The Thermodynamics and Kinetics of Metallic Corrosion

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Mar de Alborão
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AVEIRO
6 Km

CORROSION

International standard definition of corrosion*:

"Physicochemical interaction between a *metal* and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part".

*ISO 8044 -1986 - Corrosion of metals and alloys - Terms and definitions

International Union of Pure and Applied Chemistry (IUPAC) :

“Corrosion is an irreversible interfacial reaction of a *material* (metal, ceramic, polymer) with its environment which results in consumption of the material or in dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively physical or mechanical processes such as melting or evaporation, abrasion or mechanical fracture are not included in the term corrosion”.

Pure & Appl. Chem. 61 (1989) 19

Fire

Weather

Acid Rain

UV radiation

Living organisms

(rodents, insects, bacteria, fungi,…)

CORROSION OF METALS

versus

DEGRADATION OF MATERIALS

COSTS OF CORROSION

DIRECT

- Implementation of anticorrosive measures
- Repainting (when corrosion prevention is the prime objective)
- Maintenance of cathodic and anodic protection
- Replacement of corroded structures or machinery

All studies and surveys give values between
1 - 5% of Gross Domestic Product
varying with the industrial level of the country
(more industry → more costs)

COSTS OF CORROSION

INDIRECT

- **Loss of production** due to shutdown of industrial units
  - because of malfunction caused by corrosion
  - for replacement of corroded parts

- **Loss of product**
  - product leakage from corroded pipes and tanks
  - product contamination with corrosion products

- **Loss of efficiency**
  - of heat transfer through accumulated corrosion products
  - or pumping capacity because of clogging of pipes

- **Overdesign**

  Equipment is often designed heavier and thicker than needed

COSTS OF CORROSION

In addition, we must face the human lives lost or injured by unpredictable catastrophic failures due to material corrosion

Aloha Airlines Flight 243, April 28th 1988

WHY CARE ABOUT CORROSION?

- ECONOMY

Reduce the money spent in:

- **replacing materials and equipment,**
- **overdesigning structures,**
- **loss of production and efficiency,**
- **disproportionate anticorrosive measures.**

- SAFETY

Prevent loss of human lives and injuries due to unexpected material failure.

- SAVE NATURAL RESOURCES

Avoid unnecessary waste in ore, water, energy and human labour

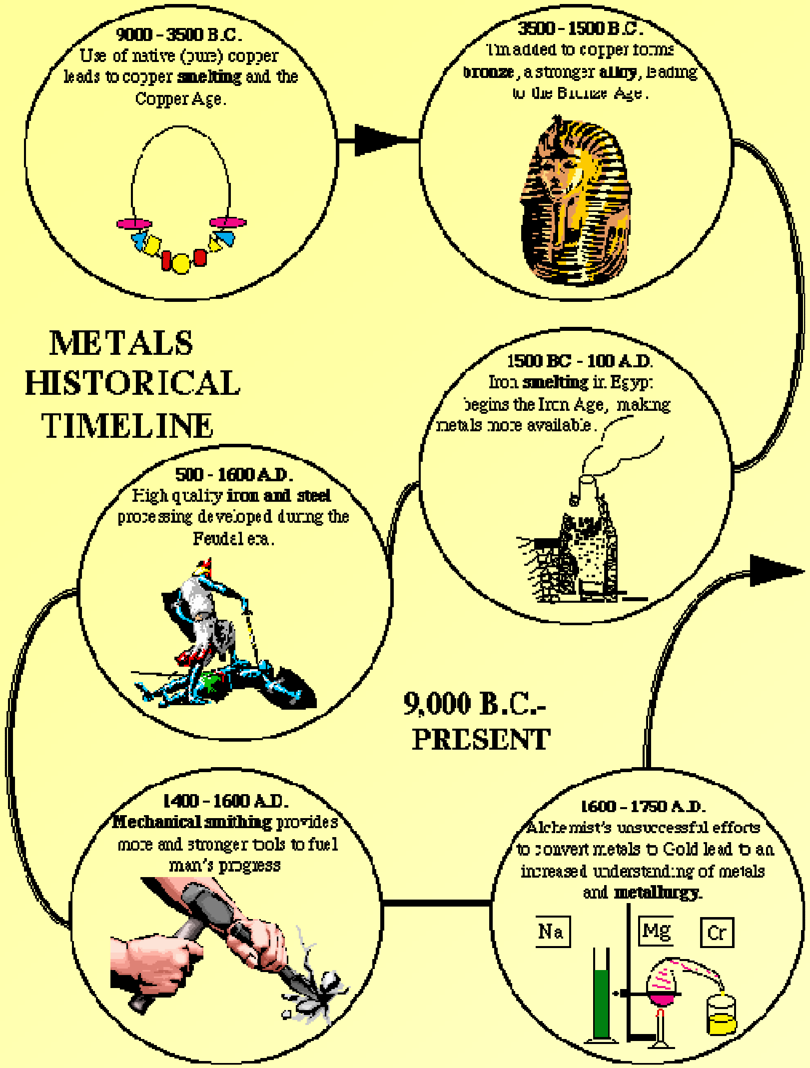
- SCIENTIFIC CURIOSITY

CLASSIFICATION OF CORROSION

- **DRY / WET**
- **HIGH / LOW TEMPERATURE**

Object of this presentation

WHY METALS CORRODE?



METALS HISTORICAL TIMELINE

9,000 B.C.- PRESENT

9000 - 3500 B.C. Use of native (pure) copper leads to copper **smelting** and the Copper Age.

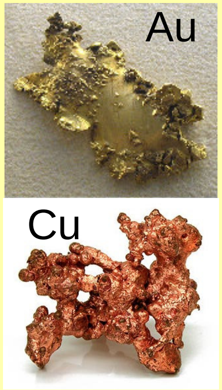
3500 - 1500 B.C. Tin added to copper forms **bronze**, a stronger **alloy**, leading to the Bronze Age.

1500 BC - 100 A.D. Iron **smelting** in Egypt begins the Iron Age, making metals more available.

500 - 1600 A.D. High quality **iron and steel** processing developed during the Feudal era.

1400 - 1600 A.D. **Mechanical smithing** provides more and stronger tools to fuel man's progress

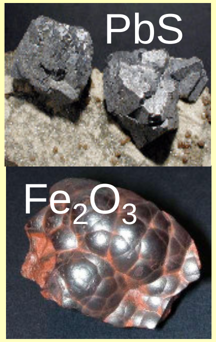
1600 - 1750 A.D. Alchemist's unsuccessful efforts to convert metals to Gold lead to an increased understanding of metals and **metallurgy**.



Relative position according to the energy necessary to convert ore into metal

↑ energy

Na
Mg
Al
Zn
Fe
Ni
Sn
Cu
Ag
Pt
Au



<u>86 known metals</u>

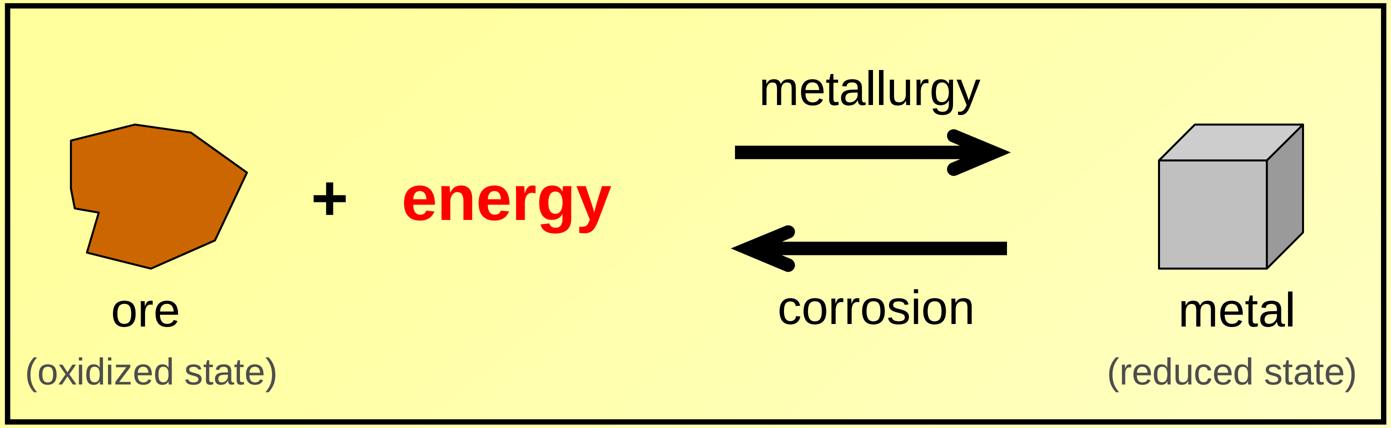
12 until XVII century

12 in XVIII century

43 in XIX century

19 in XX century

WHY METALS CORRODE?

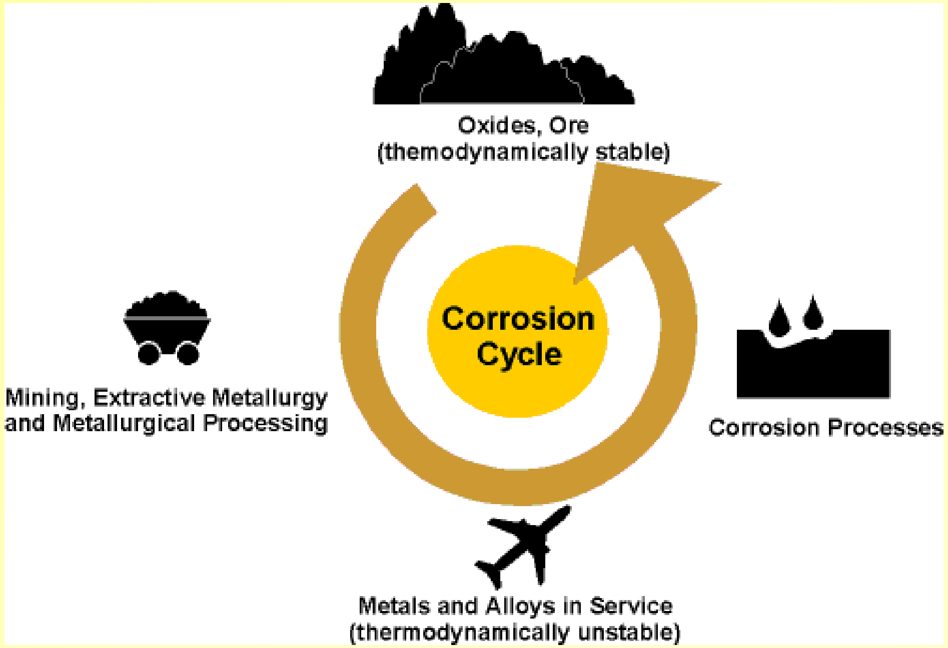


ore + **energy** $\xrightarrow{\text{metallurgy}}$ metal

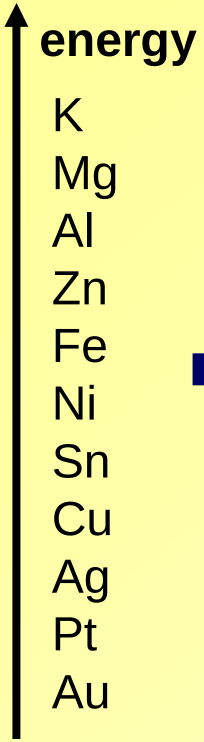
ore $\xleftarrow[\text{corrosion}]{}$ metal

ore (oxidized state)

metal (reduced state)

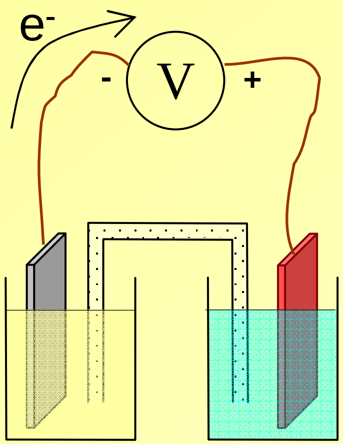


List of corrosivity



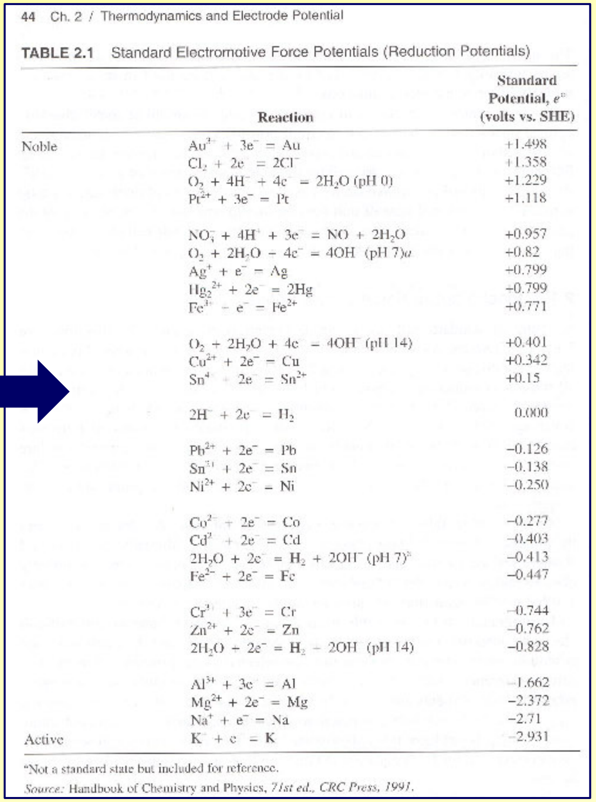
energy

K
Mg
Al
Zn
Fe
Ni
Sn
Cu
Ag
Pt
Au



More active metals have more negative potentials

List of potentials



44 Ch. 2 / Thermodynamics and Electrode Potential

TABLE 2.1 Standard Electromotive Force Potentials (Reduction Potentials)

