JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY, ANANTAPUR
COLLEGE OF ENGINEERING, (Autonomous)
ANANTHAPURAMU - 515 002 (A.P.) INDIA

ACADEMIC RECORD BOOK

Academic Year : 2020-21

Class and Semester : IV B.Tech – II semester

Course : Corrosion Engineering

Branch : Chemical Engineering

Name and Designation of Staff Member handling the course } Dr. B. Dilip Kumar
Assistant Professor
Dept of Chemical Engg
JNTUA CE, Anantapur

Signature of Concerned staff Member :

JNTUA College of Engineering (Autonomous), Ananthapuramu

IV Year B.Tech. Chem. Engg. II-Sem

L	T	P	C
3	0	0	3

ELECTIVE-IV
CORROSION ENGINEERING (17A80803c)

Course Outcomes:

At the end of the course, the student will be able to:

CO1	Understand the electrochemical and metallurgical behavior of corroding systems
CO2	Apply the electrochemical and metallurgical aspects of combating eight forms of corrosion
CO3	Select or choose the testing procedures for corroding systems
CO4	Evaluate the polarization behavior of corroding systems
CO5	Design of suitable materials, methods to combat corrosion
CO6	Predict the function of corrosion inhibitors

Course Articulation Matrix

Course Outcomes	PO1	PO2	PO3	PO4	PO5	PO6	PO7	PO8	PO9	PO10	PO11	PO12
CO1	3	-	-	-	-	-	3	-	3	-	-	3
CO2	3	-	-	-	-	2	3	-	3	-	-	3
CO3	3	3	-	-	-	3	2	-	3	-	-	3
CO4	3	3	-	-	-	2	1	-	3	-	-	3
CO5	3	-	3	-	-	3	3	-	3	-	-	3
CO6	3	-	-	-	-	2	2	-	3	-	-	3

OBJECTIVES:

The course will enable the students to:

1. Be introduced to the principles of electrochemistry as well as the essential elements of electrochemical corrosion.
2. Lay a foundation for understanding the forms of corrosion, the mechanisms of corrosion, electrochemical methods.
3. Develop the thermodynamic and kinetic aspects of electrochemistry, including potential-pH (Pourbaix) diagrams, mixed potential theory, and the theory and application of polarization.
4. Design methods for combating corrosion, the principles and methods leading to mitigation of corrosion problems that might occur in engineering practice.

JNTUA College of Engineering (Autonomous), Anantapuramu

IV Year B.Tech. Chem. Engg. II-Sem

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CO1	3	-	-	-	-	-	3	-	3	-	-	3
CO2	3	-	-	-	-	2	3	-	3	-	-	3
CO3	3	3	-	-	-	3	2	-	3	-	-	3
CO4	3	3	-	-	-	2	1	-	3	-	-	3
CO5	3	-	3	-	-	3	3	-	3	-	-	3
CO6	3	-	-	-	-	2	2	-	3	-	-	3

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1. Be introduced to the principles of electrochemistry as well as the essential elements of electrochemical corrosion.
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4. Design methods for combating corrosion, the principles and methods leading to mitigation of corrosion problems that might occur in engineering practice.

UNIT- I:

Introduction

Definitions of Corrosion - Overall classification of types of corrosion-Basic electrochemistry – Galvanic and electrolytic cells – Potential measurements - EMF and Galvanic series – Galvanic corrosion and bimetallic contacts – Eh – pH diagrams, Cost of Corrosion, Metallurgical properties influencing corrosion.

UNIT-II:

Forms of Corrosion

Uniform attack, galvanic, crevice, pitting, Inter granular, selective leaching, erosion and stress corrosion – Mechanisms, testing procedures and their protection.

UNIT- III:

Electrode kinetics and polarization phenomena

Electrode – solution interface – Electrode kinetics and polarization phenomena – Exchange current density – Polarization techniques to measure corrosion rates – Mixed potential theory – Activation and diffusion controlled mixed electrodes.

UNIT IV:

Methods of corrosion prevention and control

Design, coatings and inhibition – Cathodic protection – Stray current corrosion – Passivity phenomena and development of corrosion resistant alloys – Anodic control.

UNIT-V:

Industry Approach

Selection for a given Chemical Engineering Service Environment- Materials for Chemical Engineering Industry to resist the given chemical Environment.-Ferritic, Austenitic steels and stainless steels- Copper and its alloys-Brasses, bronzes, Nickel and its alloys- Monel alloys-materials for a petroleum refinery industry.

TEXT BOOKS:

1. M. G. Fontana, Corrosion Engineering (Third Edition) McGraw-Hill Book Company.
2. Denny A Jones, Principles and Prevention of Corrosion (second edition), Prentice-Hall, N. J. (1996).

REFERENCE:

1. H. H. Uhlig and R. W. Revie, Corrosion and Corrosion Control, Wiley (NY) (1985).

JNTUA COLLEGE OF ENGINEERING (AUTONOMOUS) ANANTHAPURAMU
DEPARTMENT OF CHEMICAL ENGINEERING
IV B.TECH- II SEMESTER (AY: 2020-21) R17
CLASS TIME TABLE

Day	1st Hour (8AM-9AM)	2nd Hour (9AM-10AM)	3rd Hour (10 AM-11AM)	4th Hour (11AM-12PM)	5th Hour (12 PM- 1 PM)	1PM - 2 PM	6th Hour (2-3 PM)	7th Hour (3-4 PM)	8th Hour
MON	PRP	FE	CE	*Project Work*	*Project Work*	L	Internship		
TUE	BCE	PRP	CE	FE	MOOC- II	U	Internship		
WED	FE	BCE	CE	PRP	MOOC- II	N	Internship		
THU	FE	CE	BCE	PRP	MOOC- II	C	Internship		
FRI	BCE	CE	*Project Work*	PRP	*Project Work*	H	Internship		
SAT	FE	PRP	*Project Work*	BCE	*Project Work*		Internship		

Acronym	Subject	Subject Code	Staff Name	Contact
BCE	Elective II : Bio-Chemical	17A80801	Mr. M. Murali Naik	7702840728
FE	Elective III: Fluidization	17A80802	Mr. K. Peddintaiah	9000487374
CE	Elective IV: Corrosion	17A80803	Dr. B. Dilip Kumar	9247192692
PRP	Elective V: Petroleum Refining & Petrochemicals	17A80804	Mr. V. Ramanjaneyulu	9052960454
Project Work	Project Work	17A80806	All the faculty	...
MOOC- II	MOOC- II	17A89906	...	...

