Tutorials : Corrosion

Part 1: Theory and basics

Theory and basics of corrosion

A. Definition and effects of corrosion

B. General thermodynamics and kinetics in electrochemistry

C. Thermodynamics and kinetics in corrosion

A. Corrosion : What is it ?

D.A. Jones : « Destructive result of a chemical reaction between a metal and its environment »

M.G. Fontana : « Deterioration of a material because of reaction with its environment »

If a degradation of a material is only physical and does not involve chemical mechanisms it is not considered to be corrosion.

Corrosion is an unwanted spontaneous electrochemical reaction that can lead to the structural degradation of a material.

A. Corrosion : Unwanted

Recent studies (2002) estimate the direct cost of corrosion in the United States to be nearly $300 billion dollars per year or 3,1% of US GNP.

Corrosion has been the cause of many catastrophic damages.

Famous example : 1999, Sinking of the Erika, broke in two 70 kilometers from the coast of Brittany, France, whilst carrying approximately 30 000 tons of heavy fuel oil. Some 19 800 tons were spilled.

Holes due to corrosion were found on the main deck coaming, the inert gas system risers, the «watertight » ship's doors...

A. Corrosion : Electrochemical

An electrochemical reaction is the sum of two half-reactions :

. An oxidation (electrons loss) $Red \rightarrow Ox + ne^-$

. A reduction (electrons gain) $Ox + ne^- \rightarrow Red$

In an oxidation, the oxidation number (o.n.) of the concerned element increases.

In a reduction, the o.n. of the concerned element decreases.

The oxidation number characterizes in which electronic state an element is.

o.n. = 0, the element is in its elementary state (Fe, Ni, O_2 H_2...)

o.n. > 0, the element is positively charged (one or more electrons are gone) : Fe^{2+}, H^+, Na^+, Cu^{2+}, Al^{3+}...

o.n. < 0, the element is negatively charged (one or more electrons are in excess) : Cl^-, O^{2-}...

A. Corrosion : Electrochemical

In corrosion, the oxidation reaction is **ALWAYS** the destructive oxidation of the metal :

$$M \rightarrow M^{z+} + ze^-$$

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

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

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

In corrosion, the reduction reactions mostly are :

Water (proton) reduction : $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Dissolved oxygen reduction : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

A complete corrosion reaction is written as the sum of the partial reaction

(ex : Fe in an acidic solution)

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

If either the oxidation **or** the reduction cannot occur,then the **corrosion is inhibited**.

A. Corrosion : Electrochemical

Two fundamental aspects to consider in corrosion (and electrochemistry) :

. Thermodynamics : which reactions will occur ?

. Kinetics : how fast these reactions will occur ?

B. General thermodynamics

Consider the following reaction written as an equilibrium:

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

In the case where an electrode made of the metal M is immersed in a solution containing the cation M^{z+} this electrochemical reaction reaches an **equilibrium** and the electrode M takes a potential called the equilibrium potential $\mathbf{E_{eq}}$.

The potential of an electrode is always defined *vs.* a reference potential.

The Nernst equation is used to calculate this equilibrium potential observed in specific conditions.

B. General thermodynamics

For the general reaction :

$$aA + bB + ne^- \leftrightarrow cC + dD$$

In a dilute solution, the activity is equal to the concentration, the Nernst equation writes:

$$E_{eq} = E^0 + \frac{RT}{nF} \ln \frac{[A]^a [B]^b}{[C]^c [D]^d} \qquad (1)$$

With :
E^0 the equilibrium potential in the standard conditions*
R the perfect gas constant (8.315 $J.K^{-1}.mol^{-1}$)
T the temperature (K)
n the number of exchanged electrons
F the Faraday constant (96487 $C.mol^{-1}$)
$[x]$ the concentration of the species x ($mol.L^{-1}$)

*standard conditions : pure solids, gases at 1 atm pressure, dissolved species at 1 $mol.L^{-1}$ concentration, 0°C

B. General thermodynamics

Each species has a different equilibrium potential.

It is generally given in the standard conditions and *vs.* the standard hydrogen reference electrode.

Such a table is used to determine which reactions are likely to occur.

From D.A. Jones

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.*

B. General kinetics

Let us consider again the following electrochemical reaction at an equilibrium :

$$M^{n+} + ne^- \underset{I_{red}}{\overset{I_{ox}}{\rightleftharpoons}} M$$

An electrochemical reaction involves an electron flow *i.e.* an electrical current.

