

أيها الطلبة الأعزاء نظرا للظروف التي يعيشها العالم بصفة عامة والجامعة بصفة خاصة وبطلب من وزارة التعليم العالي فانه تقرر وضع الدروس في الأرضية الالكترونية للجامعة حتى يتسنى للطلبة متابعة الدروس

سوف تجدون الملف ملخص لمادة تآكل المعادن يطلب منكم الاطلاع عليه و يمكنكم الاتصال بي على الرقم 0667519087 في حالة وجود اي استفسار يتعلق بهذا الموضوع و شكرا .

الاستاذ: عسوس بوبكر

## **Atmospheric Corrosion**

### **Atmospheric Types**

Because corrosion rates are affected by local conditions, atmospheres are generally divided into the following major categories:

- Rural
- Industrial
- Marine

For all practical purposes, the more rural the area, with little or no heavy manufacturing operations, or with very dry climatic conditions, the less will be the problem of atmospheric corrosion. In an industrial atmosphere, all types of contamination by sulfur in the form of sulfur dioxide or hydrogen sulfide are important. The burning of fossil fuels generates a large amount of sulfur dioxide that is converted to sulfuric and sulfurous acid in the presence of moisture. Combustion of these fossil fuels and hazardous waste products should produce only

carbon dioxide, water vapor, and inert gas as combustion products. This is seldom the case. Depending on the impurities contained in the fossil fuel, the chemical composition of the hazardous waste materials incinerated, and the combustion conditions encountered, a multitude of other compounds may be formed.

In addition to the most common contaminants previously mentioned, pollutants such as hydrogen chloride, chlorine, hydrogen fluoride, and hydrogen bromide are produced as combustion products from the burning of chemical wastes. When organophosphorus compounds are incinerated, corrosive phosphorous compounds are produced. Chlorides are also a product of municipal incinerators.

Road traffic and energy production lead to the formation of  $\text{NO}_x$  that may be oxidized to  $\text{HNO}_3$ .

Marine environments are subject to chloride attack resulting from the deposition of fine droplets of crystals formed by evaporation of spray that has been carried by the wind from the sea. The quantity of chloride deposition from marine environment is directly proportional to the distance from the shore. The closer to the shore, the greater the deposition and corrosive effect. The atmospheric test station at Kure Beach, North Carolina shows that steels exposed 80

feet from the ocean corrode 10–15 times faster than steels exposed 800 feet from the ocean.

## **Factors Affecting Atmospheric Corrosion**

Atmospheric corrosion is an electrochemical process and, as such, depends on the presence of an electrolyte. The usual electrolyte associated with atmospheric corrosion is water resulting from rain, fog, dew, melting snow, or high humidity. Because an electrolyte is not always present, atmospheric corrosion is considered a discontinuous process. Corrosion takes place only during the time of wetness. It can be described by the equation:

$$K = \sum_L^h t_n V_k(n)$$

$K$  accumulated corrosion effect

$t_n$  time of wetness (the period with an electrolyte layer on the surface)

$V_k$  average corrosion rate during the individual periods of wetness, the composition of the electrolyte, and the temperature determines the corrosion rate; factors affecting the time of wetness, and the composition of the electrolyte film will be discussed later.

## **Time of Wetness**

The term time of wetness refers to the length of time during which the metal surface is covered by a film of water that renders significant atmospheric corrosion possible. The actual time of wetness will vary with climatic conditions at the location. It is dependent on the relative humidity of the atmosphere (being greatest when the relative humidity is R80%), the temperature of the air and the metal surface above 328F/08C, the duration and frequency of rain, fog, dew, and melting snow, as well as the hours of sunshine and wind speed.