Head of the department

Vice- principal

Principal

B.Tech. IV Year II Semester AY: 2020 - 2021

Lesson Plan for "Corrosion Engineering"

Faculty Name: Dr. B. Dilip Kumar, Asst. Prof,

Department of Chemical Engineering

S. No	Topics to be covered	No. of Periods	Cumulative No. of Periods
1	**UNIT-I : Introduction** Definitions of Corrosion	1	1
2	Overall classification of types of corrosion	1	2
3	Basic electrochemistry	1	3
4	Basic electrochemistry, Galvanic and electrolytic cells	1	4
5	Potential measurements - EMF and Galvanic series	1	5
6	Galvanic corrosion and bimetallic contacts – Eh – pH diagrams	1	6
7	Cost of Corrosion,		7
8	Metallurgical properties influencing corrosion	1	8
9	**UNIT- II: Forms of Corrosion** Uniform attack, galvanic	1	9
10	Crevice, Pitting , Inter granular , Selective leaching	1	10
11	Erosion and stress corrosion – Mechanisms	1	11
12	Testing procedures , Protection	1	12
13	**UNIT-III : Electrode kinetics and polarization phenomena** : Electrode – solution interface	1	13
14	Electrode kinetics , Polarization phenomena	1	14
15	Exchange current density, Polarization techniques to measure corrosion rates	1	15
16	Polarization techniques to measure corrosion rates	1	16
17	Mixed potential theory, Activation and diffusion controlled mixed electrodes	1	17
18	**UNIT- IV: Methods of corrosion prevention and control :** Design, coatings and inhibition	1	18
19	Design, coatings and inhibition, Cathodic protection	1	19
20	Stray current corrosion, Stray current corrosion , Passivity phenomena	1	20
21	development of corrosion resistant alloys, Anodic control	1	21
22	**UNIT-V: Industry Approach** Selection for a given Chemical Engineering Service Environment	1	22
23	Materials for Chemical Engineering Industry to resist the given chemical Environment	1	23
24	Materials for Chemical Engineering Industry to resist the given chemical Environment	1	24
25	Ferritic, Austenitic steels and stainless steels, , Monel alloys	1	25
26	Copper and its alloys-Brasses, bronzes,	1	26
27	Nickel and its alloys	1	27
28	Materials for a petroleum refinery industry.	1	28

CE   2017 admitted

14-07-2021

Academic Year: 2021-22   **Date of Examination: ~~13-04-2022~~**

Name of the teacher:

Admission Number ☐☐☐☐☐☐☐☐☐☐

JNTUA COLLEGE OF ENGINEERING (AUTONOMOUS), ANANTHAPURAMU
DEPARTMENT OF CHEMICAL ENGINEERING
B.Tech IV Year II Semester First Internal Examinations(Objective Type)
Corrosion Engineering (Elective Course)

Max. Marks: 20   **Duration: 20 min**

Answer all questions.

Each question carries one mark.

Course Outcomes:

CO-1: Understand the electrochemical behaviour of corroding systems

CO-2: Classify various corrosion forms and the mechanisms involved.

CO-3: Apply the electrochemical aspects of combating eight forms of corrosion

CO-4: Design of suitable materials& methods to combat corrosion

CO-5: Evaluate the polarization behaviour of corroding systems

1.	The units of Faradays Constant F are**(CO-1)** a) mole/Coulomb b) Coulomb/mole c) Joule/mole d) mole/joule. Volt	[ ]
2	_______is unstable in oxygenated solutions and is oxidized to ____**(CO-1)** a) Ferrous hydroxide, Ferric hydroxide b)Ferric hydroxide, Ferrous hydroxide c) Ferrous hydroxide, Iron Oxide d) Iron Oxide, Ferrous hydroxide	[ ]
3.	Corrosion of mild steel is high in _____environmental conditions**(CO-2)** a) dry b) Marinec) Humid with other oxidizing d) None of the above	[ ]
4	Which of the following metal can be used for cathodic protection:**(CO-2)** a) Al b) Cd c) Cu d) Pt	[ ]
5	As compare to iron, aluminum has**(CO-2)** a) higher tendency to oxidize b) less tendency to oxidize c) equal tendency to oxidize d) None of above	[ ]
6	The stainless steels owe their resistance to the presence of**(CO-4)** a) C b) S c) Mn d) Cr	[ ]
7	Standard hydrogen electrode (SHE) is assigned a zero potential ____temperatures. **(CO-3)** a) 0C b) 0K c) 25C d) at all	[ ]
8	Poubiax diagrams are generated for equilibrium conditions at _____temperature**(CO-3)** a) 0K b) 25C c)0C d) None of the above	[ ]
9	In most instances Concentration polarization during metal dissolution is usually_______and____; it is only important during_____. **(CO-5)**	[ ]

Academic Year: 2021-22 **Date of Examination: 13-04-2022**

Name of the teacher:

Admission Number ☐☐☐☐☐☐☐☐☐☐

	a) high, can be neglected, oxidation reactions b) small, can be neglected, reduction reactions c) high, cannot be neglected, reduction reactions d) small, cannot be neglected, oxidation reactions	
10	Tarnishing of silver is due to the formation of______**(CO-4)** a) Silver Sulphide b) Silver Sulphate c) Silver Carbonate d) Silver Nitrate	[ ]
11	_____help to undergo vigorous corrosion for Titanium**(CO-4)** a) dry chlorine b) moist chlorine c) H_2SO_4 d) HNO_3	[ ]
12	In mpy expression, the area of specimen is in____units**(CO-3)** a) Sq. inch b) Sq. m c) Sq. cm d) Sq. mm	[ ]
13	Oxygen reduction reaction in acid solutions yield**(CO-4)** a) Water molecule b) OH- radical c) Hydrogen d) None of the above	[ ]
14	The corrosion of Zinc in aerated HCl involves_____no of cathodic reactions **(CO-2)** a) One b) Two c) Three d) Zero	[ ]
15	When small anodic metals touch a large cathode, corrosion ______ **(CO-4)** a) occurs at much higher rateb) occurs at lower rate c) is zerod) None of the above	[ ]
16	In standard emf series, ________is the strongest oxidizing agentwhile______is the weakest reducing agent. **(CO-3)** a) lithium metal, lithium ion b) lithium ion, lithium metal c) fluoride ion , fluorine gas d) fluorine gas, fluoride ion	[ ]
17	In standard emf series, ________ is the weakest oxidizing agent while ______is the most powerful reducing agent**(CO-4)** a) lithium metal, lithium ion b) lithium ion, lithium metal c) fluoride ion, fluorine gas d) fluorine gas, fluoride ion	[ ]
18	When reactants and products are equally favored, the Gibbs Free energy ΔG^0, K and E^0 are __________respectively**(CO-3)** a) 0, >1, -ve b) +ve, <1, -ve c) 0, 1, 0 d) 0, >1, +ve	[ ]
19	According to standard emf series, the most stable states (as per thermodynamics) of Lithium and Fluorine elements are____**(CO-3)** a) Li^+, F^- b) Li, F_2 c) Li^+, F_2 d) Li, F^-	[ ]
20	Down the series in standard emf series, the species are __________active in nature and hence act as ______**(CO-3)** a) decreasingly, anodic b) decreasingly, cathodic c) increasingly, anodic d) increasingly, cathodic	[ ]

Key

Academic Year: 2020-21 Date of Examination: 14-07-2021

Name of the teacher:

Admission Number

JNTUA COLLEGE OF ENGINEERING (AUTONOMOUS), ANANTHAPURAMU
DEPARTMENT OF CHEMICAL ENGINEERING
BTechIV Year II Semester First Internal Examinations(Descriptive Type)
Corrosion Engineering (Elective Course)

Max.Marks: 30 Duration: 90 min

Answer any Three Questions Choosing one from each Unit
All questions carry equal marks.

Unit - I

2 1.a) Is it possible to carry out aqueous reactions with Fluorine? If not, explain the reasoning in perspective of electrochemistry?

3 b) When carbon di-oxide is bubbled into water, less than 1% is converted to carbonic acid when the reaction reached equilibrium. However, in carbonated beverages there is high percentage of carbon di-oxide in water exist. How is this possible? Explain the concept thermodynamically.

5 c) Write mechanism of Fe Corrosion with chemical reactions (CO-1)

(or)

3 2.a) What do you mean by passivity? Explain the concept of metal oxide formation in inhibiting the further corrosion in case of metals

3 b) Explain why few materials undergo active, passive and trans-passive modes with a neat graph and examples

4 c) In case of Iron metal, when Iron oxide formation occurs which diffusion among the following is faster? Give explanation

(i) Fe^{+2} ions crossing MO/oxide scale barrier to the gas phase

(ii) O^{2-} ions crossing MO/oxide scale barrier to metal surface (CO-2)

Unit-I/Unit-II

4 3.a) Why corrosion of iron is a spontaneous reaction? Explain the concept thermodynamically

3 b) Explain with a neat graph, the effect of oxidizer on corrosion rate with few realistic material examples showing different tendencies

3 c) Why sodium chloride (salt) will increase the corrosion rate of Fe? Explain with logical reasoning/reactions if any (CO-2)

(or)

3 4. a) Explain concept of Galvanic corrosion or coupling? How Fe will be protected via cathodic protection technique

3 b)Fish can have difficulty breathing at elevated temperatures. What is the most likely explanation for this problem?

4 c) What is the surface area effect in corrosion? Explain which material will be corroded for the following combinations

i) Aluminum bolt (larger area) connected to copper nut (smaller area)

ii) Steel bolt (larger area) connected to copper nut (smaller area) (CO-2)

Academic Year: 2020-21 **Date of Examination: 14-07-2021**

Name of the teacher:

Admission Number ☐☐☐☐☐☐☐☐☐☐

Unit-I/Unit-II

4 5.a) What is polarization? Distinguish concentration and activation polarizations briefly

3 b) Explain the mechanism of Corrosion of Zinc in aerated HCl with all electrochemical reactions

~~5~~ 3 c) Write the entropy change in the following cases

(i) $Cl_{2(g)} \rightarrow Cl_{2(l)}$

(ii) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

(iii) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

(iv) $AgNO_3(aq) + NaCl(aq) \rightarrow 2NaNO_{3(aq)} + AgCl_{(s)}$.

(v) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

(CO-1)

(or)

3 6.a) What are the values of Gibbs Free energy ΔG^0, equilibrium constant K and standard electrode potential E^0 for the following reactions

i) $Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$

ii) $NaNO_{3(s)} \rightarrow Na+_{(aq)} + NO_3^-{}_{(aq)}$

3 b) Is photosynthesis reaction is spontaneous? Explain

4 c) Write ATP to ADP electrochemical reaction inside human body along with Gibbs free energy changevalue

(CO-1)

Academic Year: 2020-21 **Date of Examination:24-07-2021**

Name of the teacher:

Admission Number ☐☐☐☐☐☐☐☐☐☐

JNTUA COLLEGE OF ENGINEERING (AUTONOMOUS), ANANTHAPURAMU
DEPARTMENT OF CHEMICAL ENGINEERING
B.TechIV Year II Semester Second Internal Examinations(Objective Type)
Corrosion Engineering (Elective Course)

Max. Marks: 20 **Duration: 20 min**

Answer all questions.Each question carries one mark.