At the equilibrium, a current of equal magnitude flows in both directions.

$$I_{net} = I_{ox} + I_{red} = 0$$

$$I_{ox} = |I_{red}| = I_0$$

I_0 is the exchange current, which is equivalent to a reversible reaction rate at the equilibrium.

The exchange current density i_0 (= I_0/A) depends on the catalytic properties of the material used for the electrode. For the proton reduction, i_0 varies over 9 orders of magnitude[1].

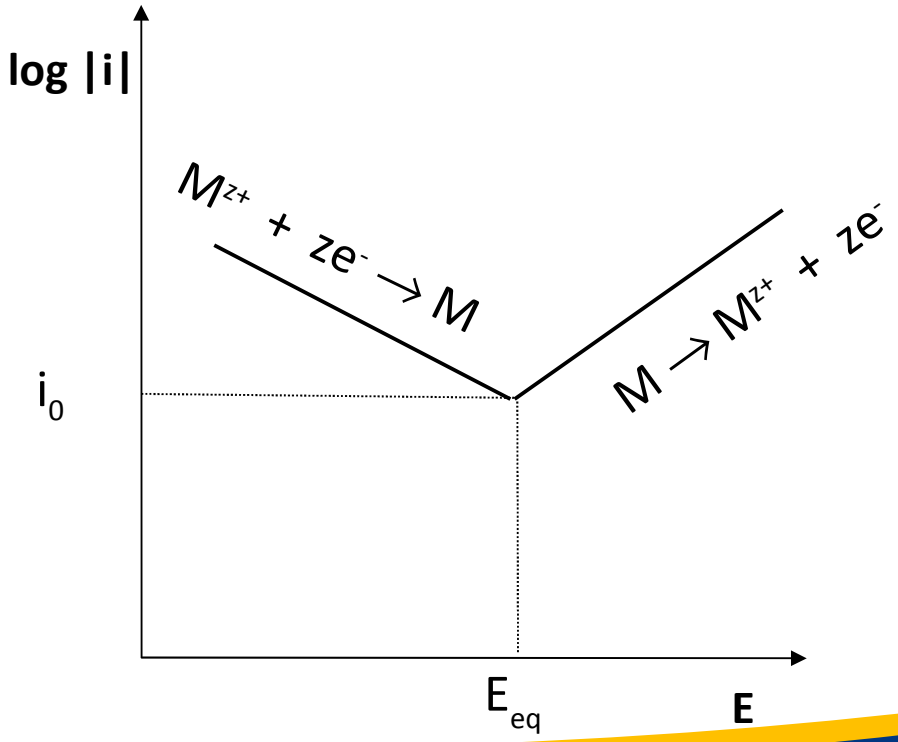
1. Table 3.2, J. M. West, Electrodeposition and Corrosion Processes, Van Nostrand 1965

B. General kinetics

What happens when the potential of the electrode moves away from the equilibrium potential of the considered reaction ?

1. If the potential is above E_{eq} (anodic potential), there is OXIDATION
2. If the potential is below E_{eq} (cathodic potential) there is REDUCTION.

Depending on how far the potential is from E_{eq}, the oxidation or reduction current will change.



B. General kinetics

Moving away from the equilibrium potential of an electrode = **POLARIZING**

η the overpotential is defined as E-E_{eq}

We assume that the current only depends on the rate of electron transfer across the charged interface.

Charge transfer at the metal/electrolyte interface does not follow the Ohm's law due to the very high electric field present there (on the order of 10^7 V/cm).

It is given by a law called the **Butler-Volmer** relationship.

$$I = I_0\left(\exp\left(\frac{\alpha_o nF}{RT}(E - E_{eq})\right) - \exp\left(\frac{-\alpha_r nF}{RT}(E - E_{eq})\right)\right) \qquad (2)$$

where α_o is the oxidation symmetry factor and α_r is the reduction symmetry factor ($\alpha_o + \alpha_r = 1$)

B. General kinetics

$$I = I_0 \exp\left(\frac{\alpha_o nF}{RT}(E - E_{eq})\right) - I_0 \exp\left(\frac{-\alpha_r nF}{RT}(E - E_{eq})\right)$$