Moisture on the surface of the metal resulting from high humidity of the atmosphere and the chemical and physical properties of the corrosion products produces an adsorption layer of water. Phase layers of water are the result of rain, fog, wet or melting snow, or dew formed by condensation on cold metallic surfaces. The total time of wetness ( $T_{tw}$ ) may be divided into the periods when the metal is moistened due to adsorption of water vapor on the surface ( $T_{aw}$ ) and the periods when the surface is covered by a phase layer of water ( $T_{ph}$ ) resulting from rain, fog, dew, or wet or melting snow:

$$T_{tw} = T_{ad} + T_{ph}.$$

It is difficult to distinguish experimentally between the two categories of time of wetness because there is no sharp boundary.

## **Adsorption Layers**

The amount of water adsorbed on a metal surface depends on the relative humidity of the atmosphere and on the chemical and physical properties of the corrosion products. The metal surface may be wetted if hygroscopic salts, deposited or formed by corrosion, absorb water from the atmosphere.

## **Phase Layers**

Phase layers may arise from precipitation of rain, fog, or wet or melting snow, or from dew formed by condensation on cold metallic surfaces.

## **Dew**

Dew formation occurs when the temperature of the metal surface is below the dew point of the atmosphere. This may occur outdoors during the night, when the surface temperature may decrease by radiant heat transfer between the structure and the sky. Another reason for dew formation may be the conditions in the early morning, when the temperature of the air increases faster than the temperature of the metal, especially if the mass, and thus the heat capacity, of the metal is great. Dew may also form when metal products are brought into warm storage after cold transport.

## **Rain**

Rain creates even thicker layers of electrolyte on the surface than dew. The thickness of the water layer retained on the surface has been estimated to be approximately 100 g/m<sup>2</sup>. Precipitation in the form of rain affects corrosion by giving rise to a phase layer of moisture on the material surface and by adding corrosion stimulators in the form of, e.g., HC and SO<sub>2</sub>K<sub>4</sub>. On the otherhand, rain also washes away pollutants deposited on the surface during the preceding dry period. Whereas the first two processes promote corrosion, the third—at least in the case of steel—decreases corrosion. The significance of the two latter processes is dependent on the ratio between the dry and wet deposition of pollutants. In a strongly polluted atmosphere, corrosion on the skyward side of steel plates is substantially lower than on the downward side. In a strongly polluted atmosphere where dry deposition is considerably greater than deposition of sulfur pollutants, the washing effect of rain predominates. In a less-polluted area, the situation is reversed, which indicates that the corrosive action of rain, in this case, is more important. The pH value of precipitation seems to be of significance for metals whose corrosion resistance may be ascribed to a protective layer of basic carbonates or sulfates, as on zinc or copper. If the pH of rainwater falls to values close to 4 or even lower, this may lead to accelerated dissolution of the protective coatings.

## **Fog**

Especially high acidity and high concentrations of sulfates and nitrates can be found in fog droplets in areas of high air pollution. In California, the pH of fog water has been found to be in the range of 2.2–4.0. The processes controlling the fog water chemistry appear to be condensation of water vapor on, and its evaporation from, preexisting aerosol, and scavenging of gas-phase nitric acid.

## **Dust**

On a weight basis in many locations, dust is the primary air contaminant. When in contact with metallic surfaces and combined with moisture, dust can promote corrosion by forming galvanic or differential cells that, because of their hygroscopic nature, form an electrolyte on the surface. Suspended particles of carbon and carbon compounds, metal oxides, sulfuric acid, ammonium sulfate, sodium chloride, and other salts will be found in industrial atmospheres. It is these materials, when combined with moisture, that initiate corrosion. The settled dust may promote corrosion by absorbing sulfur dioxide and water vapor from the air. Hygroscopic salts such as chlorides or sulfates form a corrosive electrolyte on the surface. Carbonaceous particles can start the corrosion process by forming cathodes in microcells with a steel surface. Dust-free air is less likely to cause corrosion.



## **Composition of Surface Electrolyte**

### **Oxygen**

Oxygen is readily absorbed from the air; therefore, at least the outer region of the thin water film on the metal surface may be considered saturated with oxygen.