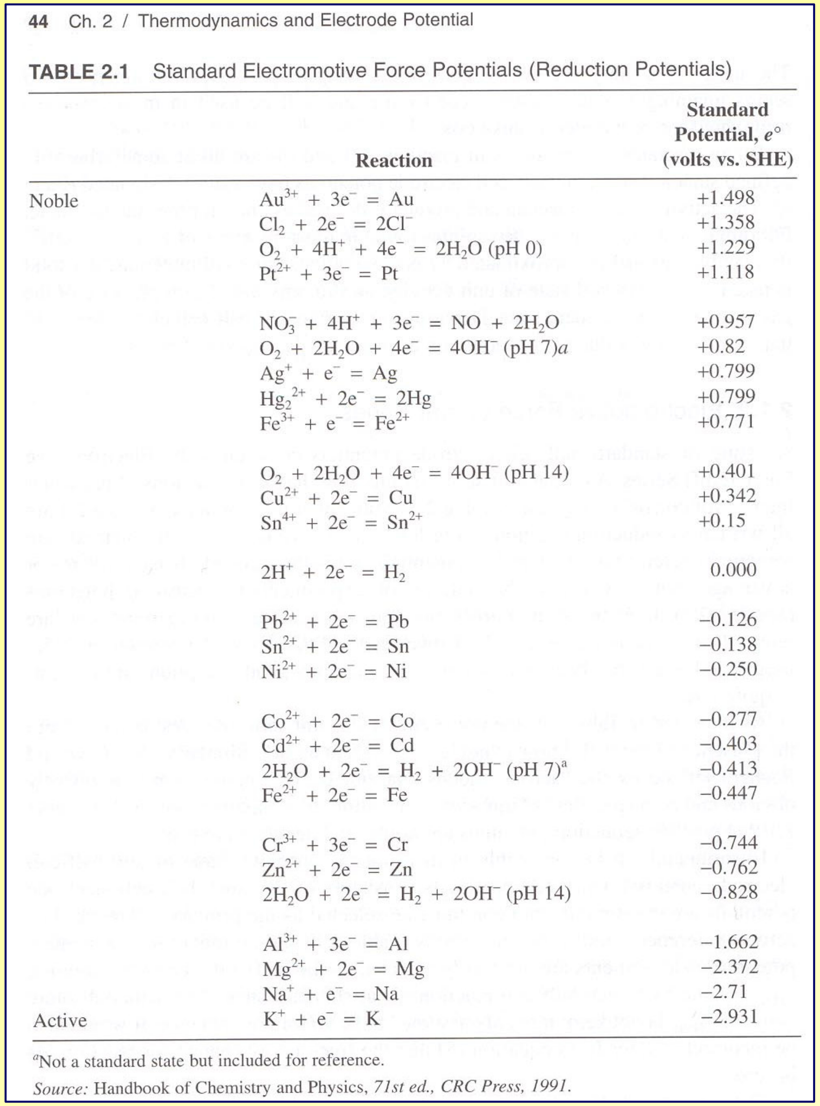
	Reaction	Standard Potential, e° (volts vs. SHE)
Noble	$Au^{3+} + 3e^- = Au$	+1.498
	$Cl_2 + 2e^- = 2Cl^-$	+1.358
	$O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0)	+1.229
	$Pt^{2+} + 3e^- = Pt$	+1.118
	$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$	+0.957
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 7)a	+0.82
	$Ag^+ + e^- = Ag$	+0.799
	$Hg_2^{2+} + 2e^- = 2Hg$	+0.799
	$Fe^{3+} + e^- = Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 14)	+0.401
	$Cu^{2+} + 2e^- = Cu$	+0.342
	$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15
	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	−0.126
	$Sn^{2+} + 2e^- = Sn$	−0.138
	$Ni^{2+} + 2e^- = Ni$	−0.250
	$Co^{2+} + 2e^- = Co$	−0.277
	$Cd^{2+} + 2e^- = Cd$	−0.403
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 7)a	−0.413
	$Fe^{2+} + 2e^- = Fe$	−0.447
	$Cr^{3+} + 3e^- = Cr$	−0.744
	$Zn^{2+} + 2e^- = Zn$	−0.762
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 14)	−0.828
	$Al^{3+} + 3e^- = Al$	−1.662
	$Mg^{2+} + 2e^- = Mg$	−2.372
	$Na^+ + e^- = Na$	−2.71
Active	$K^+ + e^- = K$	−2.931

[a] Not a standard state but included for reference.

Source: Handbook of Chemistry and Physics, *71st ed., CRC Press, 1991.*

Standard electrode potentials

Order of polarity



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Alphabetic order

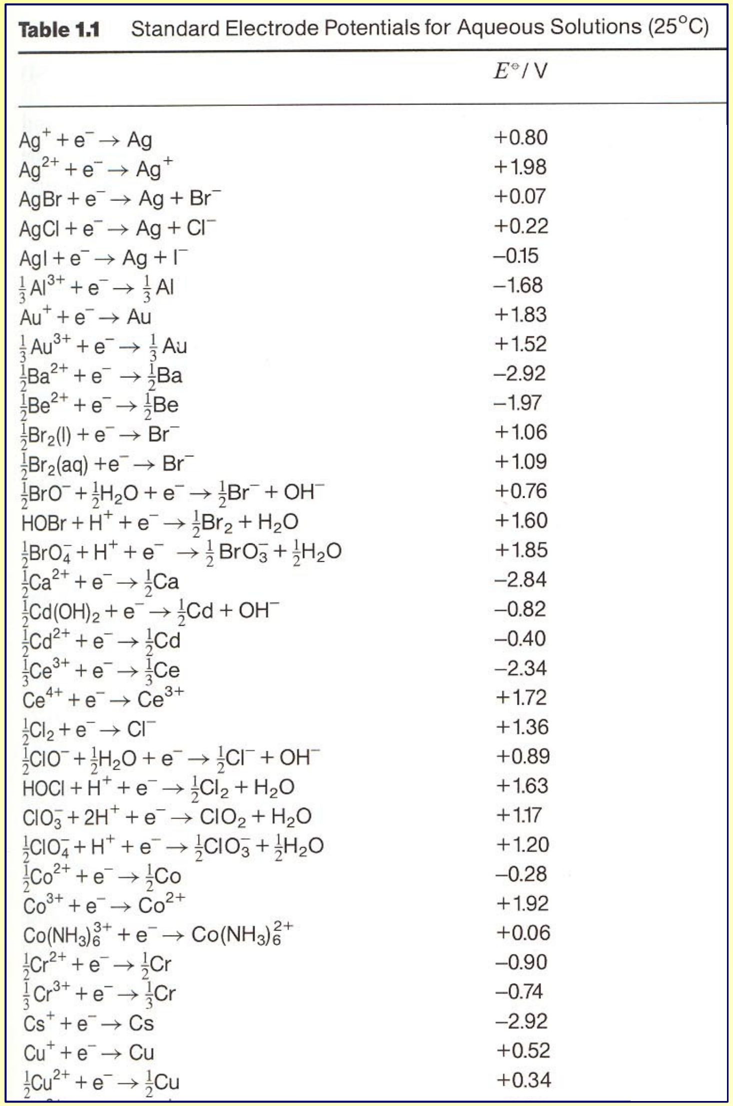


Table 1.1 Standard Electrode Potentials for Aqueous Solutions (25°C)

	$E^\ominus / V$
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Ag^{2+} + e^- \rightarrow Ag^+$	+1.98
$AgBr + e^- \rightarrow Ag + Br^-$	+0.07
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$AgI + e^- \rightarrow Ag + I^-$	–0.15
$\frac{1}{3}Al^{3+} + e^- \rightarrow \frac{1}{3}Al$	–1.68
$Au^+ + e^- \rightarrow Au$	+1.83
$\frac{1}{3}Au^{3+} + e^- \rightarrow \frac{1}{3}Au$	+1.52
$\frac{1}{2}Ba^{2+} + e^- \rightarrow \frac{1}{2}Ba$	–2.92
$\frac{1}{2}Be^{2+} + e^- \rightarrow \frac{1}{2}Be$	–1.97
$\frac{1}{2}Br_2(l) + e^- \rightarrow Br^-$	+1.06
$\frac{1}{2}Br_2(aq) + e^- \rightarrow Br^-$	+1.09
$\frac{1}{2}BrO^- + \frac{1}{2}H_2O + e^- \rightarrow \frac{1}{2}Br^- + OH^-$	+0.76
$HOBr + H^+ + e^- \rightarrow \frac{1}{2}Br_2 + H_2O$	+1.60
$\frac{1}{2}BrO_4^- + H^+ + e^- \rightarrow \frac{1}{2}BrO_3^- + \frac{1}{2}H_2O$	+1.85
$\frac{1}{2}Ca^{2+} + e^- \rightarrow \frac{1}{2}Ca$	–2.84
$\frac{1}{2}Cd(OH)_2 + e^- \rightarrow \frac{1}{2}Cd + OH^-$	–0.82
$\frac{1}{2}Cd^{2+} + e^- \rightarrow \frac{1}{2}Cd$	–0.40
$\frac{1}{3}Ce^{3+} + e^- \rightarrow \frac{1}{3}Ce$	–2.34
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.72
$\frac{1}{2}Cl_2 + e^- \rightarrow Cl^-$	+1.36
$\frac{1}{2}ClO^- + \frac{1}{2}H_2O + e^- \rightarrow \frac{1}{2}Cl^- + OH^-$	+0.89
$HOCl + H^+ + e^- \rightarrow \frac{1}{2}Cl_2 + H_2O$	+1.63
$ClO_3^- + 2H^+ + e^- \rightarrow ClO_2 + H_2O$	+1.17
$\frac{1}{2}ClO_4^- + H^+ + e^- \rightarrow \frac{1}{2}ClO_3^- + \frac{1}{2}H_2O$	+1.20
$\frac{1}{2}Co^{2+} + e^- \rightarrow \frac{1}{2}Co$	–0.28
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.92
$Co(NH_3)_6^{3+} + e^- \rightarrow Co(NH_3)_6^{2+}$	+0.06
$\frac{1}{2}Cr^{2+} + e^- \rightarrow \frac{1}{2}Cr$	–0.90
$\frac{1}{3}Cr^{3+} + e^- \rightarrow \frac{1}{3}Cr$	–0.74
$Cs^+ + e^- \rightarrow Cs$	–2.92
$Cu^+ + e^- \rightarrow Cu$	+0.52
$\frac{1}{2}Cu^{2+} + e^- \rightarrow \frac{1}{2}Cu$	+0.34

A LITTLE BIT OF THERMODYNAMICS

General reaction

$$w\,\mathrm{W} + x\,\mathrm{X} + \ldots \rightarrow y\,\mathrm{Y} + z\,\mathrm{Z} + \ldots$$

Reaction quotient

$$Q = \frac{a_{\mathrm{Y}}^{y}\, a_{\mathrm{Z}}^{z}}{a_{\mathrm{W}}^{w}\, a_{\mathrm{X}}^{x}}$$

Change in Gibbs free energy

$$\Delta G = \Delta G^{o} + RT \ln Q$$

Spontaneous reaction $\Delta G < 0$

For electrochemical reactions

$$\Delta G = -nFE$$

Combining the above equations

$$E = E^{o} - \frac{RT}{nF} \ln Q$$ **Nernst Equation**

$\Delta G < 0$ (spontaneous) when $\Delta E > 0$

At equilibrium

$$\Delta G = 0$$

$$\Delta G^{o} = -RT \ln K$$

K = equilibrium constant

$$\Delta G^{o} = -nFE^{o}$$

$$E^{o} = \frac{RT}{nF} \ln K$$

$$K = e^{\frac{nFE^{o}}{RT}} = e^{-\frac{\Delta G^{o}}{RT}}$$

SILVER, COPPER, IRON. TENDENCY TO OXIDIZE?

Iron nail in copper sulphate solution?

$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $E^{o} = 0{,}342$ V

$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$ $E^{o} = -0{,}447$ V

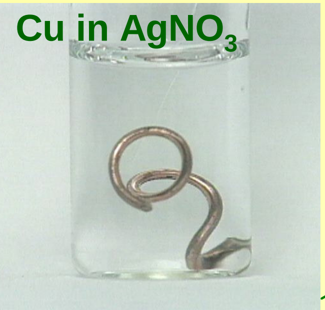
Cu has more tendency to be reduced than Fe
Cu will be reduced, Fe will oxidize.

What about Cu in $FeSO_4$?

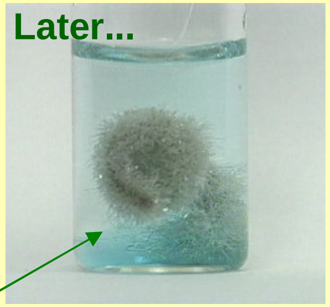
... and in $AgNO_3$?