1.	________is the percentage purity of a metal, _____is the rate of corrosion. (CO1) a) Faster, lesser b) moderate, lesser c) Lesser, faster d) lesser, moderate	[ ]
2	The________the grain size of the metal or alloy, the ________will be its corrosion (CO1) a) smaller, moderate b) greater, moderate c) greater, smaller d) smaller, greater	[ ]
3.	When the metal is higher up in the galvanic series, ______is its tendency to become ______and hence greater is the rate of corrosion (CO2) a) smaller, cathodic b) greater, anodic c) smaller, anodic d) greater, cathodic	[ ]
4	With _______of temperature of environment, the reaction as well as diffusion rate________, thereby corrosion rate is generally enhanced. (CO2) a) increase, decrease b) increase, increase c) decrease, decrease d) decrease, increase	[ ]
5	In the electrochemical corrosion, if the corrosion product is _______in corroding medium, then corrosion proceeds at a _____rate (CO1) a)soluble, moderate b) soluble, slower c) soluble, faster d) insoluble, faster	[ ]
6	When cathodic area is smaller, the demand for electrons will be _____and this result in the _______rate of dissolution of metal at anodic regions. (CO4 a) constant, decreased b) constant, increased c) less, decreased d) more, decreased	[ ]
7	The ______is humidity, the _____is the rate and extent of corrosion (CO2) a) greater, greater b) greater, lesser c) greater, constant d) lesser, constant	[ ]
8	In Tin can (food) containers, steel is coated with Sn, wherein, ____is sacrificed to protect ______ (CO4) a) Steel, Sn b) Sn, Steel c) Steel, food d) Sn, food	[ ]
9	_________converts to silver, under boiled water in presence of baked soda during	[ ]

Academic Year: 2020-21 Date of Examination:24-07-2021

Name of the teacher:

Admission Number

	cleaning of silver ornaments a) Silver sulphate b) Silver sulphide c) Silver chloride d) Silver oxide	(CO4)	
10	High carbon steel is called _____ a) Mild steelb) Stainless steel c) chromium steeld) tool steel	(CO4)	[
11	Which of the following is absent in SS (stainless steel) 400 series a) Manganese b) Iron c) Chromium d) Nickel	(CO4)	[
12	Stainless Steel is badly attacked in hours by _____Acid a) Perchloric b) Polythionic c) Sulfuric d) Hydrochloric	(CO4)	[
13	Under which corrosion category, the "underfilm corrosion" falls a) Stress b) Crevice c) Pitting d) Erosion	(CO3)	[
14	Metals loose strength when Hydrogen is absorbed through surface, especially along __________in hydrogen embrittlement a) planes b) dislocations c) grain boundaries d) grain boundaries and dislocations	(CO4)	[
15	Brass is an alloy of _____% Cu and _____% Zn approximately a) 40, 60 b) 30, 70 c) 70, 30 d) 60, 40	(CO4)	[
16	For extremely powerful oxidizing conditions, ______ & its alloy are commonly used to combate corrosion a) Zn b) Cr c) Ti d) Ni	(CO4)	[ ]
17	Which of the following is an Oxygen Scavenger a) Sodium Sulphate b) Sodium Phosphate c) Sodium Sulphite d) Sodium Chloride	(CO4)	[ ]
18	The compounds containing ______groups act as adsorption inhibitors. a) -CN b) $-NH_2$ c) -OH d) $-CH_2$	(CO5)	[ ]
19	Tafel equation is the relationship between _____and ______for activation polarization a) Overvoltage, concentration b) Concentration, current density c) overvoltage, temperature d) reaction rate, overvoltage	(CO5)	[ ]
20	The limiting diffusion current density (i_L) is a function of_____ a) Diffusion coefficient b) Film Thickness c) Bulk concentration d) All the above	(CO5)	[ ]

Academic Year: 2020-21 Date of Examination:24-07-2021

Name of the teacher:

Admission Number

JNTUA COLLEGE OF ENGINEERING (AUTONOMOUS), ANANTHAPURAMU
DEPARTMENT OF CHEMICAL ENGINEERING
B.TechIV Year II Semester Second Internal Examinations(Descriptive Type)
Corrosion Engineering (Elective Course)

Max.Marks: 30 Duration: 90 min

Answer any Three Questions Choosing one from each Unit
All questions carry equal marks.

Unit – III

1. a) Define Exchange Current density? Write equation for Over-voltage in both cases and for combined polarization? Explain the significance CO-2
b) Why Zinc corrodes slower than Fe in galvanic coupling (Galvanizing)? Explain the importance of exchange current density in supporting above argument CO-2

(or)

2. a) What is polarization? Discuss Activation and Concentration polarization concepts with a neat sketch CO-2
b) What is Mixed potential theory? Draw the Evans diagram for Fe, Zn separately CO-2

Unit – IV

3. a) What is Cathodic protection? Explain the concept with a neat diagram CO-3
b) Which materials are preferred in Anodic protection of corrosion prevention? Explain CO-3

(or)

4. a) Discuss briefly material selection, design and metallic coatings in combating corrosion CO-4
b) Write the eight important engineering design rules for prevention of corrosion CO-4

Unit –V

5. a) Write brief note on “Materials for Chemical Engineering Industry to resist the given chemical Environment” CO-4
b) What are Monel alloys? Explain briefly with examples CO-4

(or)

6. a) Write the classification of steel and cast iron. Discuss briefly about mild steel CO-4
b) Explain briefly Brass, Bronze and Other Nickel Alloys CO-4

Name of the Faculty: Dr. B. Dilip Kumar

Adm. No.										