### **SO<sub>x</sub>**

The main part of anthropogenic SO<sub>x</sub> pollution is caused by combustion of fossil fuels. The pollutants change during their transport in the atmosphere. The sulfur dioxide is oxidized on moist particles or in droplets of water to sulfuric acid.

### **NO<sub>x</sub>**

Emissions of NO<sub>x</sub> originate primarily from different combustion processes, road traffic, and energy production.

### **Chlorides**

Chlorides are deposited mainly in the marine atmosphere as droplets or as crystals formed by the evaporation of spray carried by the wind from the seas.

### **CO<sub>2</sub>**

Carbon dioxide occurs in the atmosphere in a concentration of 0.03–0.05% by volume, varying slightly with the time of day and the season of the year due to its cycle in nature.

## **Concentrations of Different Species**

The concentrations of the various species in the electrolyte on the surface vary greatly with respect to such parameters as deposition rates, corrosion rate, intervals between rain washings, presence of rain shelter, and drying conditions. The pH of the water film is difficult to specify. A moisture film in contact with an atmosphere highly polluted with SO<sub>x</sub> may initially have a pH value as low as 2. Due to acid rain or fog, the moisture film may also have a low pH value. Because of reaction with the metal and the corrosion products, the pH value will usually increase. When a steady state has been reached, the pH is generally on the order of 5–6

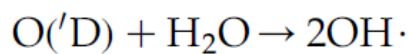
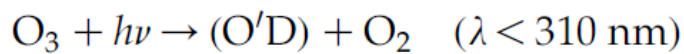
### **Nature of Corrosion Products**

The atmospheric corrosion rate is influenced by many parameters, one of the more important being the formation and protective ability of the corrosion products formed. The composition of the corrosion products depends on the participating dissolved metal ions and the access to anions solved in the aqueous layer. The eventual thickening of the film of corrosion products can be described in a sequence of consecutive steps—dissolution, coordination, reprecipitation. Where the dissolution step is acid-dependent, the coordination is based on the hard and soft acid base (HSAB) principle, and reprecipitation depends on the activities of the species involved.

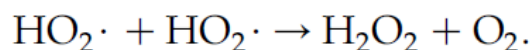
### **Pollutants Present**

One of the most important factors affecting atmospheric corrosion is the presence of specific pollutants. It has been proven that

the following gaseous constituents are of significant importance in contributing to atmospheric corrosion:  $O_2$ ,  $H_2O_2$ ,  $SO_2$ ,  $H_2S$ ,  $COS$ ,  $NO_2$ ,  $HNO_3$ ,  $NH_3$ ,  $HCl$ ,  $Cl_2$ ,  $HCHO$ , and  $HCOOH$ . Typical ranges of these materials as found under outdoor and indoor conditions are given in Table 2.1 and Table 2.2. All of the species are reactive and as such have a certain average lifetime that is limited by the ability to react with atmospheric oxidizers, primarily the hydroxyl radical,  $OH\cdot$ , and  $O_3$ .  $OH\cdot$  is generated by photoinduced dissociation of  $O_3$  (ozone) and the subsequent reaction of the electronically excited, energy-rich oxygen atom  $O(^1D)$  and water vapor:



It is possible for the  $OH$  molecules to oxidize several of the species, such as  $SO_2$ ,  $H_2S$ , and  $NO$ . However, a large portion of the  $OH$  molecules are consumed through reactions with hydrocarbon molecules, producing an end-product of  $HO_2\cdot$  (the hydroperoxyl radical). This radical converts to hydrogen peroxide ( $H_2O_2$ ) and  $O_2$  according to



$H_2O_2$  is highly soluble in aqueous environments and is a powerful oxidizing agent.