Anodic term

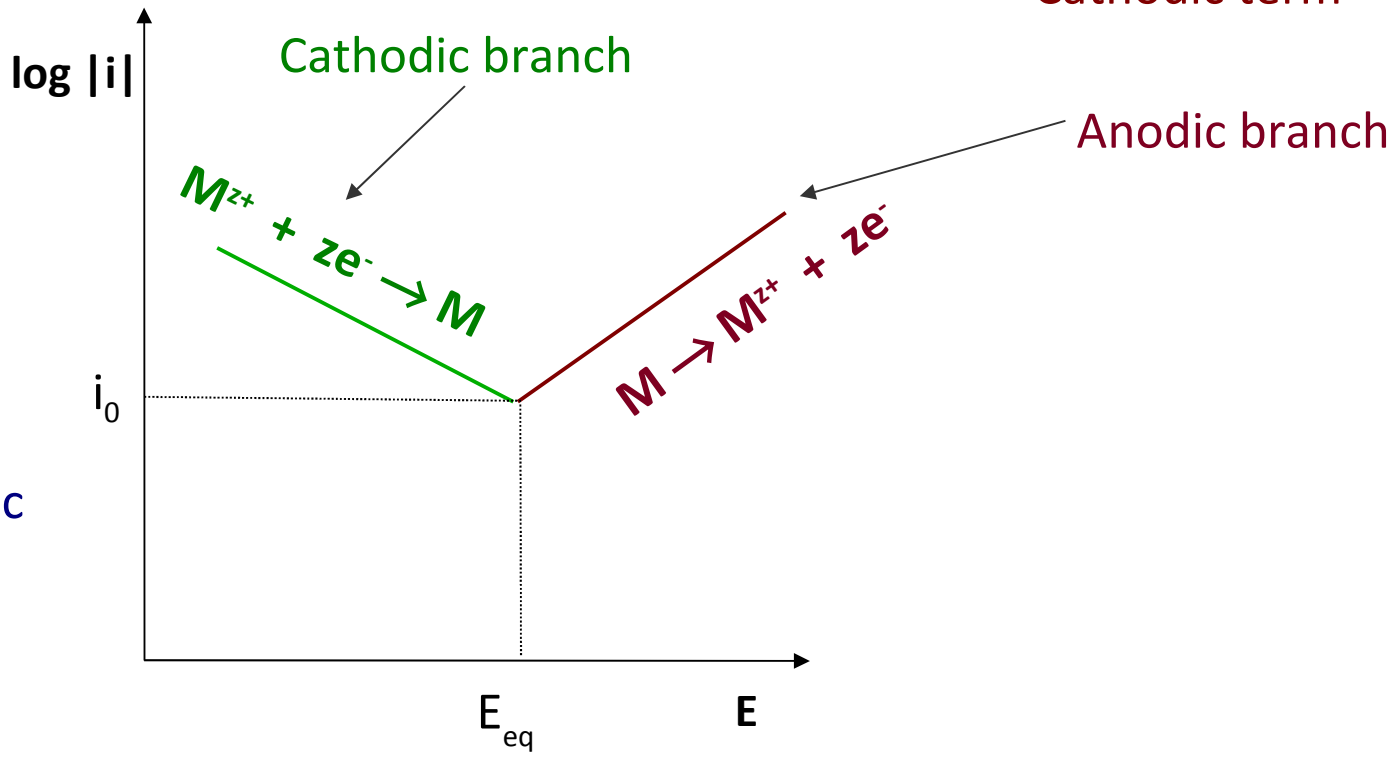
Cathodic term

Considering the absolute values :

At E_{eq} the anodic term is equal to the cathodic term.

At $E > E_{eq}$, the anodic term is larger than the cathodic term

At $E < E_{eq}$, the cathodic term is larger than the anodic term.



BV relationship is valid only if the current is not limited by mass transport.

C. Thermodynamics and kinetics applied to corrosion

The relations derived before were valid for only one redox couple M^{n+}/M.

The oxidation and the reduction half reactions involve the same species.

In corrosion, as seen above, two different redox couples are involved in the oxidation and reduction half reaction, as most of the time, the electrolyte does not contain the metallic cation corresponding to the electrode metal.

The electrolyte most of the time contains dissolved O_2 or H^+ (H_2O)

Oxidation of the metal M : $M \rightarrow M^{n+} + ne^-$

Water (proton) reduction : $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Dissolved oxygen reduction : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

C. Thermodynamics and kinetics applied to corrosion : Mixed potential theory

When a metallic electrode immersed in an aqueous media in which the oxidized species is not the metallic cation, its potential is called $\mathbf{E_{corr}}$, the corrosion potential.