$Cu^{2+}|Cu$ vs $Ag^{+}|Ag$

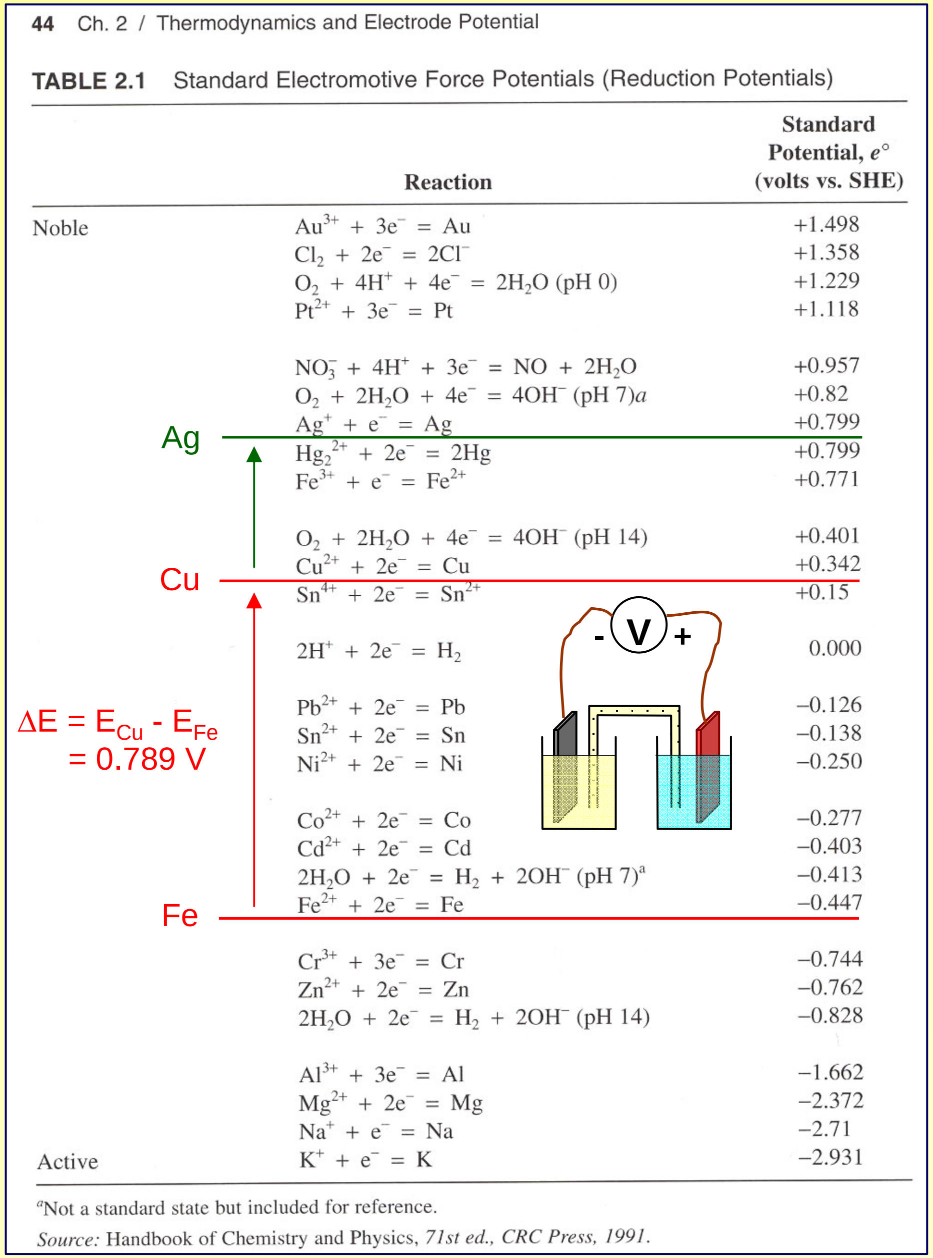
Cu in $AgNO_3$



Later...



Metallic Ag dendrites and blue copper nitrate



44   Ch. 2 / Thermodynamics and Electrode Potential

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	$Pt^{2+} + 3e^{-} = Pt$	+1.118
	$NO_3^{-} + 4H^{+} + 3e^{-} = NO + 2H_2O$	+0.957
	$O_2 + 2H_2O + 4e^{-} = 4OH^{-}$ (pH 7)a	+0.82
	$Ag^{+} + e^{-} = Ag$	+0.799
	$Hg_2^{2+} + 2e^{-} = 2Hg$	+0.799
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Active	$K^{+} + e^{-} = K$	−2.931

[a] Not a standard state but included for reference.

Source: Handbook of Chemistry and Physics, *71st ed., CRC Press, 1991.*

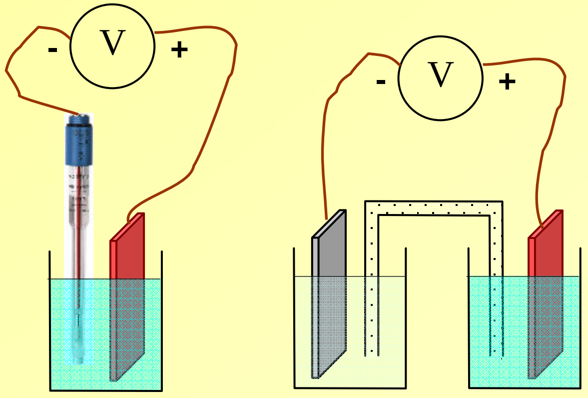
$\Delta E = E_{Cu} - E_{Fe}$
$= 0.789$ V

FOR NON-STANDARD CONDITIONS...

Tables give values for standard conditions, T = 25º C, pure metals, pure solutions with unitary activity (or fugacity if gases)NOTE. For different conditions the potential can be calculated using the **Nernst Equation**.

$$E = E^o - \frac{RT}{zF} \ln \frac{a_{Red}}{a_{Ox}} = E^o - \frac{RT}{zF} \ln \frac{a_M}{a_{M^{z+}}}$$

E^o = Standard electrode potential
a = species activity (or fugacity)
R = Gas constant (8,314 J K^{-1} mol^{-1})
T = Temperature (K)
z = nº electrons in half-reaction
F = Faraday's constant (96485 C mol^{-1})



Potential of half-cell: $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

$$E_{Fe^{2+}/Fe} = E^o_{Fe^{2+}/Fe} - \frac{RT}{2F} \ln \frac{a_{Fe}}{a_{Fe^{2+}}} = -0{,}447 - \frac{RT}{2F} \ln \frac{1}{a_{Fe^{2+}}} = -0{,}447 + \frac{RT}{2F} \ln a_{Fe^{2+}}$$

Potential of cell: $Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$

$$E_{célula} = E_{Cu^{2+}/Cu} - E_{Fe^{2+}/Fe} = E^o_{Cu^{2+}/Cu} - E^o_{Fe^{2+}/Fe} - \frac{RT}{2F} \ln \frac{a_{Fe^{2+}}}{a_{Cu^{2+}}} = 0{,}789 - \frac{RT}{2F} \ln \frac{a_{Fe^{2+}}}{a_{Cu^{2+}}}$$

NOTE: **formal potentials**, **E'**, exist as an alternative to standard potentials, Eº. They are experimentally determined using concentrations, rather then activities, which is, in many cases, more convenient.

In most corrosion situations there are no metal ions around to oxidize the metal… But, there is water and oxygen

Most important reactions in corrosion

Oxidation of metal

$M(s) \rightarrow M^{n+}(aq) + ne^-$

Reduction of H_2O

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ (acid)

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

(neutral or alkaline)

Reduction of dissolved O_2

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ (acid)

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

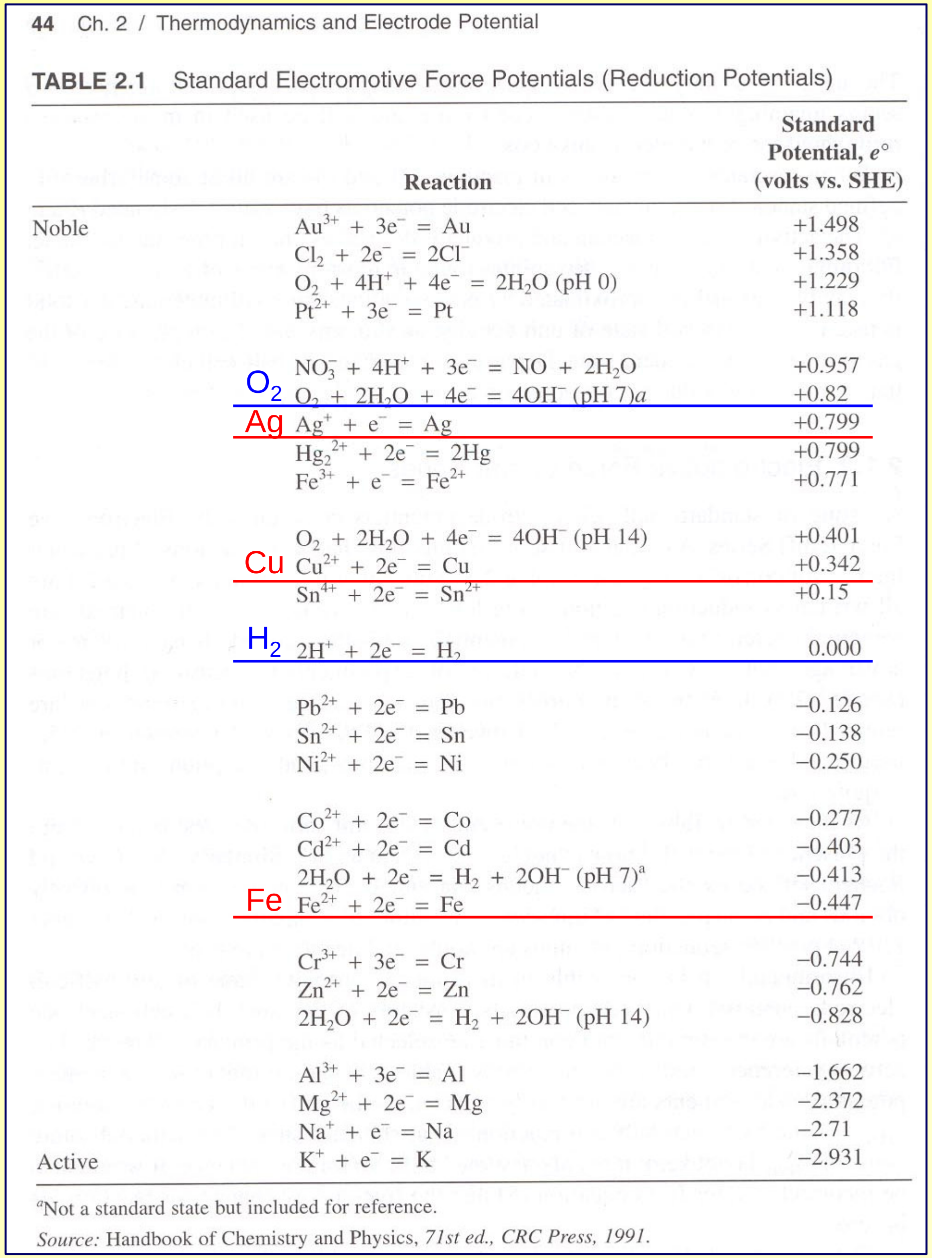
(neutral or alkaline)

Fe will be oxidized by H_2O and O_2

Cu will be oxidized only by O_2

(acids will not corrode copper)

Ag may, in principle, be oxidized by O_2



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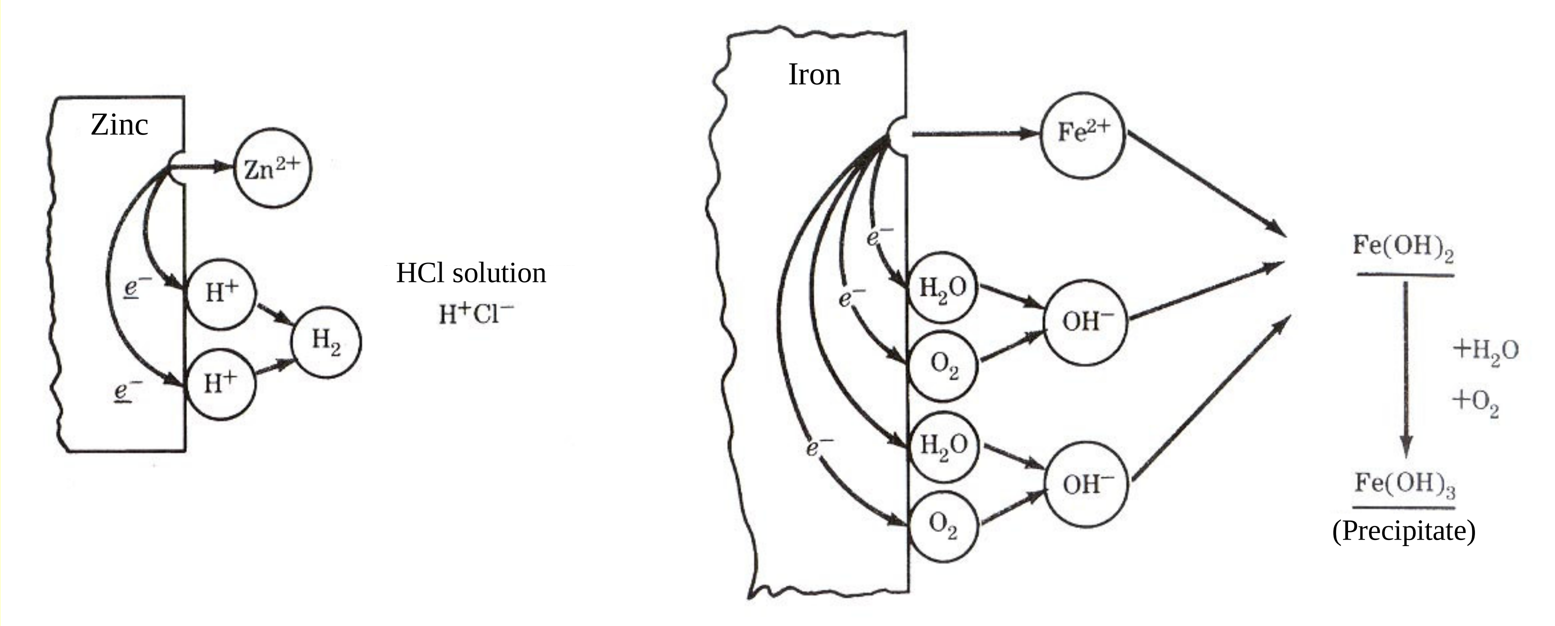
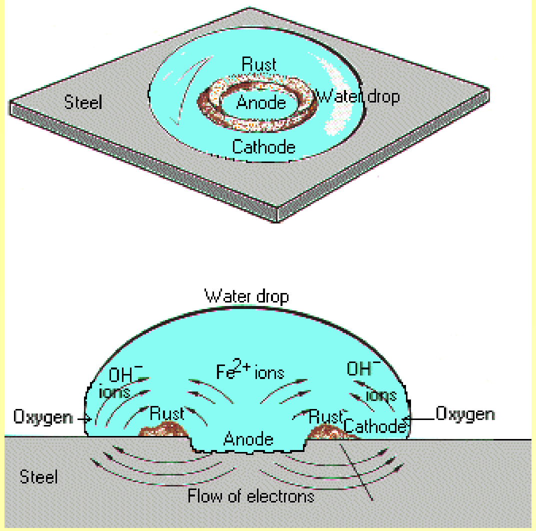
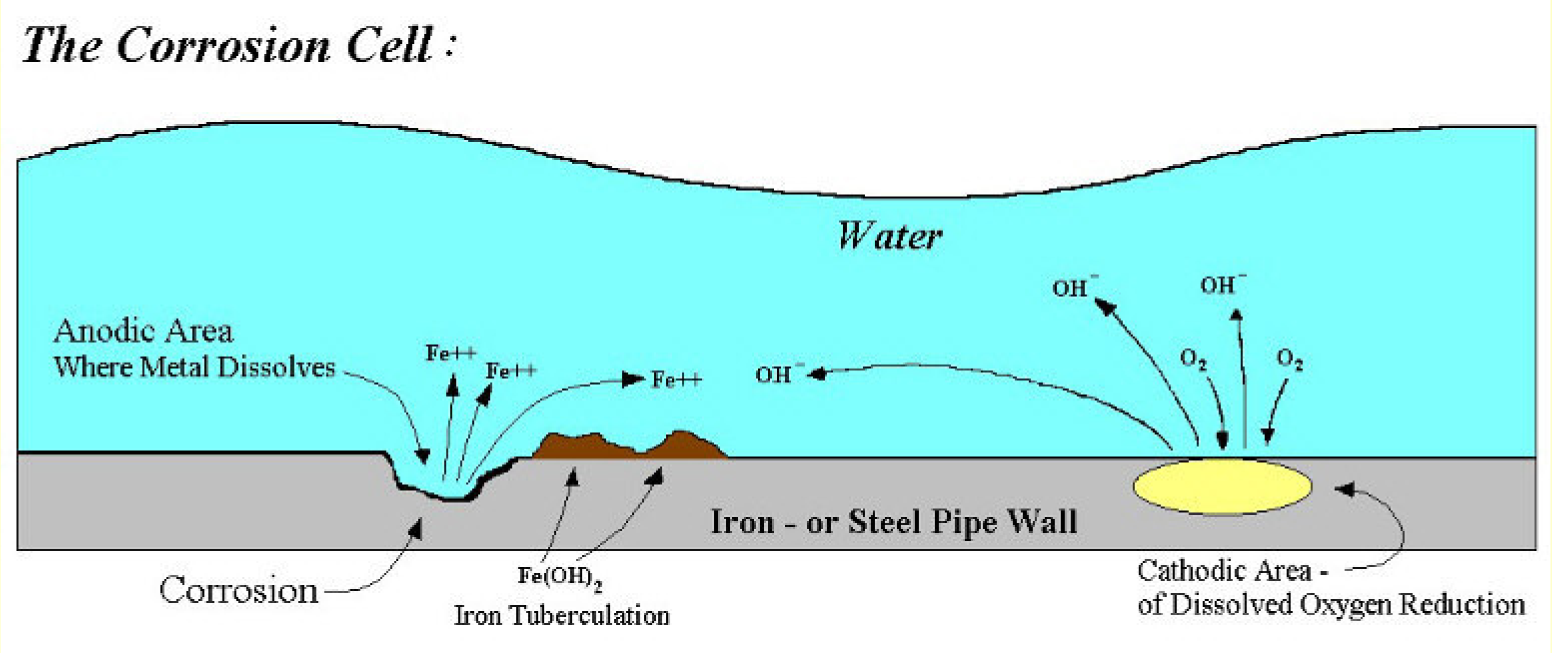
CORROSION MECHANISM



