



# **Non-Destructive Testing Methods for Metal Corrosion**

**An Online Continuing Education Course for Engineers**

**Course Number: MA-2007**  
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# Nondestructive Testing Methods for Metal Corrosion

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## INTRODUCTION

Corrosion is a deterioration of metal or alloy due to its chemical or electrochemical interaction with the environment. It may occur in two types of environment: corrosion at ambient temperature (aqueous phase or moisture) or corrosion at high temperature (reactive gases).

Corrosion has existed since the copper age, but a brief timeline of more recent historical landmarks in the study of corrosion might include the following examples:

In the 18<sup>th</sup> century, Luigi Galvani and Alessandro Volta began experimenting with electrochemistry.

In the early 19<sup>th</sup> century, Sir Humphrey Davy passed current through substances to decompose them (electrolysis).

In the 1830s, Michael Faraday, who had been Sir Davy's lab flunky but outgrew the role, developed the theory of electrochemical action and coined the following terms we now use:

- Electrode
- Electrolysis
- Ion

## Principles of Corrosion

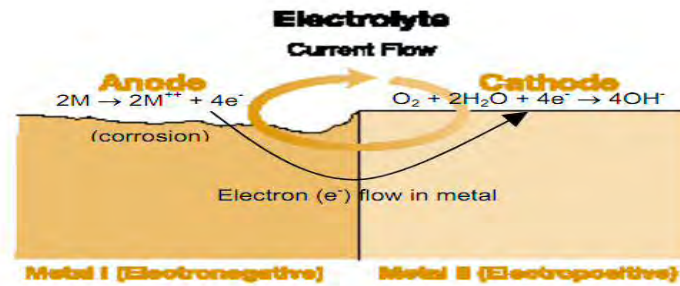
*Dry corrosion* may occur in three ways:

- Oxidation corrosion
- Corrosion by other gases
- Liquid metal corrosion

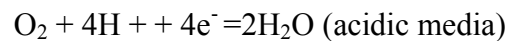
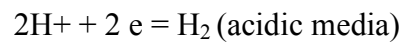
*Wet (electrochemical) corrosion* consists of

- Electronic path through metal
- Ionic path through solution (electrolyte: acidic/alkaline/neutral)
- Anode Electrode (Oxidizing – losing electrons)

- Cathode Electrode (Reducing – gaining electrons)



- Anodic Reaction:  $M = M^{+n} + ne$ . Where M represents a metal with a valency. It is a de-electronation reaction, also called oxidation.
- Cathode reaction: Also known as reduction reaction, cathode reactions can be numerous, but the principal ones may be generalized as:



## CHARACTERISTICS OF METAL CORROSION

### Thermodynamic Aspects of Corrosion

Metals extracted from ores in high energy states have a thermodynamic tendency to recombine with elements present in the environment.

Tendency of corrosion is determined by the free energy difference, i.e.,  $\Delta G = G_f - G_i$ .

For continuous corrosion to occur,  $\Delta G = G_f - G_i < 0$ .

$$\Delta G = -Q\Delta E = -nF\Delta E,$$

Where:

$\Delta E$  = the potential difference between the electrodes,

$Q$  = the transported charge,

$n$  = the number of electrons transferred within the reaction

$F$  = the Faraday Constant (96500 Coulombs/equivalent)

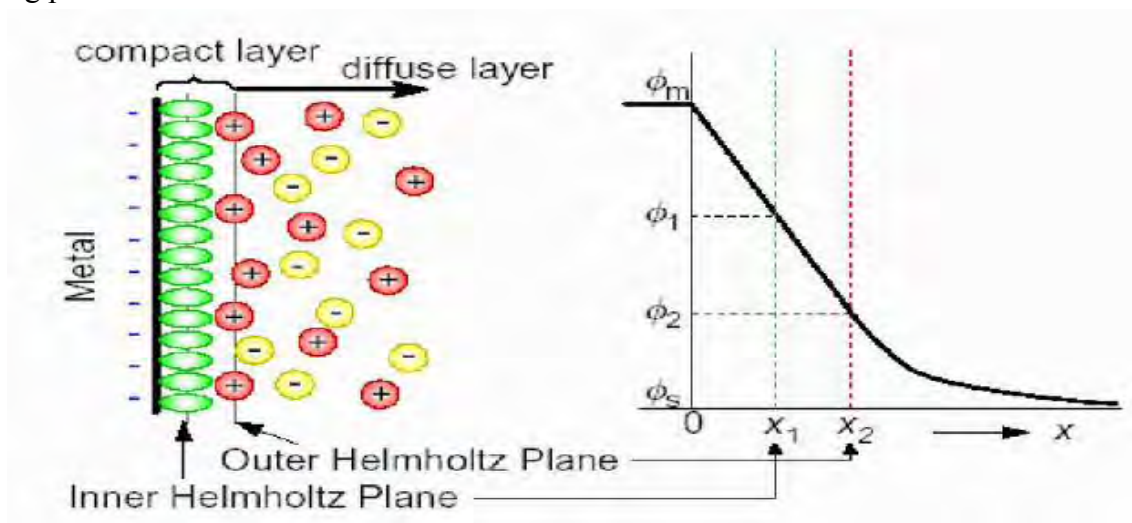
There are two reactions involved in the corrosion process: oxidation and reduction. Each reaction (anodic and cathodic) has a half-cell potential. The sum of the anodic and cathodic half-cell potentials is the total potential. The total free energy change must be negative for corrosion to occur.