## **Mechanisms of Atmospheric Corrosion of Metals**

Atmospheric corrosion takes place by means of an electrochemical process occurring in corrosion cells. A corrosion cell must have the following essential components:

1. A metal anode
2. A metal cathode

**TABLE 2.1**

## Characteristics of Selected Gaseous Air Constituents

Gas	H	M(atm)	Equilibrium Concentration ( $\mu\text{M}$ )		Deposition Velocity (cm/s)		Deposition Rate ( $\text{ng}/\text{cm}^2$ )	
			Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor
O <sub>3</sub>	1.8	(-2)	2.3 (-4)	1.7 (-4)	0.05-1	0.036	5.8 (-3)	6.8 (-4)
H <sub>2</sub> O <sub>2</sub>	2.4	(5)	4.2 (3)	1.2 (3)	—	0.07	—	5.0 (-4)
SO <sub>2</sub>	1.4	—	1.1 (-2)	2.9 (-3)	0.1-1.2	0.05	7.5 (-3)	2.7 (-4)
H <sub>2</sub> S	1.5	(-1)	6.1 (-4)	4.0 (-5)	0.38	0.03	2.2 (-3)	1.1 (-5)
NO <sub>2</sub>	7.0	(-3)	1.9 (-4)	3.8 (-5)	0.2-0.8	0.006	2.0 (-2)	6.2 (-5)
HNO <sub>3</sub>	9.1	(4)	2.9 (2)	2.7 (2)	0.1-30	0.07	1.4 (-2)	5.5 (-4)
NH <sub>3</sub>	1.0	(1)	1.1 (-1)	5.8 (-1)	0.3-2.6	0.05	6.6 (-3)	2.1 (-3)
HCl	2.0	(1)	1.5 (-2)	1.9 (-3)	—	0.04	—	5.8 (-6)
Cl <sub>2</sub>	6.2	(-2)	1.2 (-6)	1.4 (-7)	1.8-2.1	—	1.1 (-4)	—
HCHO	1.4	(4)	1.1 (2)	1.4 (2)	—	0.005	—	6.3 (-5)
HCOOH	3.7	(3)	3.3 (1)	7.4 (1)	—	0.006	—	2.3 (-4)

The equilibrium solution concentration and deposition rate values were based on correlations from Table 2.2, and using geometric mean values for the intervals 1.8 (-2) means  $1.8 \times 10^{-2}$ .