JNTUA COLLEGE OF ENGINEERING (AUTONOMOUS), ANANTHAPURAMU
DEPARTMENT OF CHEMICAL ENGINEERING
B.Tech IV Year II Semester (R17)
<Sub: Corrosion Engineering>

Submit before:

Batch: 2017-21

ASSIGNMENT- I

Answer ALL Questions. All Questions carry equal marks.

Course outcomes:

CO1	Able to understand the electrochemical and metallurgical behaviour of corroding systems
CO2	Able to apply the electrochemical and metallurgical aspects of combating eight forms of corrosion
CO3	Able to select or choose the testing procedures for corroding systems
CO4	Able to evaluate the polarization behaviour of corroding systems
CO5	Able to design of suitable materials, methods to combat corrosion

S. No.	Question	Marks	Course Outcome
1	(a) What is Corrosion? Write salient characteristics of Corrosion of Fe (b) What are the differences between EMF and Galvanic series?	5	CO1
2	(a) What is Galvanic Corrosion? Explain briefly about galvanic corrosion? (b) What is crevice corrosion? Discuss about mechanism of crevice corrosion and write the preventions of it.	5	CO2
3	(a)Why are there always a minimum of two electrochemical reactions to explain even the simplest corrosion reaction? (b) Write briefly on i) Tafel Slope ii) Mixed potential theory	5	CO3

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Corrosion Engineering

7/10

ASSIGNMENT-I

1) (a) What is corrosion? Write salient characteristics of corrosion of Fe

* corrosion is the deterioration of materials by chemical interaction with their environment.

* The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals The most widely used metal is iron (usually as steel) and the following discussion is mainly related to its corrosion

characteric of corrosion of Fe:

The rusting of iron is characterized by the formation of a layer of a red, flasky substance that easily crumbles into a powder. This phenomenon is a great example of the corrosion of metals, where the surfaces of metals are degraded into more chemically stable oxides

(b) What are the differences between EMF and Galvanic series?

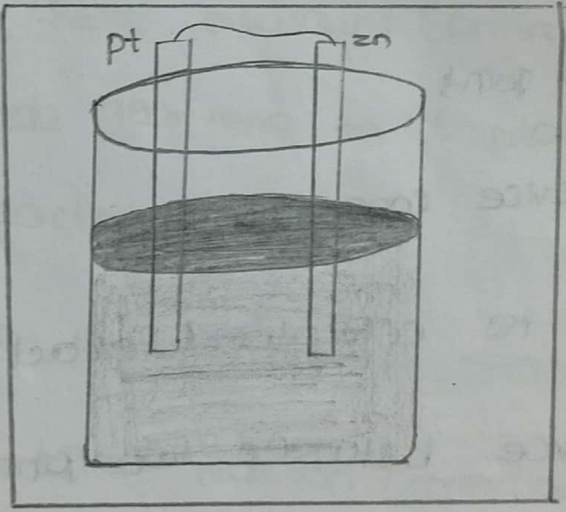
Differences between EMF and Galvanic series:

EMF series	Galvanic series
* EMF Series lists only metals Alloys not included * Electrode potentials listed calculated from thermodynamic principles * Equilibrium potentials with concentrations at unit activity. * predicts only tendency to corrode (Role of passive films and oxidation kinetic not predicted) * Effect of environment not predicted (Eg: Sn-Fe couple as in Tin cans)	* Instead of standard electrode potentials, actually measured rest potentials of metal and alloys in a given environment arranged with respect to nobility and activity * practically measured potentials vs reference electrode. * Effect of coupling of metals and alloys on corrosion rate can be predicted certain anomalies Eg: stainless steels (active and passive

What is Galvanic corrosion? Explain briefly about galvanic corrosion?

Galvanic corrosion:

Galvanic Corrosion can be defined simply as being the effect resulting from contact between two different metals or alloys in a Conducting corrosive environment. Another term employed is galvanic coupling.



When a metal is immersed in any electrolytic Solution it is possible to measure its dissolution potential with the aid of a reference electrode and a hgh input impedence millivoltmeter.
For each Solution, it is possible to establish a "galvanic series", that is, a ranking of different metals and alloys as a function of the measured potential

(b) What is crevice corrosion? Discuss about mech of crevice corrosion and write the preventions of it.

Crevice corrosion:

It is a corrosion is the corrosion produced at the region of contact of metals with metals or metals or metals with non-metals. It may occur at washers, under applied protective films, and at pockets formed by threaded joints

Mechanism of crevice corrosion:

Crevice corrosion is a localized attack on a metal adjacent to a crevice between two joining surfaces. It is considered good design practice to avoid, if possible, all shapes and joints that from crevices into which oxygen does not have ready access. various factors influence crevice corrosion are:

- Metal alloy composition, metallographic structure
- Environmental conditions such as PH, oxygen concentration, chloride concentrations and temperature.

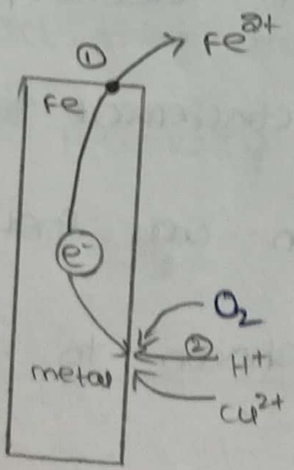
- Geometrical featores of crevices, surface roughness

prevention from crevice corrosion:

- use non-absorbable solid gaskets such as teflon
- Avoid sharp corner while designing.
- clean throughly to remove stagnant
- use butt joint instead of lap-joints

3) (a) Why are there always a minimum of two electrochemical reactions to explain even the simplest corrosion reaction?

Even the simplest corrosion reaction consists of one oxidation reaction (corrosion) and one cathodic reaction that conscomes the electrons produced by oxidation process



2(v)

① $Fe \rightarrow Fe^{2+} + 2e^-$

Fe atom at metal surface dissolves into moisture film, leaving negative charge in metal

② corrosion continues as a depolarizer removes electrons from metal.