Anodic reaction
Cathodic reaction **(amount of oxidizer)**
Electronic path **(internal resistance)**
Ionic path **(external resistance; solution conductivity)**

CORROSION MECHANISM





A simple experiment

Petri dish with agar-agar gel containing

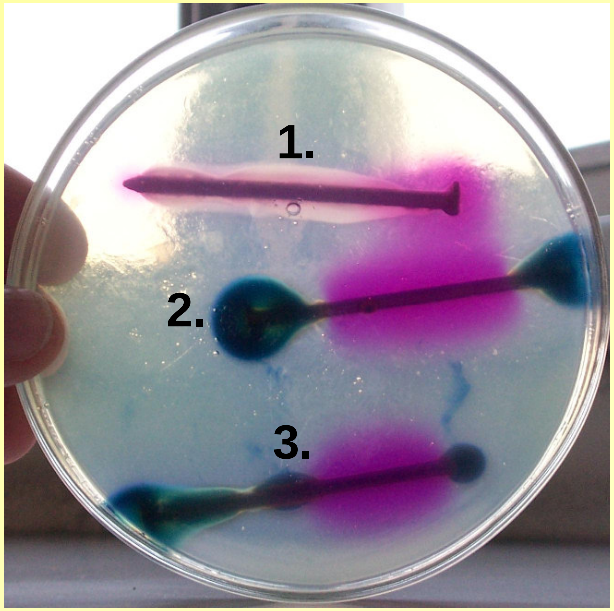
- **3% NaCl aqueous solution** (corrosive environment)**,**
- **phenolfthalein** (pH indicator, turns red at pH > 8)
- **potassium ferricianide** (ferricianide ion reacts with Fe^{2+} to give a prussian blue precipitate)

and

1. Zinc nail

2. Iron nail

3. Iron nail with copper deposited in half of its area



Anodic regions (oxidation)

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \text{ (blue)}$$

Except for zinc where Zn^{2+} is produced. Zn^{2+} does not react with ferricianide. It gives zinc hydroxide (with the OH^- produced in the cathodic process) The white deposit around the zinc nail is precipitated $Zn(OH)_2$.

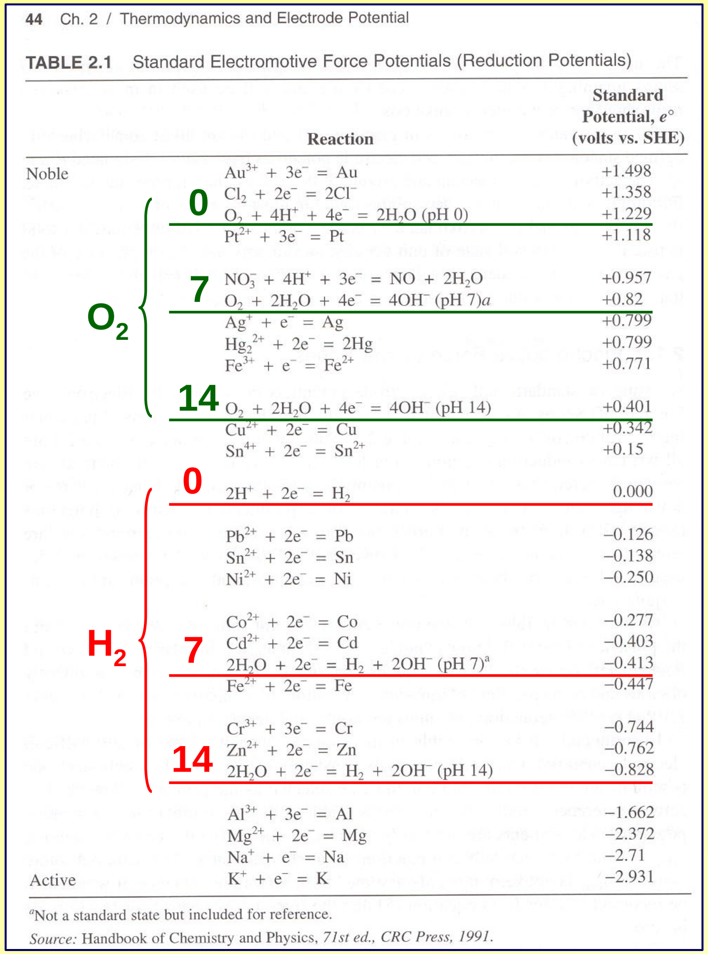
Cathodic regions (reduction)

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

This reaction occurs in all nails. The increase in OH^- concentration rises the local pH and turns red the phenolftalein. In the copper plated nail this reaction occurs preferentially in at the copper surface.

The cathodic reactions are pH dependent

So is their oxidant “power”



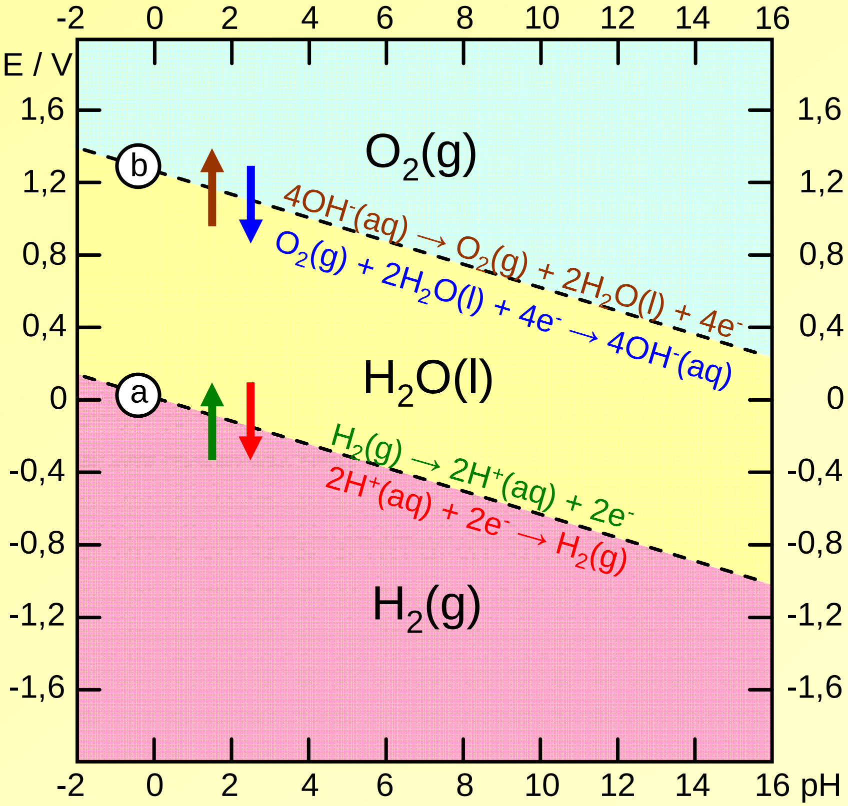
44 Ch. 2 / Thermodynamics and Electrode Potential

TABLE 2.1 Standard Electromotive Force Potentials (Reduction Potentials)

	Reaction	Standard Potential, $e°$ (volts vs. SHE)
Noble	$Au^{3+} + 3e^- = Au$	+1.498
	$Cl_2 + 2e^- = 2Cl^-$	+1.358
	$O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0)	+1.229
	$Pt^{2+} + 3e^- = Pt$	+1.118
	$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$	+0.957
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 7)*a*	+0.82
	$Ag^+ + e^- = Ag$	+0.799
	$Hg_2^{2+} + 2e^- = 2Hg$	+0.799
	$Fe^{3+} + e^- = Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 14)	+0.401
	$Cu^{2+} + 2e^- = Cu$	+0.342
	$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15
	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	−0.126
	$Sn^{2+} + 2e^- = Sn$	−0.138
	$Ni^{2+} + 2e^- = Ni$	−0.250
	$Co^{2+} + 2e^- = Co$	−0.277
	$Cd^{2+} + 2e^- = Cd$	−0.403
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 7)^a	−0.413
	$Fe^{2+} + 2e^- = Fe$	−0.447
	$Cr^{3+} + 3e^- = Cr$	−0.744
	$Zn^{2+} + 2e^- = Zn$	−0.762
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 14)	−0.828
	$Al^{3+} + 3e^- = Al$	−1.662
	$Mg^{2+} + 2e^- = Mg$	−2.372
	$Na^+ + e^- = Na$	−2.71
Active	$K^+ + e^- = K$	−2.931

^{a}Not a standard state but included for reference.

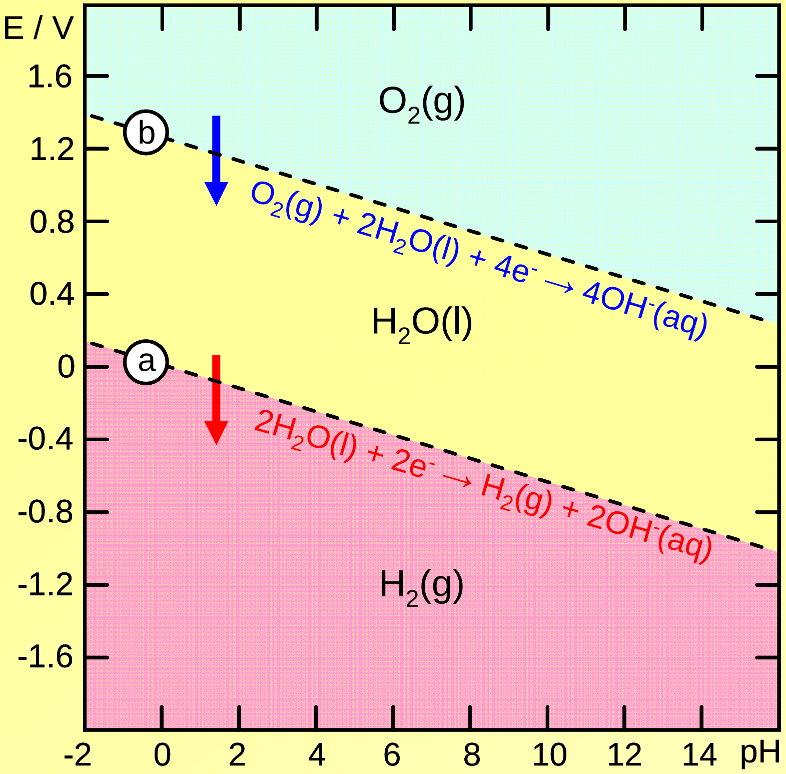
Source: Handbook of Chemistry and Physics, *71st ed., CRC Press, 1991.*