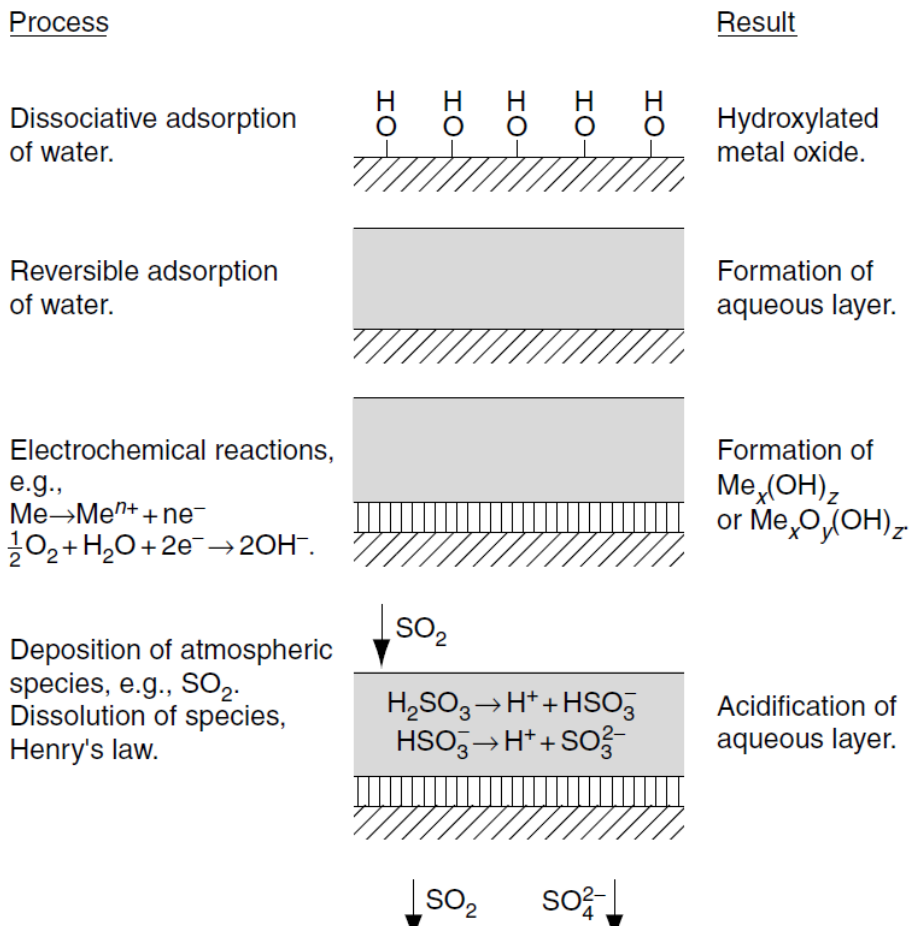
**TABLE 2.2**

Concentration of Selected Gaseous Air Constituents (ppb)

Gas	Outdoor	Indoor
O <sub>3</sub>	4–42	3–30
H <sub>2</sub> O <sub>2</sub>	10–30	5
SO <sub>2</sub>	1–65	0.3–14
H <sub>2</sub> S	0.7–24	0.1–0.7
NO <sub>2</sub>	9–78	1–29
HNO <sub>3</sub>	1–10	3
NH <sub>3</sub>	7–16	13–259
HCl	0.18–3	0.05–0.18
Cl <sub>2</sub>	<0.005–0.08 <sup>a</sup>	0.001–0.005
HCHO	4–15	10
HCOOH	4–20	20

<sup>a</sup> Corresponding to 5 wt% HCl.

**Corrosion Products**



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**TABLE 2.4**

Classification of Hard and Soft Acids and Bases

	Hard	Intermediate	Soft
<i>Acids</i>	$H^+, Na^+, Mn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Ti^{4+}$	$Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}$	$Cu^+, Ag^+$
<i>Bases</i>	$H_2O, OH^-, O^{2-}, SO_4^{2-}, NO_3^-, CU_3^{2-}$	$SO_3^{2-}, NO_2^-$	$R_2S, RSH, RS$

## Specific Atmospheric Corrodents

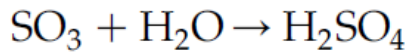
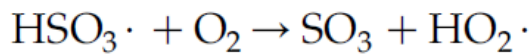
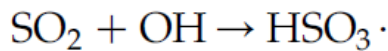
The atmospheric region closest to the earth is known as the troposphere and contains nitrogen, oxygen, and the rare gases Ne, Kr, He, and Xe.

Oxygen, because of its ability to accept electrons and its involvement in chemical transformations of the atmosphere, is particularly important to atmospheric corrosion. Other materials present in the troposphere that play a part in atmospheric corrosion are water and carbon dioxide. Water acts as an electrolyte and carbon dioxide, which has a concentration of approximately 330 ppm and is highly soluble in water, contributes to the acidity of the aqueous layer.

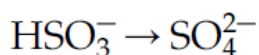
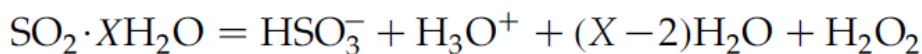
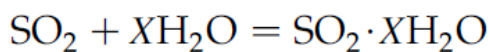
## Sulfur-Containing Compounds

The most important corrosive contaminant found in industrial atmospheres is sulfur dioxide (SO<sub>2</sub>), which results from the combustion of sulfur containing. Depending on the environment, the sulfur dioxide is capable of being oxidized in one or more of the following ways:

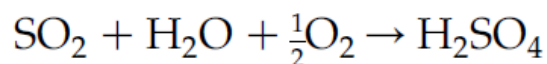
GM



where GM represents another gaseous molecule, such as nitrogen or oxygen, that collides with an HSO<sub>3</sub> molecule and removes some of the excess energy released. In the aqueous phase:



On moist particles or in droplets of water, the SO<sub>2</sub> may be oxidized to sulfuric acid:



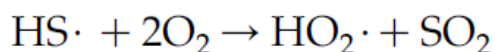
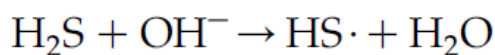
Sulfur dioxide has a lifetime in the atmosphere of 0.5–2 days. This limits the distance that the SO<sub>2</sub> may be transported to a few hundred kilometers. During this period, the sulfuric acid may be partly neutralized, particularly with ammonia that results from the biological decomposition of organic matter. When this occurs, particles containing ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> different forms of acid ammonium sulfate, such as NH<sub>4</sub>HSO<sub>4</sub> and (NH<sub>4</sub>)<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>, are formed. Atmospheric corrosion results from the deposition of these various materials on metal surfaces.



Order-of-magnitude deposition rates for SO<sub>2</sub> in various types of atmospheres are as follows:

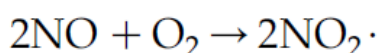
Type of Atmosphere	Deposition Rate (mg SO <sub>2</sub> /m <sup>2</sup> day)
Rural	<10
Urban	10–100
Industrial	Up to 200

Another atmospheric corrosion stimulant is hydrogen sulfide (H<sub>2</sub>S). Hydrogen sulfide can cause the tarnishing of silver and copper by the formation of tarnish films. Hydrogen sulfide can react with OHK to form SO<sub>2</sub> as follows:

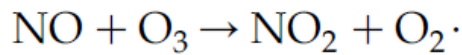


### **Nitrogen-Containing Compounds**

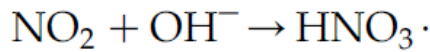
High-temperature combustion processes such as in power plants, vehicles, etc., produce NO and NO<sub>2</sub>. The combustion gas produced has a much higher percentages of NO than NO<sub>2</sub>; however, the NO is rapidly converted to NO<sub>2</sub> according to:



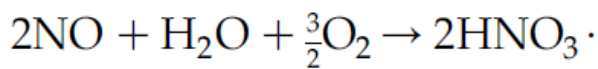
At distances further from the emission source, the NO may also form NO<sub>2</sub> through the influence of ozone (O<sub>3</sub>) as follows:



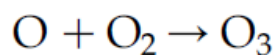
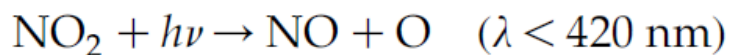
Nitrogen dioxide can be oxidized to nitric acid according to:



In addition, NO may be oxidized to nitric acid according to the total reaction:



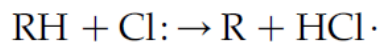
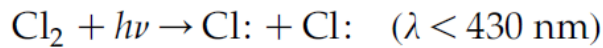
Because this reaction has a very low rate, the concentrations of HNO<sub>3</sub> and nitrates in the immediate area of the emission source are low. Nitrogen dioxide, by absorbing solar light and the subsequent formation of ozone through:



plays an important part in atmospheric chemistry. Ammonia in the aqueous phase establishes equilibrium with NH<sub>4</sub><sup>+</sup>, which results in increased pH. NH<sub>3</sub> affects the atmospheric corrosion chemistry by partly neutralizing acidifying pollutants, forming particulate ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] and acid ammonium sulfates such as NH<sub>4</sub>HSO<sub>4</sub> and (NH<sub>4</sub>)<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>.

### 2.5.3 Chlorine-Containing Compounds

In marine environments, chloride deposition is in the form of droplets or crystals formed by evaporation of spray that has been carried by wind from the sea.  $\text{Cl}_2$  can photodissociate into chlorine radicals that react with organic compounds (RH) to form HCl:



#### Carbon Dioxide ( $\text{CO}_2$ )

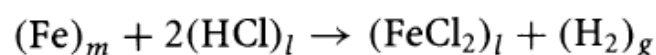
Carbon dioxide occurs naturally in the atmosphere in a concentration of 0.03–0.05% by volume.