Common depolarizers are:

oxygen:

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

acid: $2H^+ + 2e^- \rightarrow H_2$

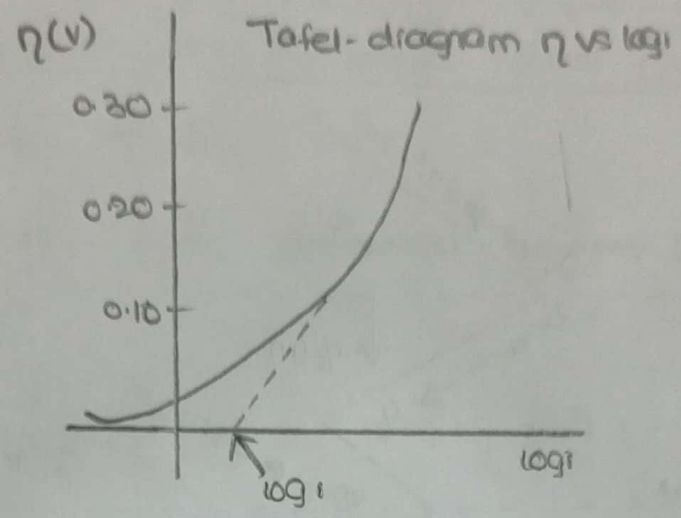
cation of more-noble metal:

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

(b) write briefly on

i) Tafel slope:

The Tafel equation in electrochemical kinetics relating the rate of an electrochemical reaction to the overpotential. The Tafel equation ... was first deduced experimentally and was later shown to have a theoretical justification.

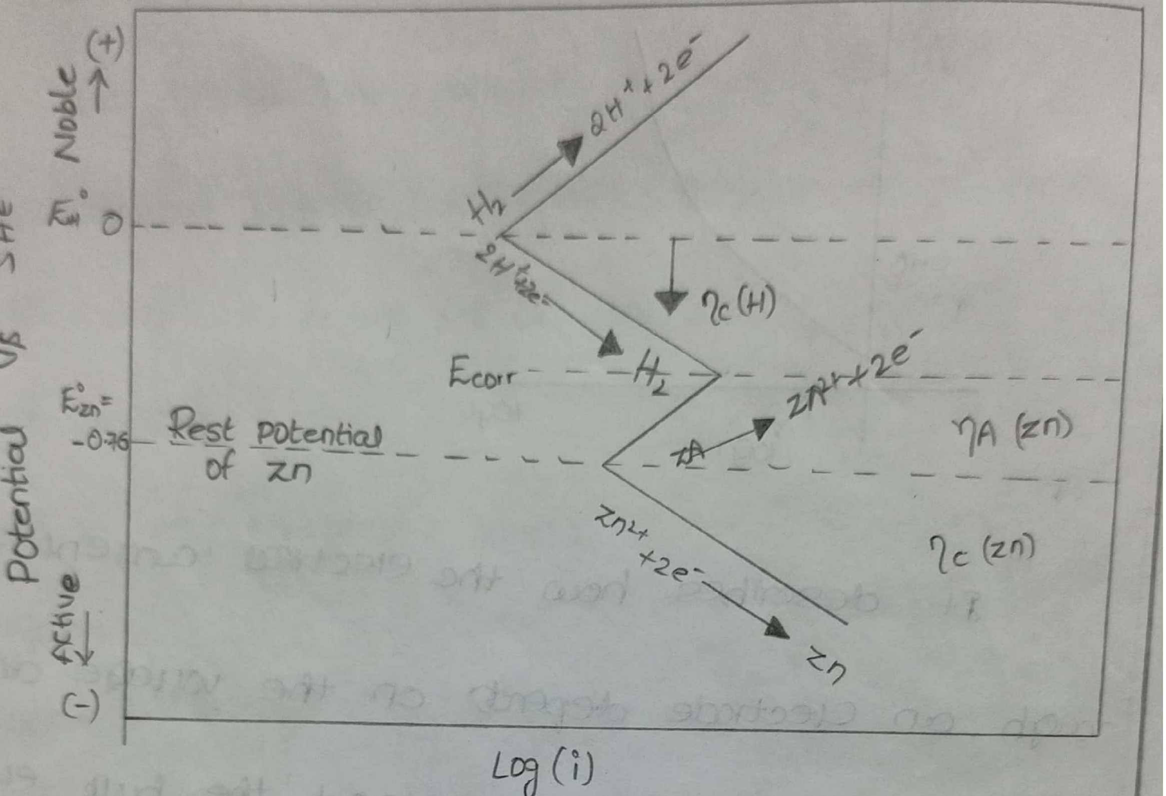


It describes how the electrical current through an electrode depends on the voltage difference between the electrode and the bulk electrolyte for a simple, unimolecular redox reaction

$$Ox + ne^- \rightleftharpoons Red$$

(ii) Mixed potential theory:

when two different metals are in physical contact, they are also in electrical in electrical contact. According to what is known as mixed potential theory.


Potential vs SHE
E° Noble → (+)
Active ← (−)
0
E°_{Zn} = −0.76
Rest potential of Zn
Ecorr
$2H^+ + 2e^-$
H_2
$2H^+ + 2e^-$
H_2
$\eta_c(H)$
$Zn^{2+} + 2e^-$
Zn
$\eta_A(Zn)$
$Zn^{2+} + 2e^-$
Zn
$\eta_c(Zn)$
Log (i)

Name of the Faculty: Dr. B. Dilip Kumar

Adm. No.

JNTUA COLLEGE OF ENGINEERING (AUTONOMOUS), ANANTHAPURAMU
DEPARTMENT OF CHEMICAL ENGINEERING
B.Tech IV Year II Semester (R17)
<Sub: Corrosion Engineering>

Batch: 2017-21

Submit before:

ASSIGNMENT- II

Answer ALL Questions. All Questions carry equal marks.