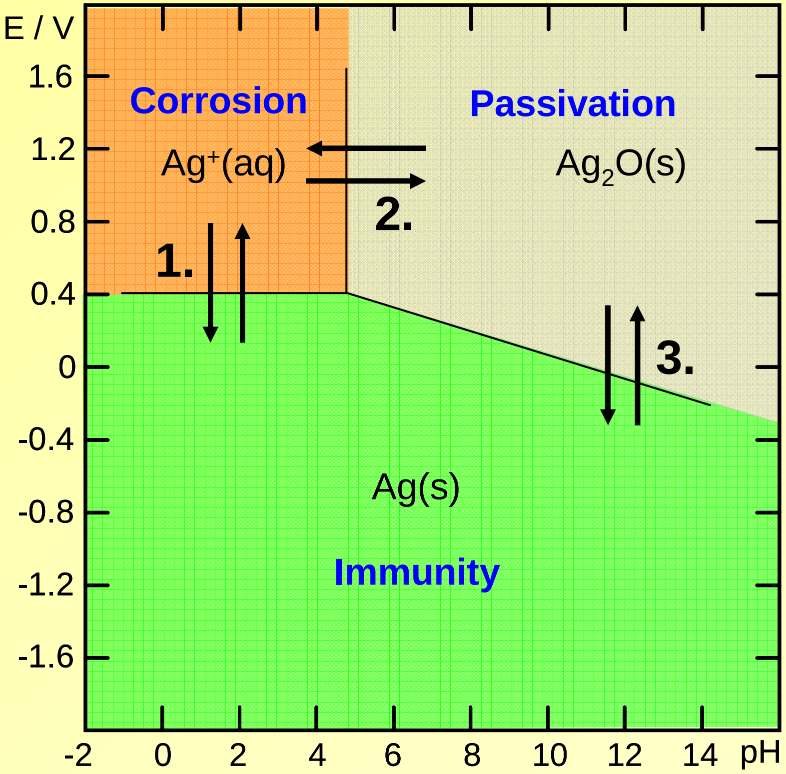


O_2: Eº = 1,228-0,0591 pH

H_2: Eº = 0,000-0,0591 pH

Pourbaix Diagrams (E-pH)





1. Ag/Ag^+

Oxidation (corrosion of silver)

$Ag(s) \rightarrow Ag^+(aq) + e^-$

Reduction (silver deposition)

$Ag^+(aq) + e^- \rightarrow Ag(s)$

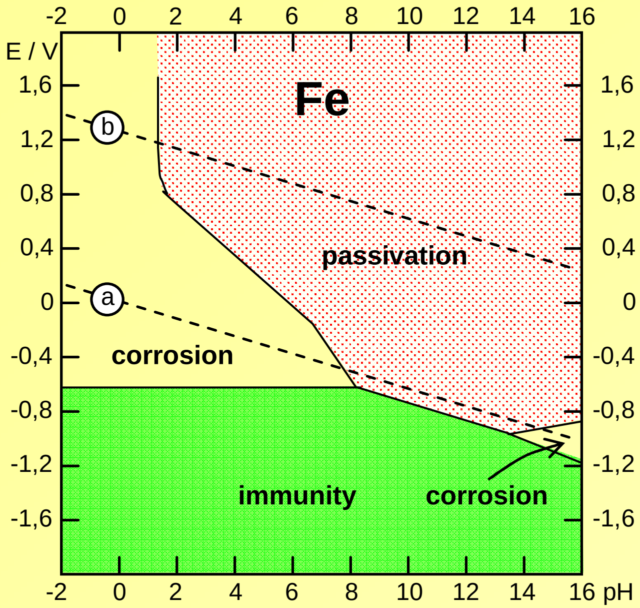
2. Ag^+/Ag_2O

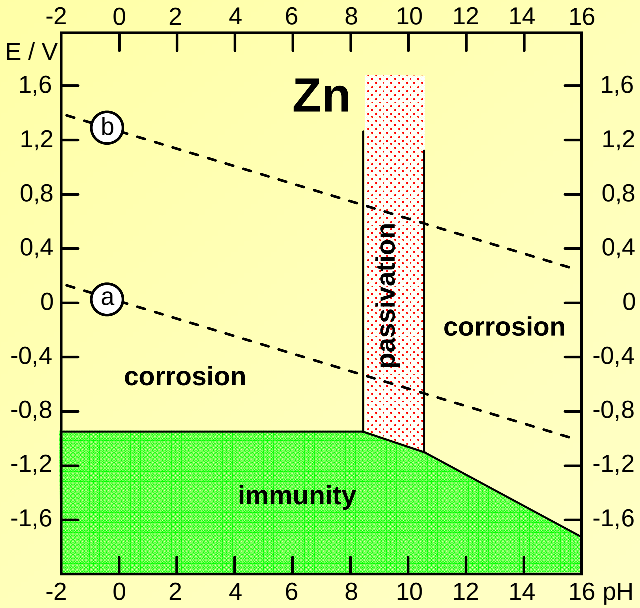
$2Ag^+(aq) + 2OH^-(aq) \Leftrightarrow Ag_2O(s) + H_2O$

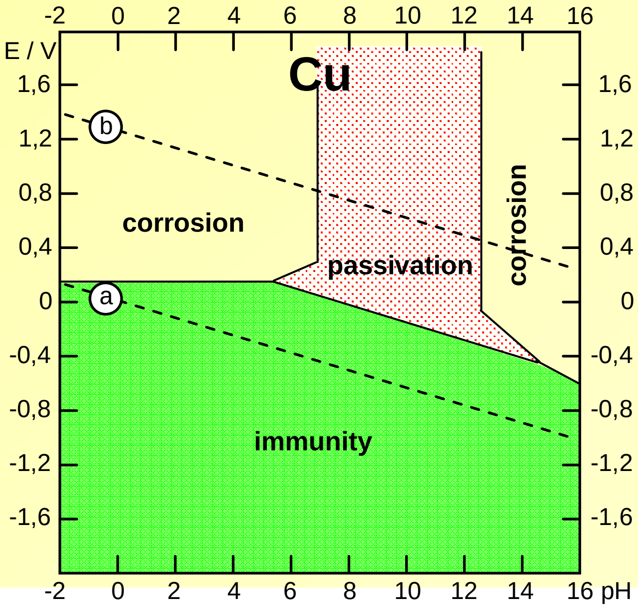
3. Ag/Ag_2O

$Ag_2O(s) + 2H^+(aq) + 2e^- \Leftrightarrow 2Ag(s) + H_2O(l)$

Pourbaix Diagrams (E-pH)







Pourbaix Diagram for Fe

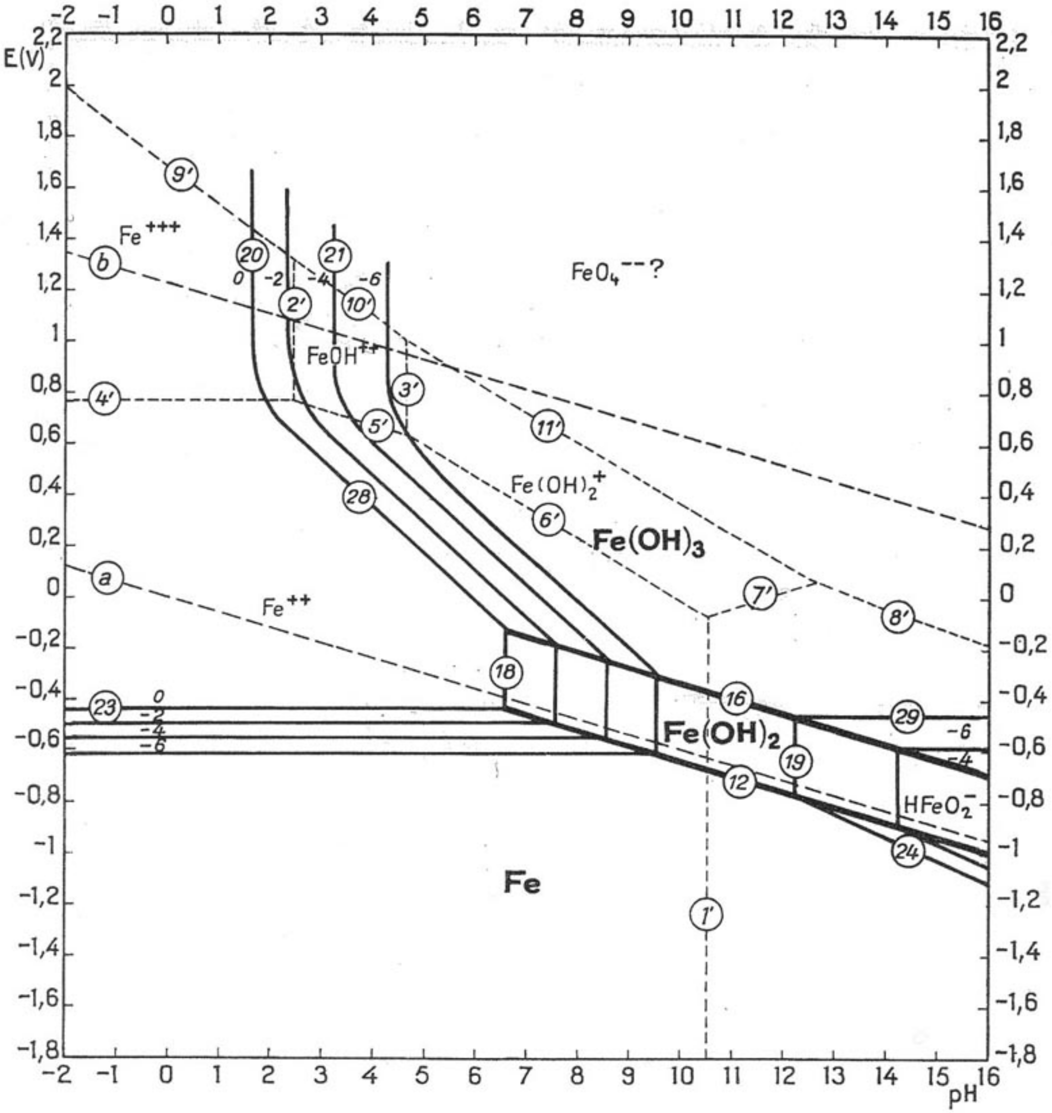


FIG. 5. Potential–pH equilibrium diagram for the system iron–water, at 25°C [considering as solid substances only Fe, $Fe(OH)_2$ and $Fe(OH)_3$].

Pourbaix Diagrams (E-pH)

Show the thermodynamic stability at different potentials and pH,

Give the reactions and reaction products at equilibrium,

Indicate the conditions where corrosion may take place and those where corrosion is either thermodynamically impossible or kinetically hindered (passivated).

Limitations

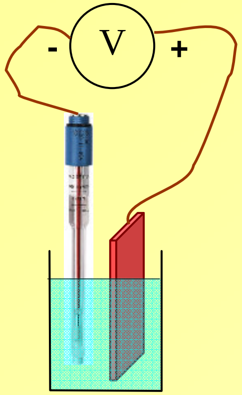
Pourbaix diagrams give only the thermodynamic possibility for corrosion to occur,
no information on corrosion rate is provided;

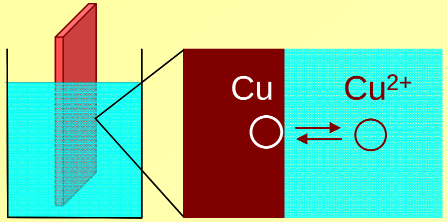
The diagrams are valid for the conditions considered, usually pure metals in water and O_2,
To consider other species (CO_2, Cl^-, etc) or temperatures ≠ 25 ºC other diagrams have to be calculated;

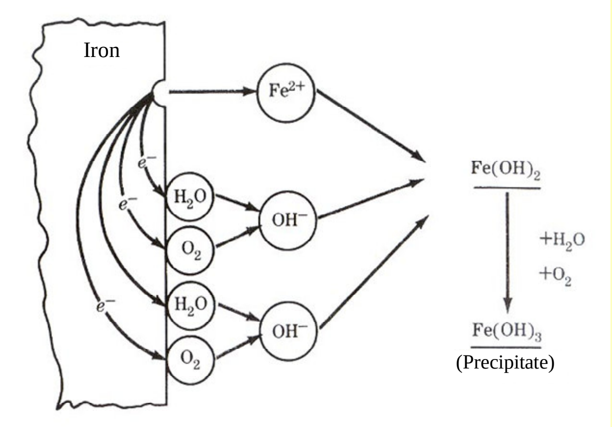
The solution pH can be different from the pH near the surface;

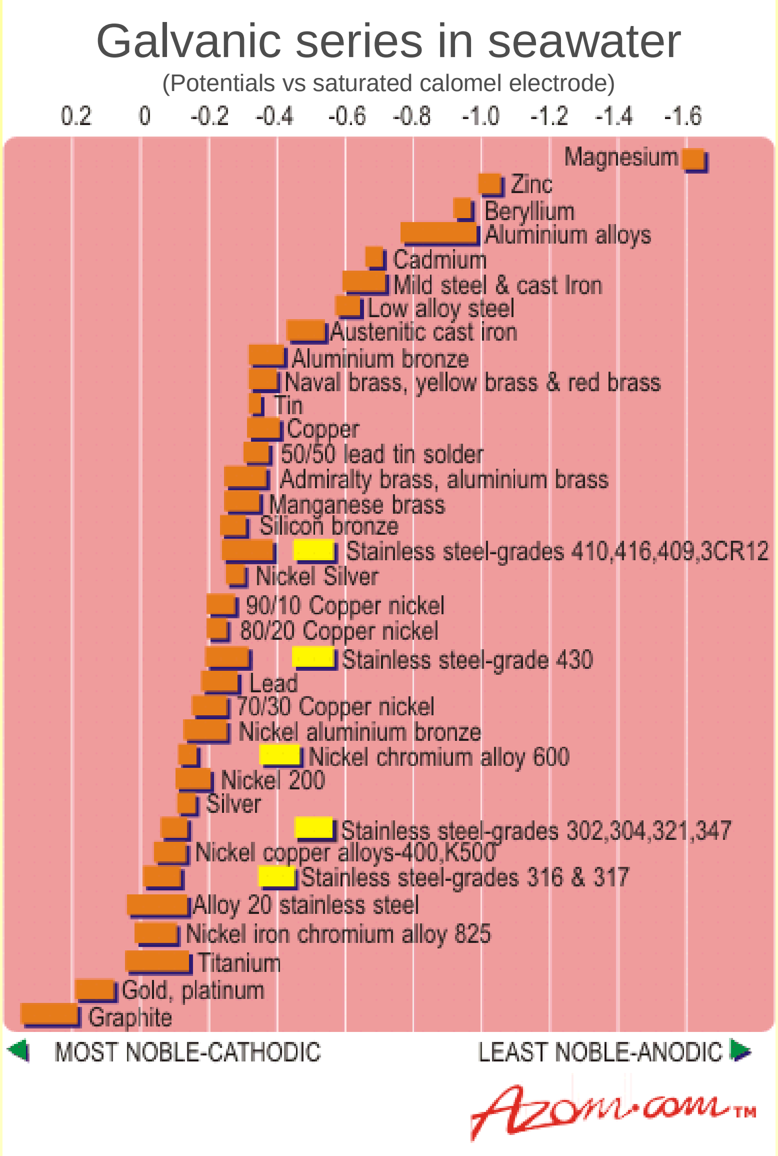
Usually the formation of corrosion products is considered as passive region,
this is only true if the products form an adherent, compact, flawless layer, protecting completely the underlying metal;