At this potential, the oxidation rate of the metal is given by $\mathbf{I_{corr}}$, the corrosion current.

$\mathbf{E_{corr}}$ and $\mathbf{I_{corr}}$ can be determined by plotting the **I *vs.* E** characteristics of each involved redox couple and using the relation dictated by the principle of charge conservation :

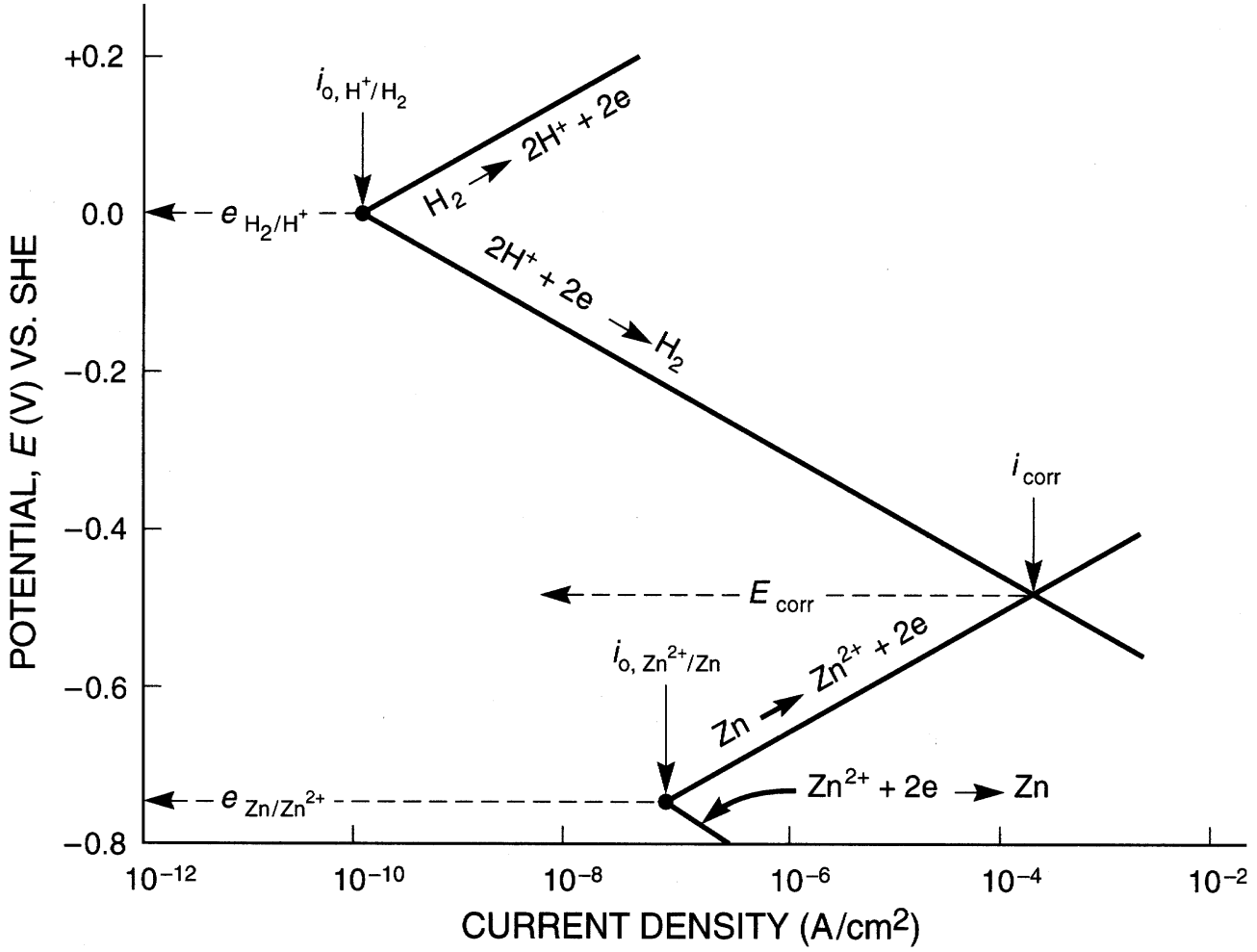
$$\mathbf{\Sigma I_{oxid} = \Sigma I_{red}}$$

The sum of the oxidation currents is equal to the sum of the reduction currents.

