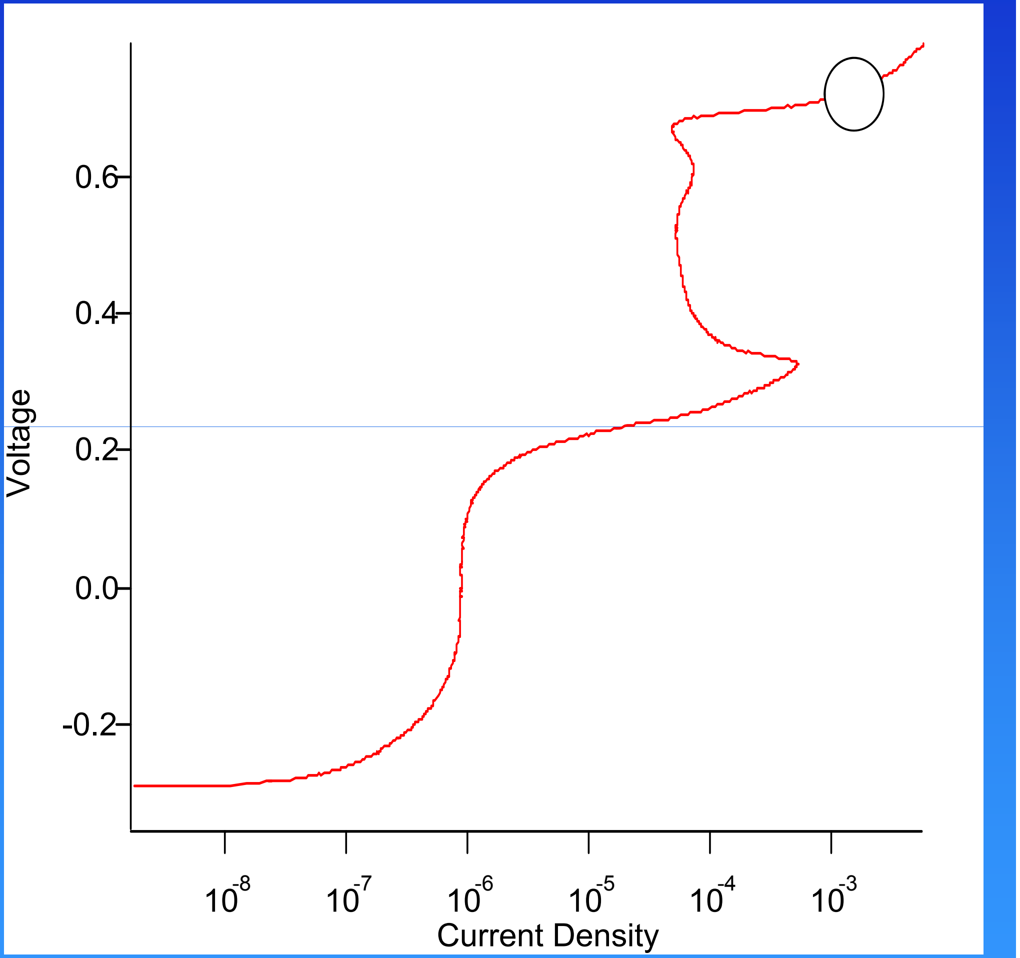
Alloy 22 Dissolution



Cr_2O_3 under spalled NiO



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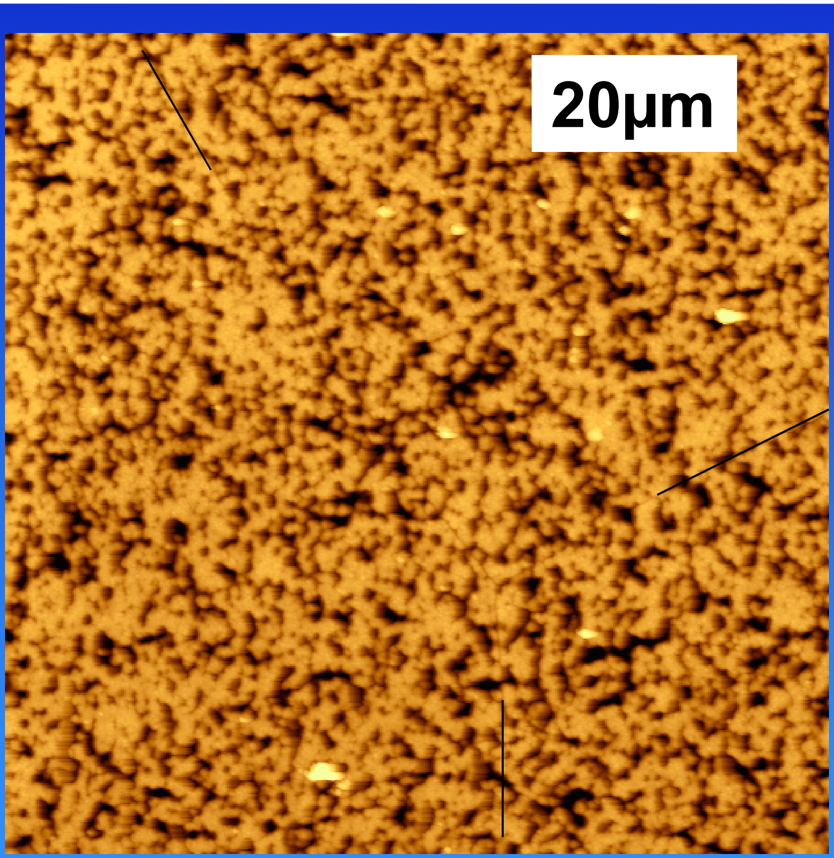
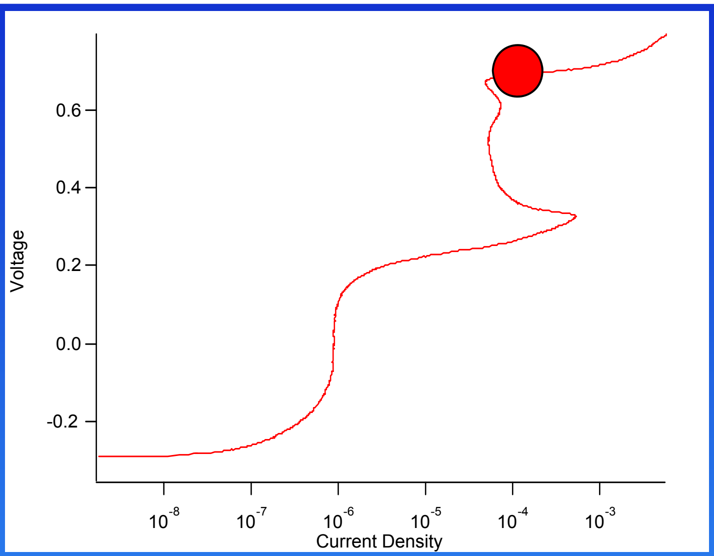
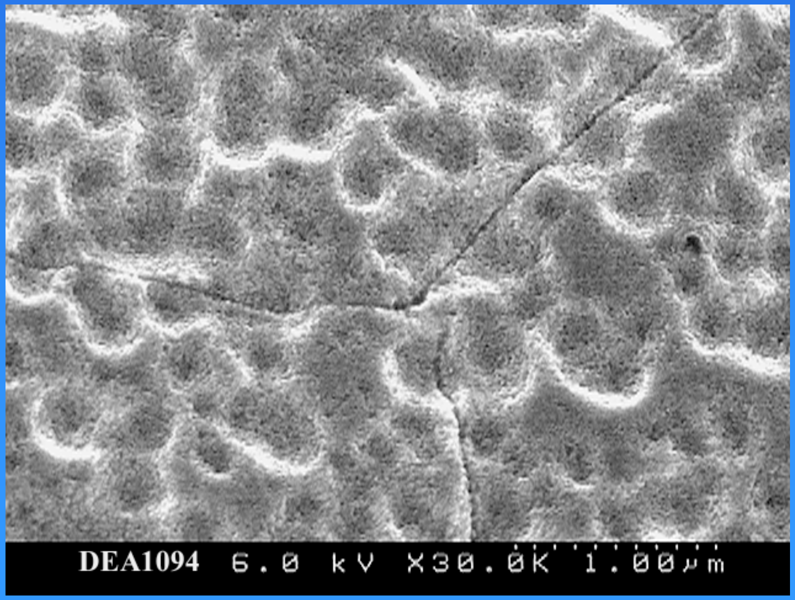
Alloy 22 General Dissolution





Etching is not preferential at grain boundaries

Occasionally identify pronounced grain boundaries



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Fundamentals Summary

- Corrosion thermodynamically almost always happens
  - Pourbaix Diagrams
- Goal is to control the kinetics of corrosion!
  - Evans Diagrams
- LWR alloys survive due to passive films on the metal surface
- These passive films are subject to local breakdown:
  - Pitting corrosion
  - Environmentally-assisted cracking (EAC)
    - Corrosion fatigue
    - Stress corrosion cracking (SCC)