Galvanic series vs Electrochemical series

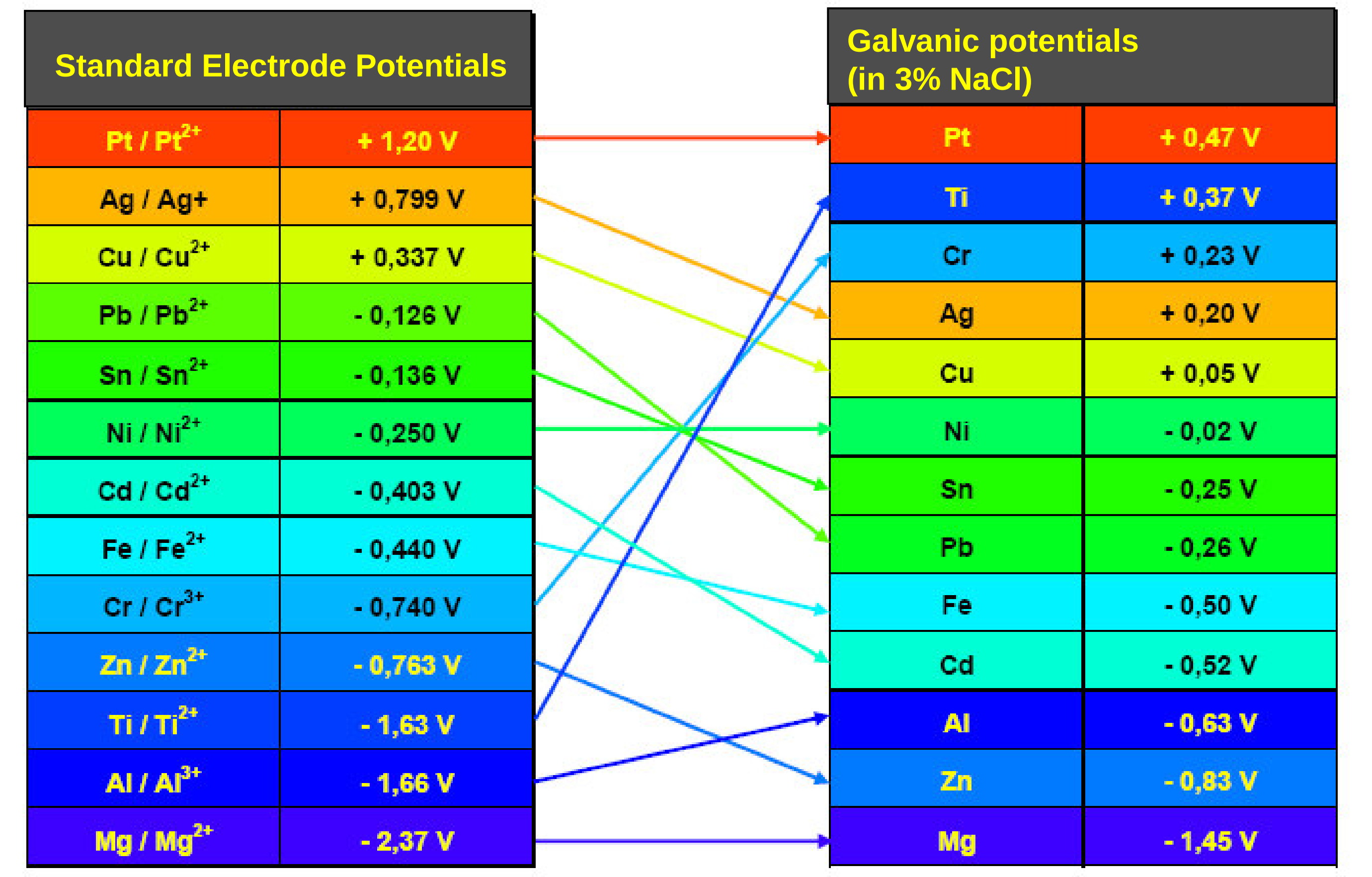








Galvanic series vs Electrochemical series



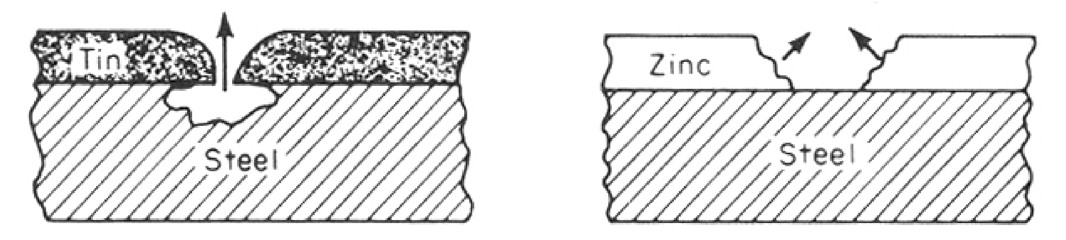
Standard Electrode Potentials	
Pt / Pt^{2+}	+ 1,20 V
Ag / Ag+	+ 0,799 V
Cu / Cu^{2+}	+ 0,337 V
Pb / Pb^{2+}	- 0,126 V
Sn / Sn^{2+}	- 0,136 V
Ni / Ni^{2+}	- 0,250 V
Cd / Cd^{2+}	- 0,403 V
Fe / Fe^{2+}	- 0,440 V
Cr / Cr^{3+}	- 0,740 V
Zn / Zn^{2+}	- 0,763 V
Ti / Ti^{2+}	- 1,63 V
Al / Al^{3+}	- 1,66 V
Mg / Mg^{2+}	- 2,37 V

Galvanic potentials (in 3% NaCl)	
Pt	+ 0,47 V
Ti	+ 0,37 V
Cr	+ 0,23 V
Ag	+ 0,20 V
Cu	+ 0,05 V
Ni	- 0,02 V
Sn	- 0,25 V
Pb	- 0,26 V
Fe	- 0,50 V
Cd	- 0,52 V
Al	- 0,63 V
Zn	- 0,83 V
Mg	- 1,45 V

Potential values vs NHE

EXAMPLE

Steel pipe protected with a metallic coating



Standard electrode potentials		Galvanic potentials in 3% NaCl	
Sn^{2+}/Sn	– 0,136 V	Cr	+ 0,23 V
Fe^{2+}/Fe	– 0,440 V	Sn	– 0,25 V
Cr^{3+}/Cr	– 0,74 V	Fe	– 0,50 V
Zn^{2+}/Zn	– 0,763 V	Zn	– 0,83 V

The electrochemical series suggests that chromium protects cathodically iron, which actually is not true. For corrosion problems the galvanic series are safer.

CORROSION RATES

The simplest way: visual inspection Just qualitative

The accurate way: mass loss Time and material consuming

Corrosion is a surface phenomenon
(proportional to the area, not the volume) $\dfrac{\Delta m}{A\,\Delta t}$

Since corrosion is an electrochemical process the mass loss can be related to the current through the Faraday laws of electrolysis

$$i = q / t$$

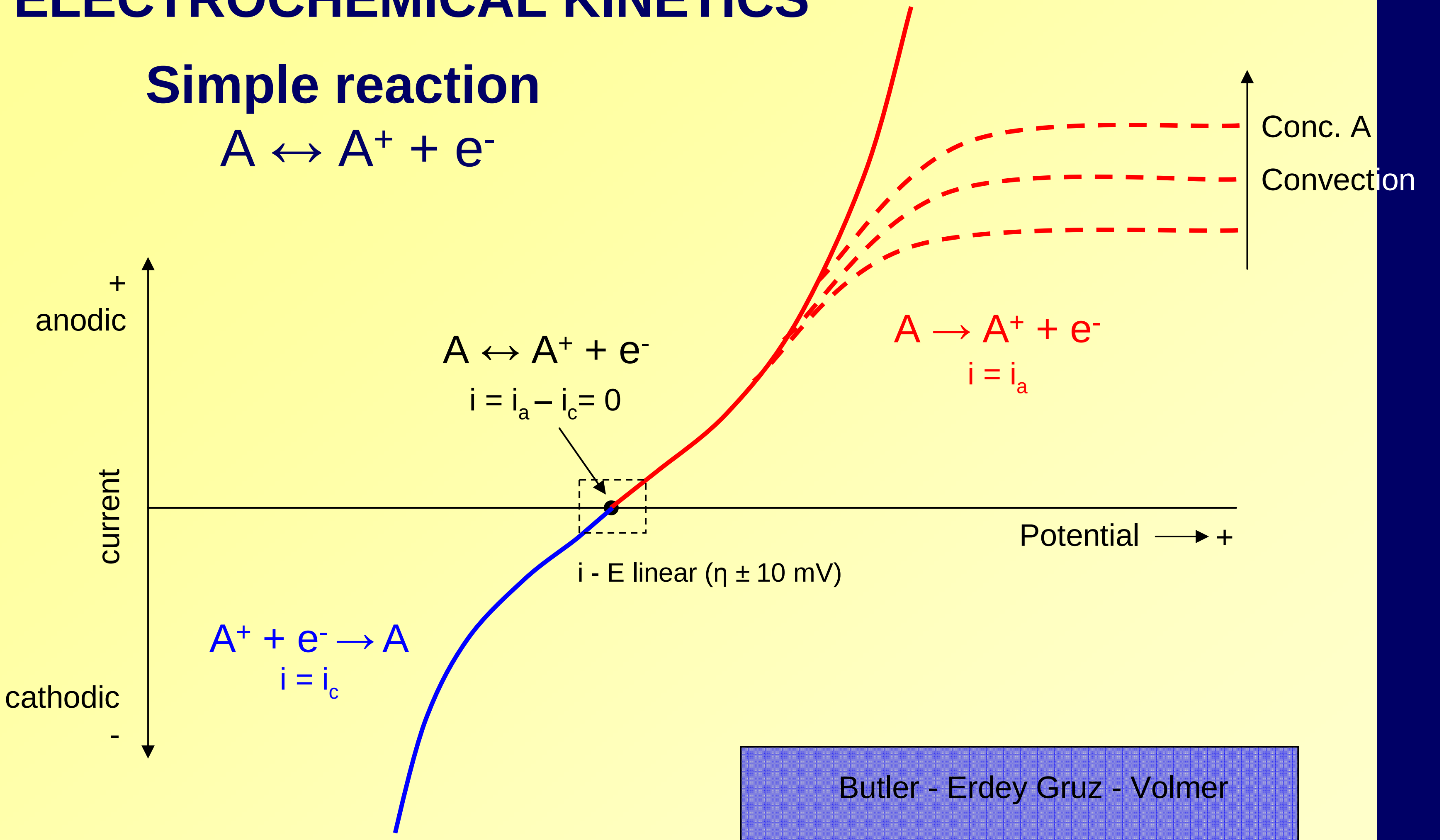
$$corr.\ rate\ (1) = \frac{m}{A\,t} = \frac{M}{z\,F}\,i \qquad (\text{mass area}^{-1}\ \text{time}^{-1})$$

$$corr.\ rate\ (2) = \frac{corr.\ rate\,(1)}{metal\ density} \qquad (\text{thickness time}^{-1})$$

ELECTROCHEMICAL KINETICS

Simple reaction

$A \leftrightarrow A^+ + e^-$



Diffusion limit equation

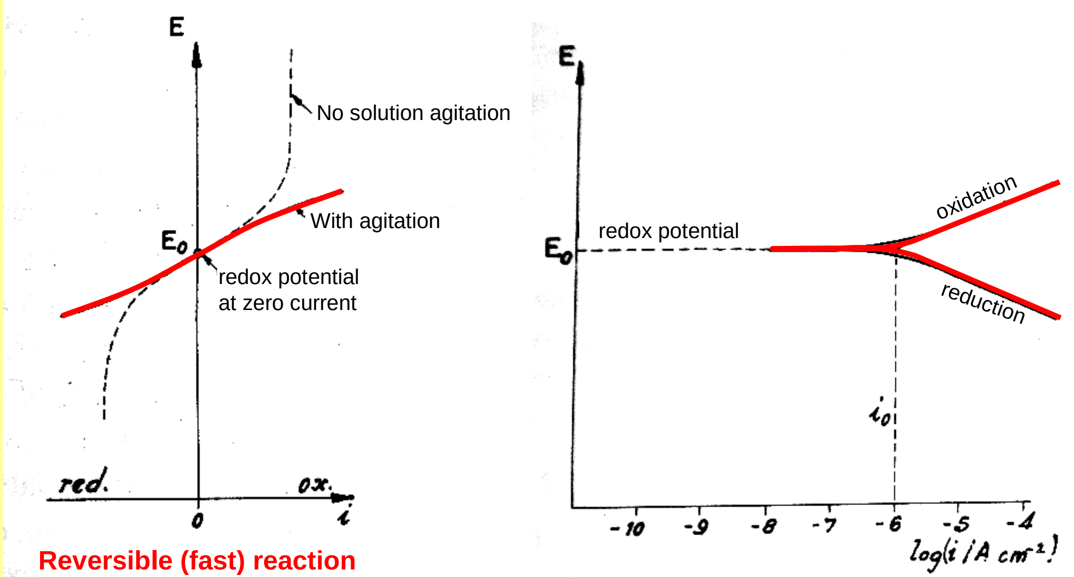
$$i_L = \frac{DnFC}{\delta}$$

Butler - Erdey Gruz - Volmer

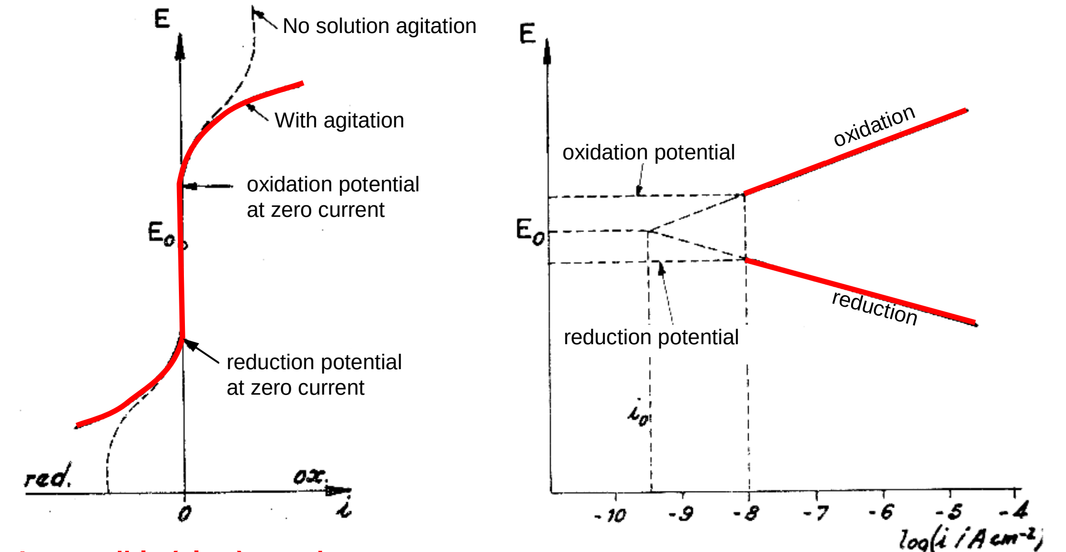
$$i = i_0 \left\{ e^{(1-\alpha) n_a f \eta} - e^{-\alpha n_c f \eta} \right\}$$