Course outcomes:

CO1	Able to understand the electrochemical and metallurgical behaviour of corroding systems
CO2	Able to apply the electrochemical and metallurgical aspects of combating eight forms of corrosion
CO3	Able to select or choose the testing procedures for corroding systems
CO4	Able to evaluate the polarization behaviour of corroding systems
CO5	Able to design of suitable materials, methods to combat corrosion

S. No.	Question	Marks	Course Outcome
1	(a) What is Poliarization? Explain the types of Polarization. (b)Detail about polarization techniques to measure corrosion rates?	5	CO4
2	Write the examples for demonstrating the area effect in selection and design of materials?	5	CO5

****

Corrosion Engineering

ASSIGNMENT-I

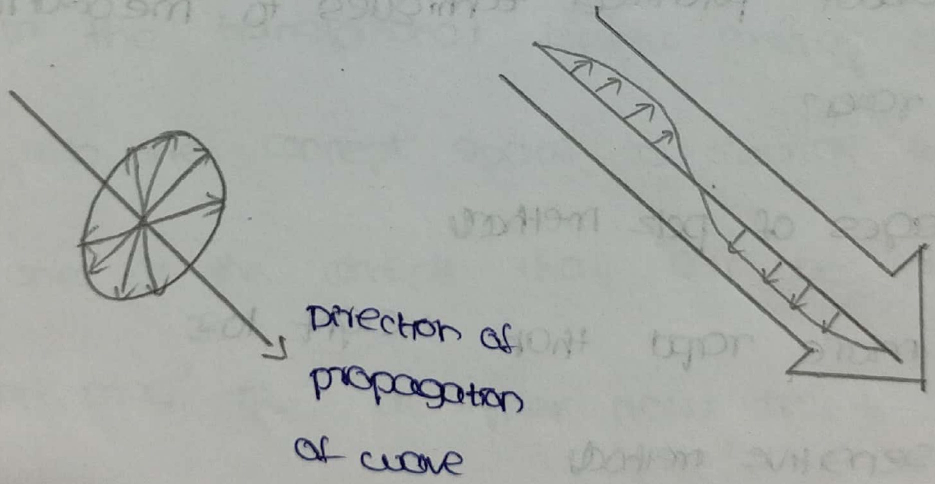
16/10

1\.
(a) What is polarization? Explain the types of polarization.

polarization:

* polarization is a characteristic of all transverse waves.

* oscillation which takes place in a transverse wave in many different directions is said to be unpolarized



Types of polarization:

- linear polarization:

Electric field vector oscillate along straight line in one plane

- circular polarization:

circularly polarized light consists of two perpendicular electromagnetic plane waves of equal amplitude and 90° difference in phase

- Elliptically polarized:

Elliptically polarized light consists of two perpendicular waves of unequal amplitude which differ in phase by 90°.

(b) Detail about polarized techniques to measure corrosion rates?

- Advantages of polz methods

- much more rapid than weight loss
- highly sensitive methods
- accelerating factors usually unneccesary
- nondestructive technique
- corrosion rates can be monitored directly in process streams, "on-line".