#### Oxygen ( $\text{O}_2$ )

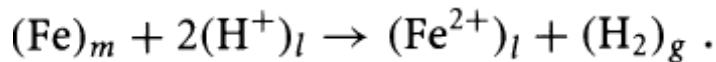
Oxygen is a natural constituent of air and is readily absorbed from the air in to a water film on the metal surface, which is considered to be saturated, thereby promoting any oxidation reactions.

### Corrosion Reactions and Corrosion Products

Considering iron in dilute hydrochloric acid solution as a typical example. The reaction equation is



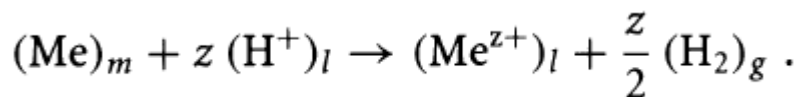
where the subscripts  $m$ ,  $l$ , and  $g$  indicate the phases Hydrogen chloride and ferrous chloride are 'strong' electrolytes, virtually completely dissociated into dissolved ions,  $H^+$ ,  $Cl^-$ , and  $Fe^{2+}$ . Substituting  $(FeCl_2)_l$  by  $(Fe^{2+})_l + 2(Cl^-)_l$  and  $(HCl)_l$  by  $(H^+)_l + (Cl^-)_l$  the terms  $(Cl^-)_l$  cancel, and the reaction equation simplifies to



Instead of hydrochloric acid, sulfuric acid can be considered just as well, and the reaction equation then is

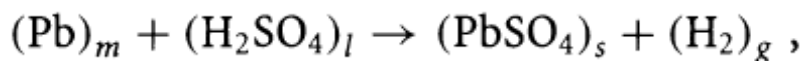


For other acids the result always is the same, and this suggests to write, for acid corrosion of any metal, Me, regardless of the nature of the acid, the reaction equation

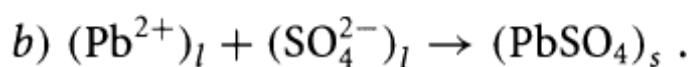
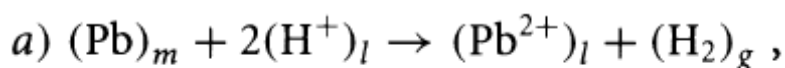


With decreasing acidity and increasing concentration of dissolved metal ions, the electrolytic solution eventually will become saturated with respect to a solid product of the corrosion reaction. A straightforward example is acid corrosion of lead in dilute sulfuric acid, where lead sulfate is scarcely soluble and very soon solid lead

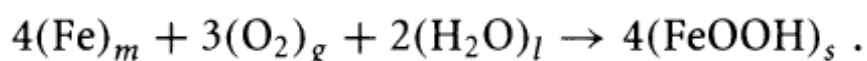
sulfate is deposited forming a protective layer blocking further corrosion



An obviously likely supposition is that this overall reaction proceeds in two consecutive steps:

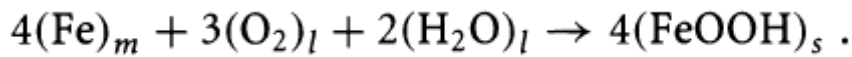


Turning to the second typical group of corrosion reactions, i.e., to *oxygen corrosion*, and particularly to rusting of iron, we recall that the overall reaction is the oxydation of iron by atmospheric oxygen, via oxygen dissolved in an aqueous solution, as for instance in an aqueous film on the surface of the metal, to what summarily is described as Fe-III-oxyhydroxide:

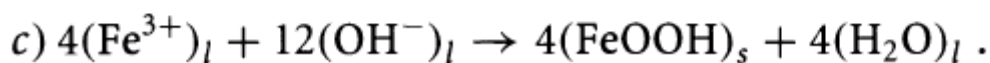
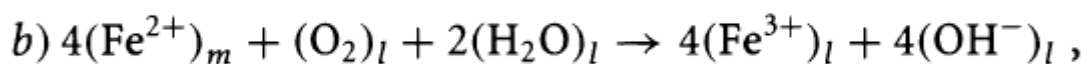
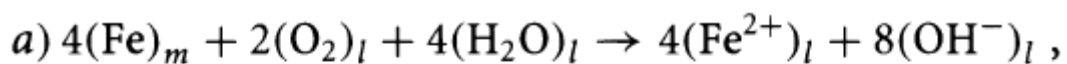


In the present context the real, normally much more complicated composition of rust is not yet the important point. Instead, we note a number of consecutive steps, into which the overall reaction very probably separates: First, the aqueous phase must absorb oxygen from the atmosphere, and in the solution the dissolved oxygen must arrive at the metal surface by either diffusion or convection. It is important to recognize that these physical, i.e. non-chemical

processes in fact are discernible steps in the overall chemical reaction. The next stage is a *phase boundary reaction*, or *interfacial reaction*, summarily written as



one may expect that the primary reaction product is dissolved FeH , followed by the oxidation to Fe<sup>3+</sup>, followed by the deposition of rust. This should cause a sequence of steps approximately as follows:

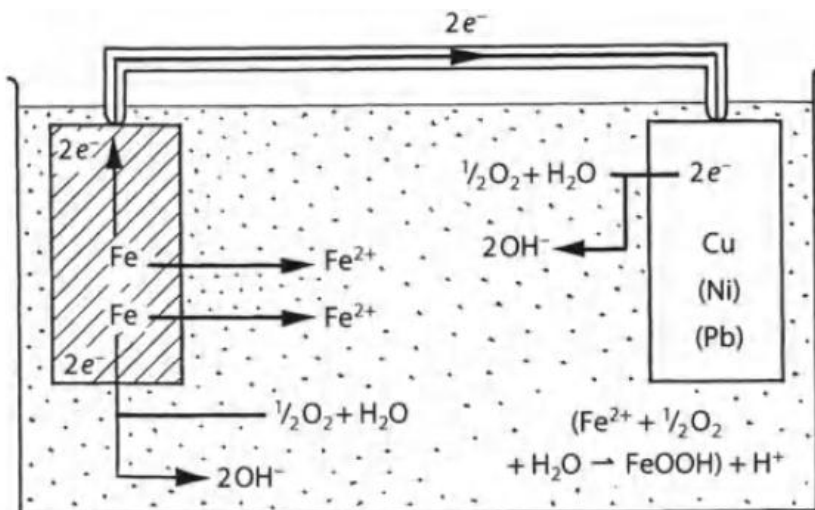


In reality, the deposition of solid rust is even more complicated, with such sub-steps as the formation of hydroxide via intermediate stepwise hydrolysis, followed by formation of polybases first dissolved, then colloidal, then solid, followed by partial dehydration of the hydroxide. Also, while the orthorhombic goethite,  $\alpha$ -FeOOH, usually is a main constituent of rust, there also are varying amounts of orthorhombic lepidokrookite,  $\gamma$ -FeOOH, rhomboedric hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and tetragonal maghemite,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, In rust, iron predominantly is trivalent, but from thermodynamics a lower valence state is expected at the rust/iron interface, that is, cubic magnetite, Fe<sub>3</sub>O<sub>4</sub>, Also, a

considerable part of the rust normally is amorphous; also, depending on environmental pollution, rust may contain iron sulfates, chlorides, and other contaminants. A rather curious intermediate constituent is 'green rust', which is mixed iron-II,III-hydroxide containing either chloride or sulfate.

## The Electrolytic Mechanism of Corrosion

Corrosion proceeds by the superposition of kinetically independent electrode half-reactions: anodic metal dissolution and cathodic reduction of an oxidizing species, such as hydrogen ions, or oxygen molecules, or others.



**Fig. 4.2.** Reaction scheme of a short-circuited galvanic iron/copper(nickel,lead) cell in a neutral aerated salt solution

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