$$\eta = E - E_{eq} \qquad f = \frac{F}{RT}$$

The Thermodynamics and Kinetics of Metallic Corrosion

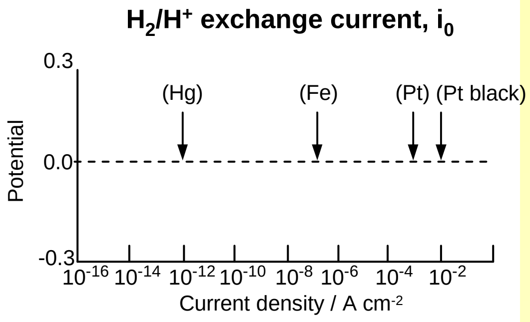


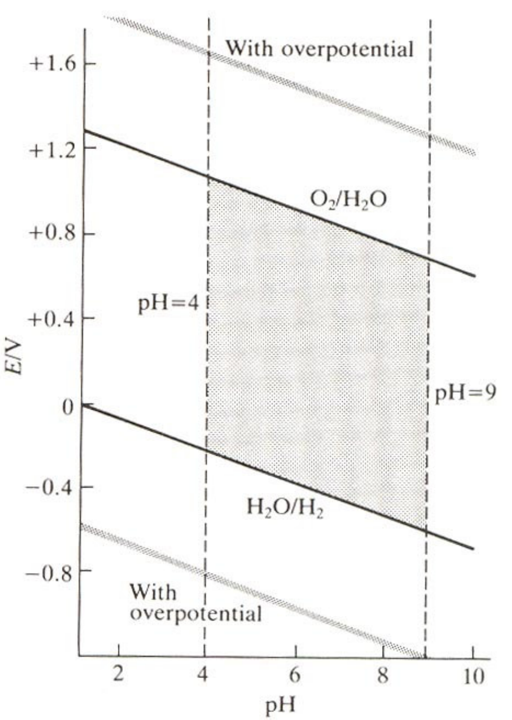
Reversible (fast) reaction



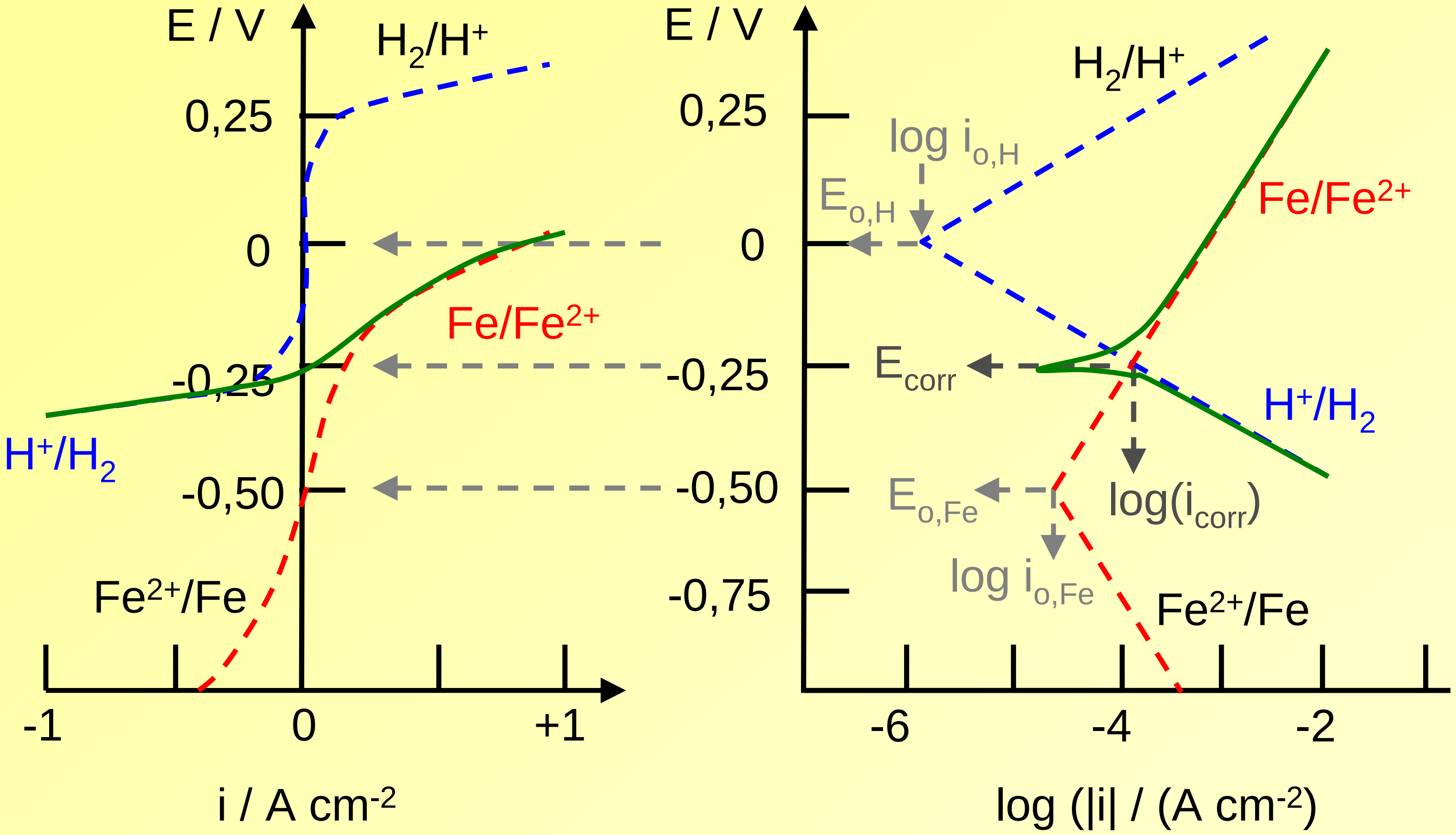
Irreversible (slow) reaction

M. Pourbaix, “*Lições de Corrosão Electroquímica,*” Lisboa, 1988, p.298.





Polarization curves of iron in a solution with 0,01g L^{-1} of Fe^{2+} and pH = 0.



N. Perez, Electrochemistry And Corrosion Science, Kluwer, 2004, p.88.
M. Pourbaix, “*Lições de Corrosão Electroquímica,*” Lisboa, 1988, p.298.

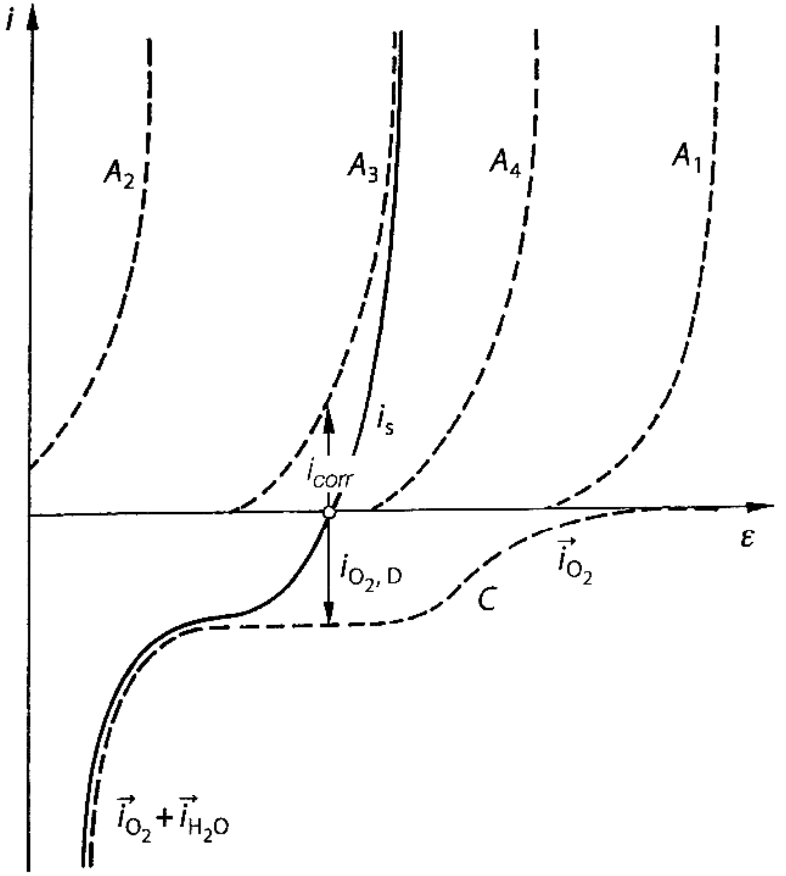
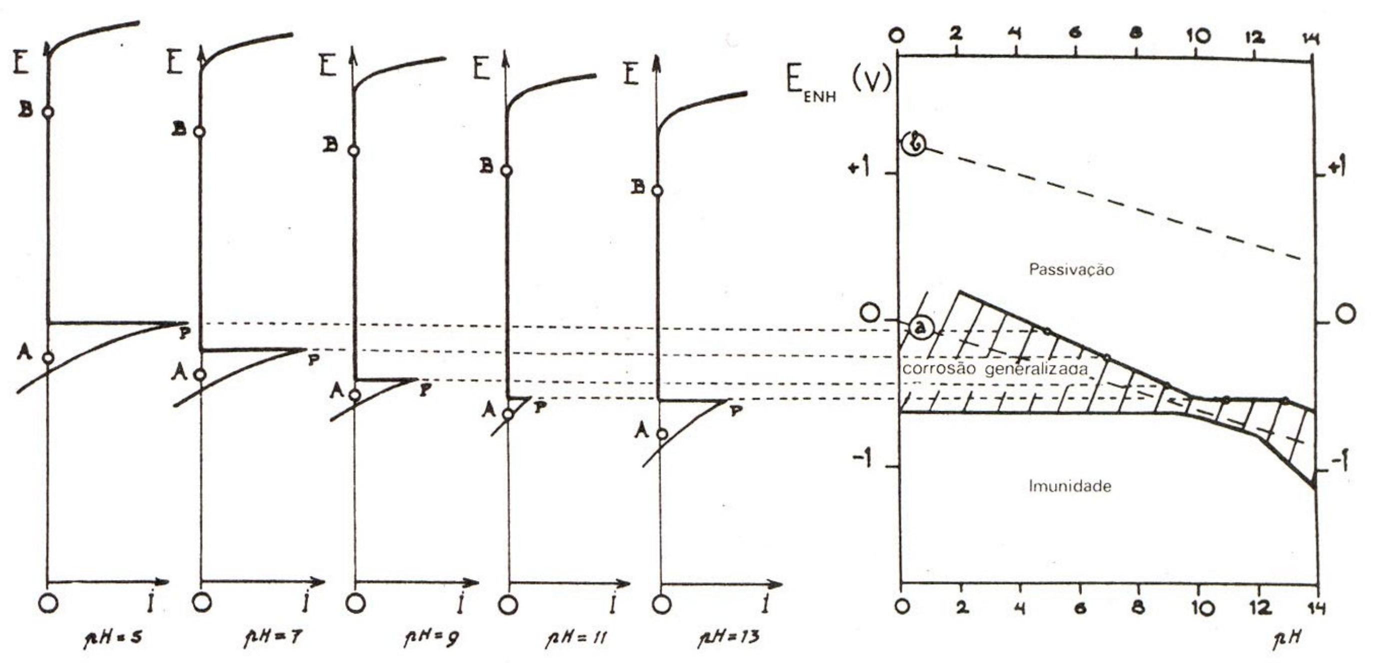