C. Thermodynamics and kinetics applied to corrosion : Mixed potential theory

Example: Zn in acidic solution

From D.A. Jones



E_{corr} and I_{corr} are the coordinates of the intersection point of the I *vs.* E characteristics of each concerned redox couple.

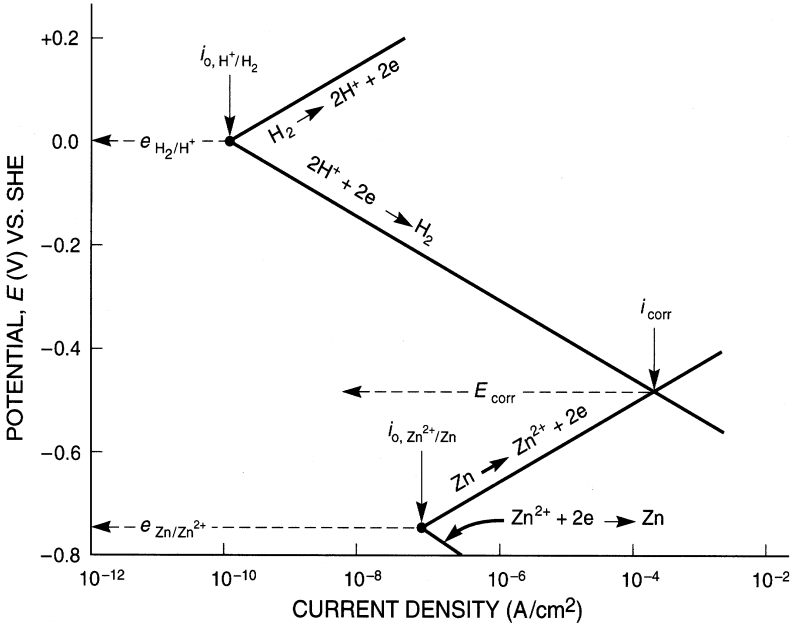
C. Thermodynamics and kinetics applied to corrosion : Stern* relationship

Example: Zn in acidic solution

Let us write the Butler-Volmer relations for the two redox couples involved :

$$I_{H^+/H_2} = I_{0\,H^+/H_2}\left(\exp\left(\frac{\alpha_{o1} n_1 F}{RT}\left(E - E_{eq\,H^+/H_2}\right)\right) - \exp\left(\frac{-\alpha_{r1} n_1 F}{RT}\left(E - E_{eq\,H^+/H_2}\right)\right)\right) \quad (3)$$

$$I_{Zn^{2+}/Zn} = I_{0\,Zn^{2+}/Zn_2}\left(\exp\left(\frac{\alpha_{o2} n_2 F}{RT}\left(E - E_{eq\,Zn^{2+}/Zn}\right)\right) - \exp\left(\frac{-\alpha_{r2} n_2 F}{RT}\left(E - E_{eq\,Zn^{2+}/Zn}\right)\right)\right) \quad (4)$$



1. At E_{corr} the anodic term of the relation (3) and the cathodic term of relation (4) are negligible.

2. Furthermore, the current I_{corr} at the Zn electrode is the sum of (3) and (4).

* also known as the Wagner-Traud relationship

C. Thermodynamics and kinetics applied to corrosion : Stern* relationship

Example: Zn in acidic solution

Following 1 and 2, I the net current at the Zn electrode is expressed as :

$$I = I_{corr}\left(\exp\left(\frac{\alpha_{o2} nF}{RT}(E - E_{corr})\right) - \exp\left(\frac{-\alpha_{r1} n_1 F}{RT}(E - E_{corr})\right)\right) \quad (5)$$

This is called the **Stern*** relationship.
It can be also written :

$$I = I_{corr}\exp\left(\frac{\alpha_{o2} n_2 F}{RT}(E - E_{corr})\right) - I_{corr}\exp\left(\frac{-\alpha_{r1} n_1 F}{RT}(E - E_{corr})\right) \quad (6)$$

With $f = \frac{F}{RT}$

$$I = I_{corr}\exp\left(\alpha_{o2} n_2 f (E - E_{corr})\right) - I_{corr}\exp\left(-\alpha_{r1} n_1 f (E - E_{corr})\right) \quad (7)$$