## Electrochemical Aspects of Corrosion

In general, an electrochemical double layer of charges exists at the interface between two conducting media: One side carries a positive excess *charge*, which is balanced by a negative excess of equal magnitude on the other side. The resulting potential drop across the interface is the double-layer potential. Two limiting cases exist: at an ideally polarizable interface the two adjacent phases cannot exchange charges; the system then behaves like a capacitor, which can be charged by applying an external potential. At an ideally non-polarizable interface the two phases can exchange charge carriers, ions or electrons, and in the stationary case the potential difference is determined by the difference of the chemical *potential* of these carriers in the two phases.

### Double layer models:

**The Helmholtz model:** Hermann Ludwig Ferdinand von Helmholtz (b. 1821 – d. 1894). Helmholtz, a German physicist, suggested that an excess charge on the metal attracts an equivalent amount of counter ions to the interface; the two opposing layers are separated by a certain distance, which determines the capacity. The simple model of a capacitor with two opposing planes is as follows:



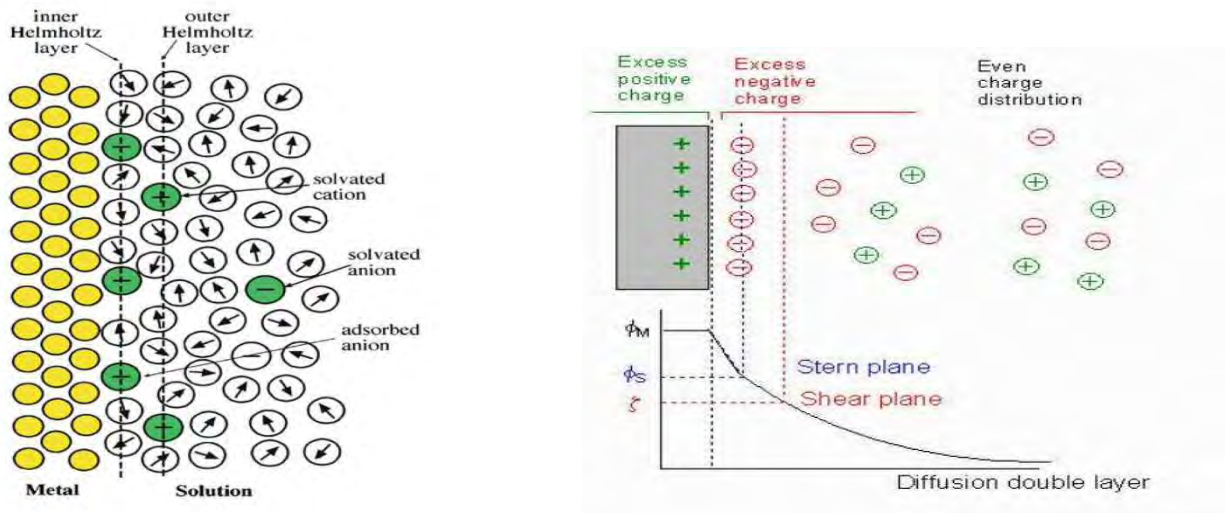
**The Gouy-Chapman model:** Louis Georges Gouy (b. 1854 – d. 1926); David Leonard Chapman (b. 1869 – d. 1958). Gouy and Chapman proposed the first statistical model. By combining electrostatics with Boltzmann statistics, they derived the Poisson–Boltzmann equation for the distribution of ions in the solution.

$$n = n_0 \exp(-ze\Psi/kT)$$

where  $n_0$  = bulk concentration  
 $z$  = charge on the ion  
 $e$  = charge on a proton  
 $k$  = boltzman constant

**The Gouy-Chapman-Stern model:** Otto Stern (b. 1888 – d. 1969). Stern won the Nobel Prize for physics in 1945 (Stern-Gerlach experiment). In this model the ions can approach the electrode surface only up to the outer Helmholtz plane; in this context, the outer Helmholtz layer is also known as the Stern or ion-free layer. Mathematically, the interface can then be described as two capacitors in series:

$$1/C = 1/C_H + 1/C_{GC}$$



### The Nernst Equation

$$\Delta G = \Delta G^\circ + RT \ln Q, \quad E = E^\circ - \frac{.059}{n} \log Q$$

$R$  is the gas constant.

$$E = E^{\circ'} + \frac{2.303 RT}{nF} \log \frac{[Ox]}{[Red]}$$

Measured E vs. Ref      Nernst Equation

The Nernst equation tells us that a half-cell potential will change by 59 millivolts per 10-fold change in the concentration of a substance involved in a one-electron oxidation or reduction; for two-electron processes, the variation will be 28 millivolts per decade concentration change.

### Potential-pH Diagram:

This diagram was introduced by Pourbaix and is known as a Pourbaix diagram. It represents the stability of a metal in an environment with respect to its oxidizing/reducing potential (y-axis) vs. pH (x-axis). It is used to predict the corrosion products, to determine the conditions that will prevent or reduce corrosion attack.

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#### Pourbaix diagram

- 1) **The corrosive region:** the metal cation or any non protective oxide will occur until the metal is completely dissolved.
- 2) **The immune region:** corrosion is thermodynamically impossible.
- 3) **The passive region:** an insoluble (hydroxide or oxide layer) is the most stable form; initial corrosion will occur until a protective layer is formed.