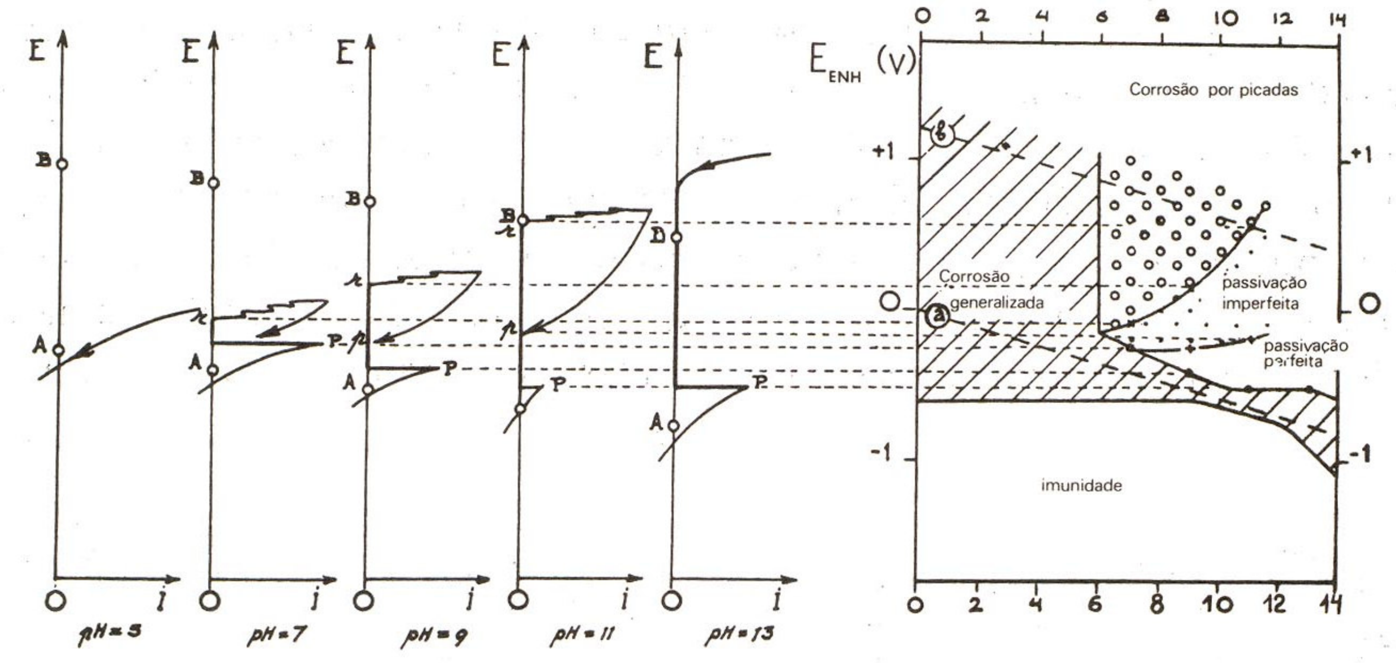
Fig. 6.6. Schematic current-potential curves for corrosion of metals in approximately neutral solutions by superposition of partial currents of anodic metal dissolution (A) and cathodic oxygen reduction and water reduction (C), assuming negligible reverse reaction for all electrode reactions. $A_{1...4}$ represent typical positions of the anodic curves depending on the magnitude of B_{Me} in Eq. (6.10), establishing the corrosion potential in the range of charge-transfer controlled oxygen reduction (A_1), charge-transfer controlled water reduction, (A_2), diffusion controlled oxygen reduction (A_3), an mixed charge-transfer/diffusion controlled oxygen reduction (A_4), respectively. Cases A_1 and A_2 reflect behaviour of copper and sodium, respectively, both A_3 and A_4 that of iron and mild steel

H.Kaesche, Corrosion of Metals, Springer, 2003

Fe in H_2O

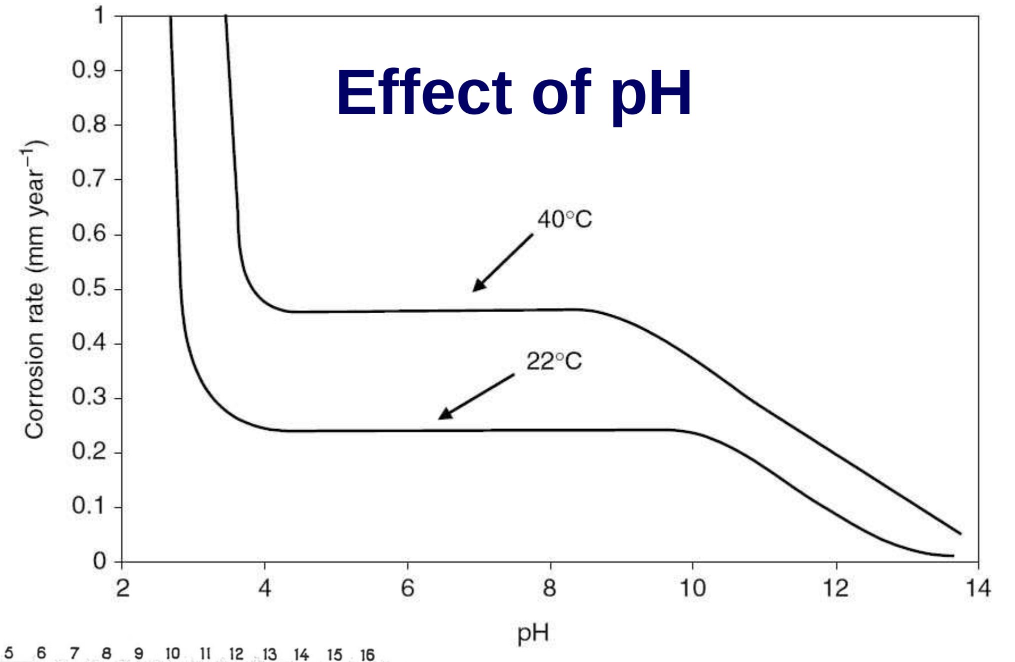


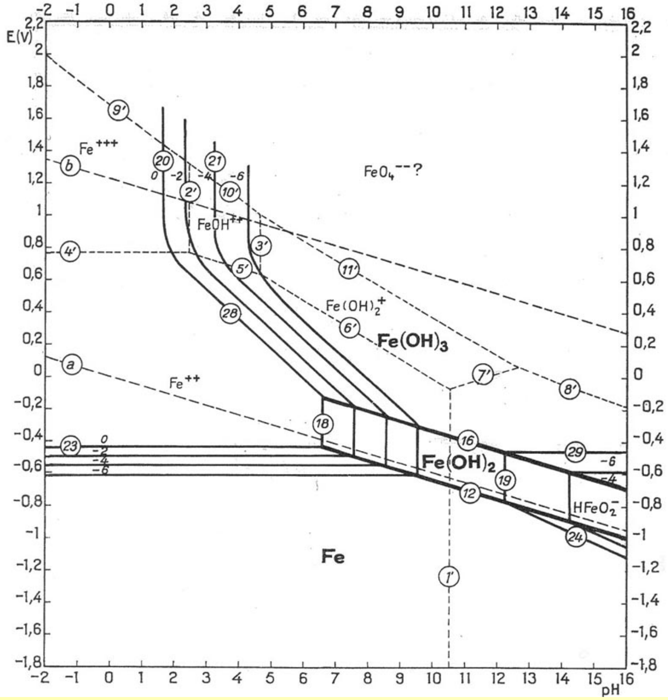
Fe in 10^{-2} M NaCl

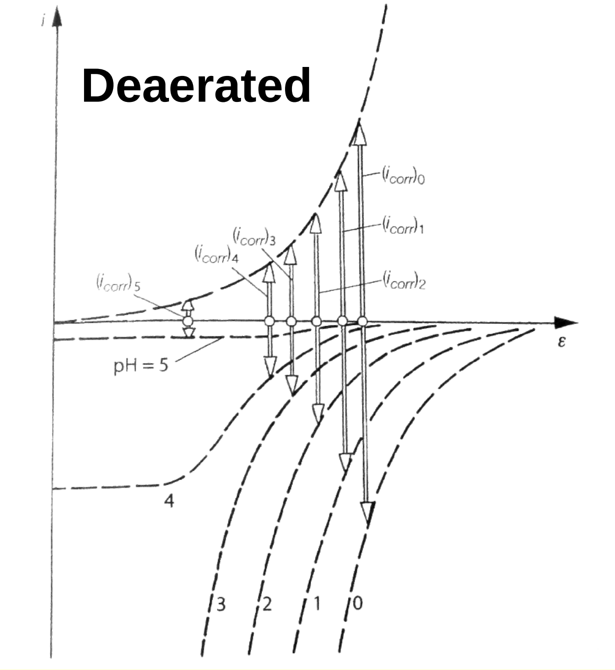


M. Pourbaix, “*Lições de Corrosão Electroquímica,*” Lisboa, 1988, p.298.

Effect of pH






Deaerated

Effect of O_2

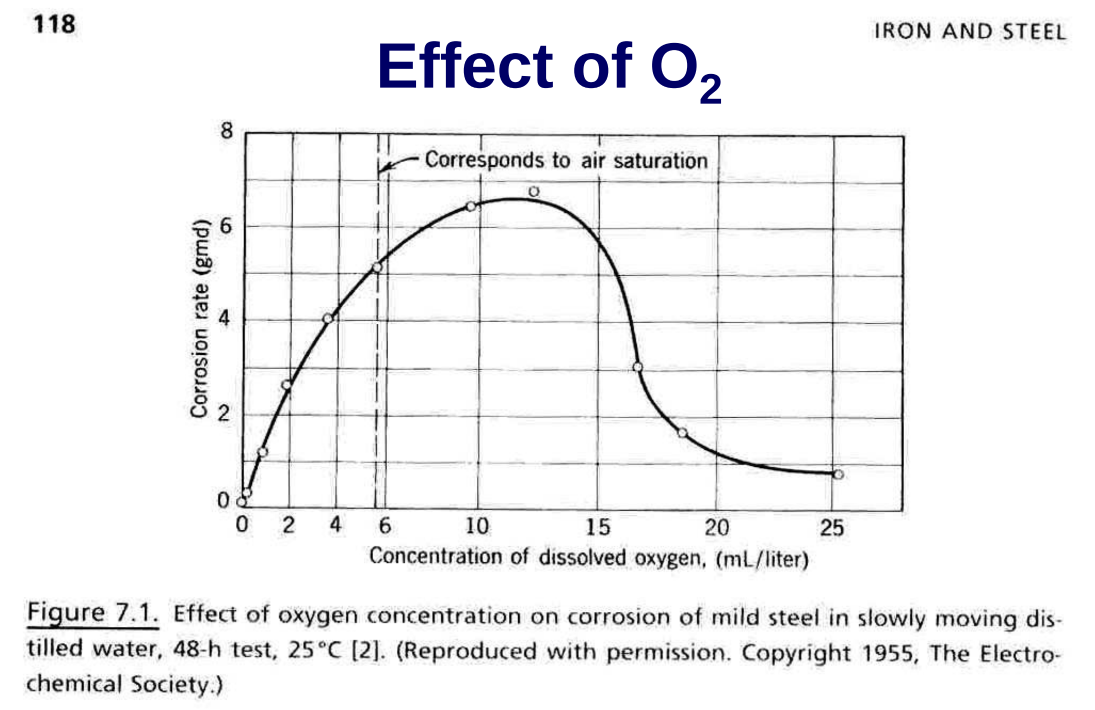


Figure 7.1. Effect of oxygen concentration on corrosion of mild steel in slowly moving distilled water, 48-h test, 25°C [2]. (Reproduced with permission. Copyright 1955, The Electrochemical Society.)

Effect of Salinity

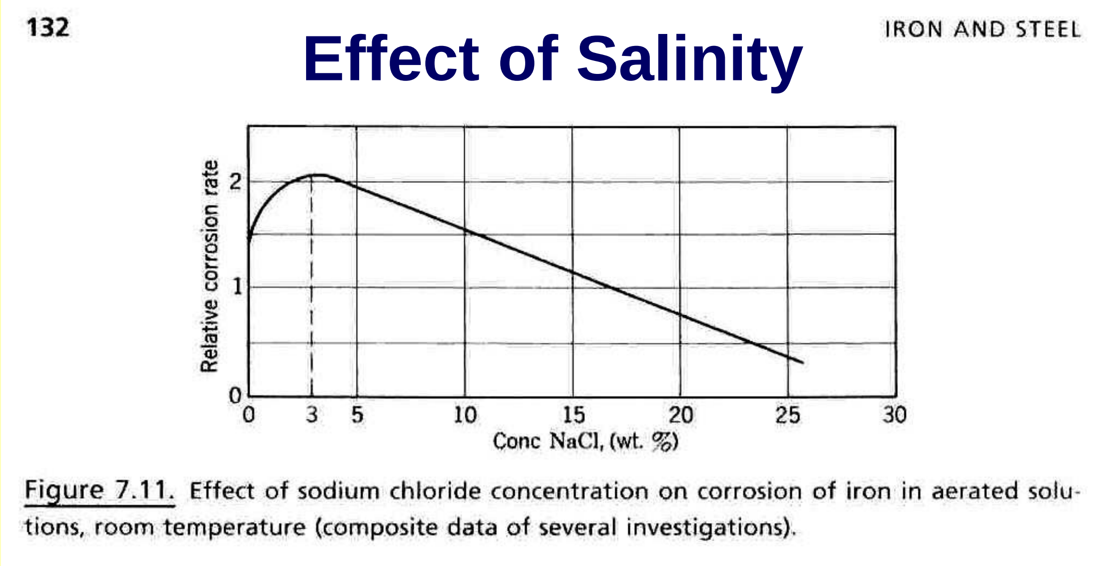
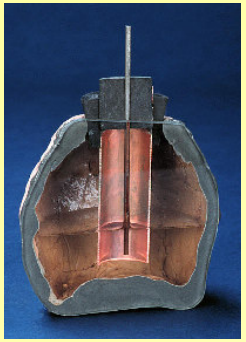


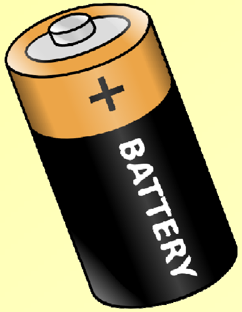
Figure 7.11. Effect of sodium chloride concentration on corrosion of iron in aerated solutions, room temperature (composite data of several investigations).

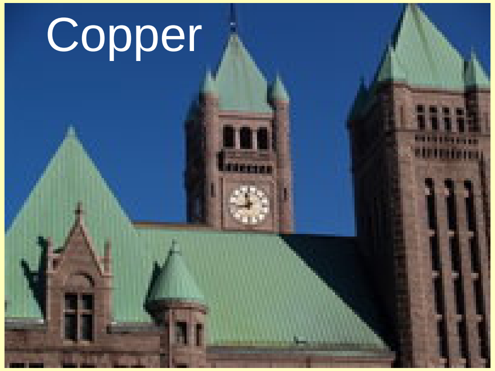
R.W.Revie, H.H.Uhlig, Corrosion and Corrosion Control 4th Ed, Wiley, 2008

Cor-Ten
Weathering steel

Batteries







Copper