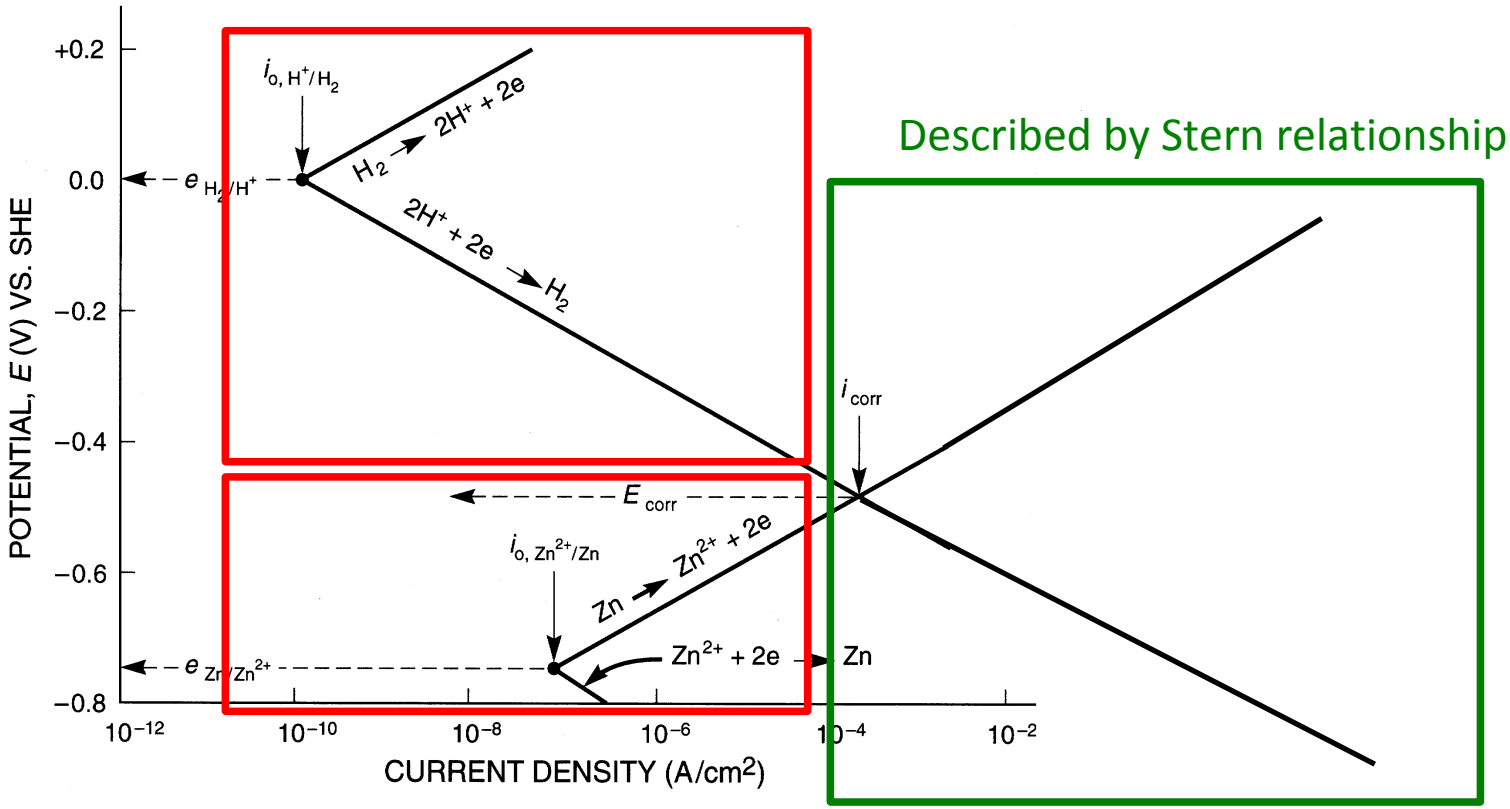
* also known as the Wagner-Traud relationship

C. Thermodynamics and kinetics applied to corrosion : Stern* relation

Example: Zn in acidic solution

Described by Butler-Volmer relationship

Described by Stern relationship



* also known as the Wagner-Traud relationship

C. Thermodynamics and kinetics applied to corrosion : Summary

Fundamental	Corrosion
1 redox couple	2 redox couples
Equilibrium potential E_{eq}	Corrosion potential E_{corr}
Exchange current I_0	Corrosion current I_{corr}
Butler-Volmer	Stern (Wagner-Traud)
α_o, α_r ($\alpha_o + \alpha_r = 1$)	α_{o2}, α_{r1} ($\alpha_{o2} + \alpha_{r1}$ not always = 1)