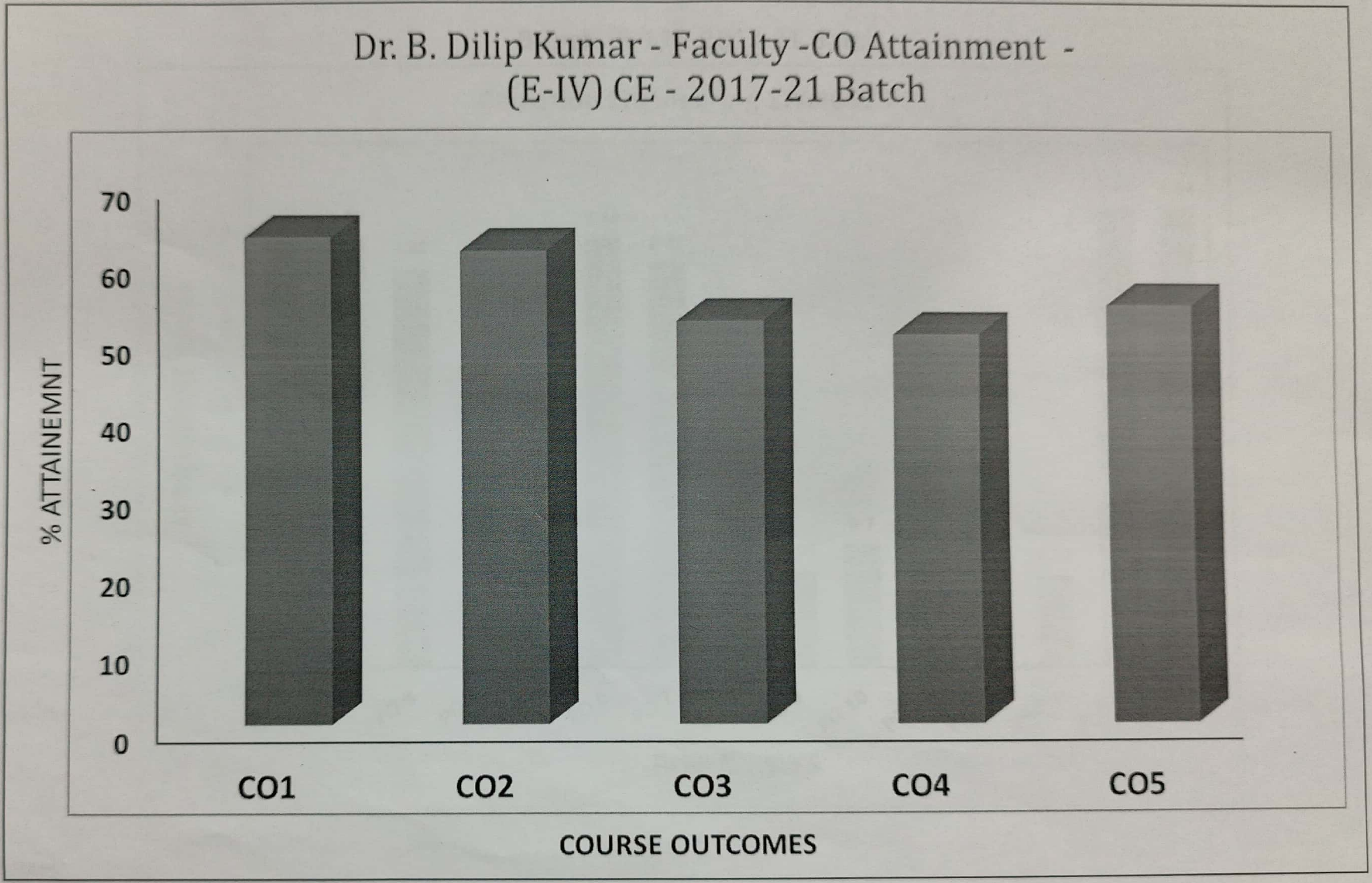
- Two polz methods are available

  - Tafel extrapolation
  - linear polarization

2) Write the examples for demonstrating the area effect in selection and design of materials

Let us consider the example of the design of the brakes for a car. when the designer brings the critical lowest-level FR, "transform the translational kinetic energy of the car", into the concept space to search for concepts, one of the concepts that can be identified is "Air Drag." The designer now tries to embody the concept. One of the embodiments for air drags is a flat plate. The designer then identifies the critical parameter for the configuration, which will be "the area of the plate normal to the flow." The designer abstracts, from the the critical parameter, the need to "maximize the area that is normal to the flow" and searches for concepts.

Continuing with the discussion on the design of the brakes for a car. The designer identifies the concept of 'coulomb fiction' for the FR, "transform the translational kinetic energy of the car." The designer evaluates this concept to check if it can fundamentally satisfy the CRs by doing an order of magnitude calculation and finds that the concept has the potential of satisfying the need. "Two surfaces rubbing against each other where the kinetic energy is used to do work against the friction force between the two surfaces, thus producing heat energy."



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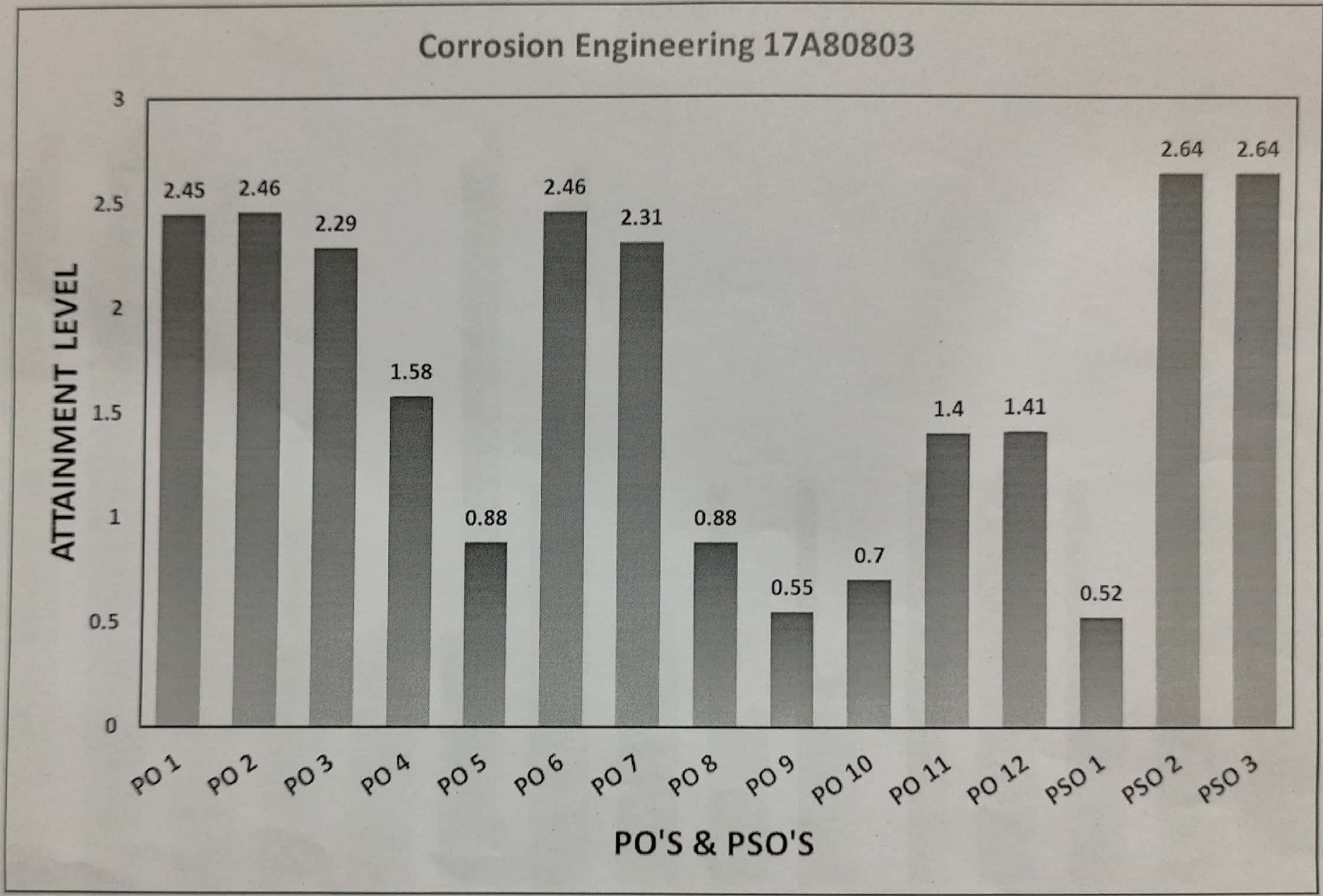
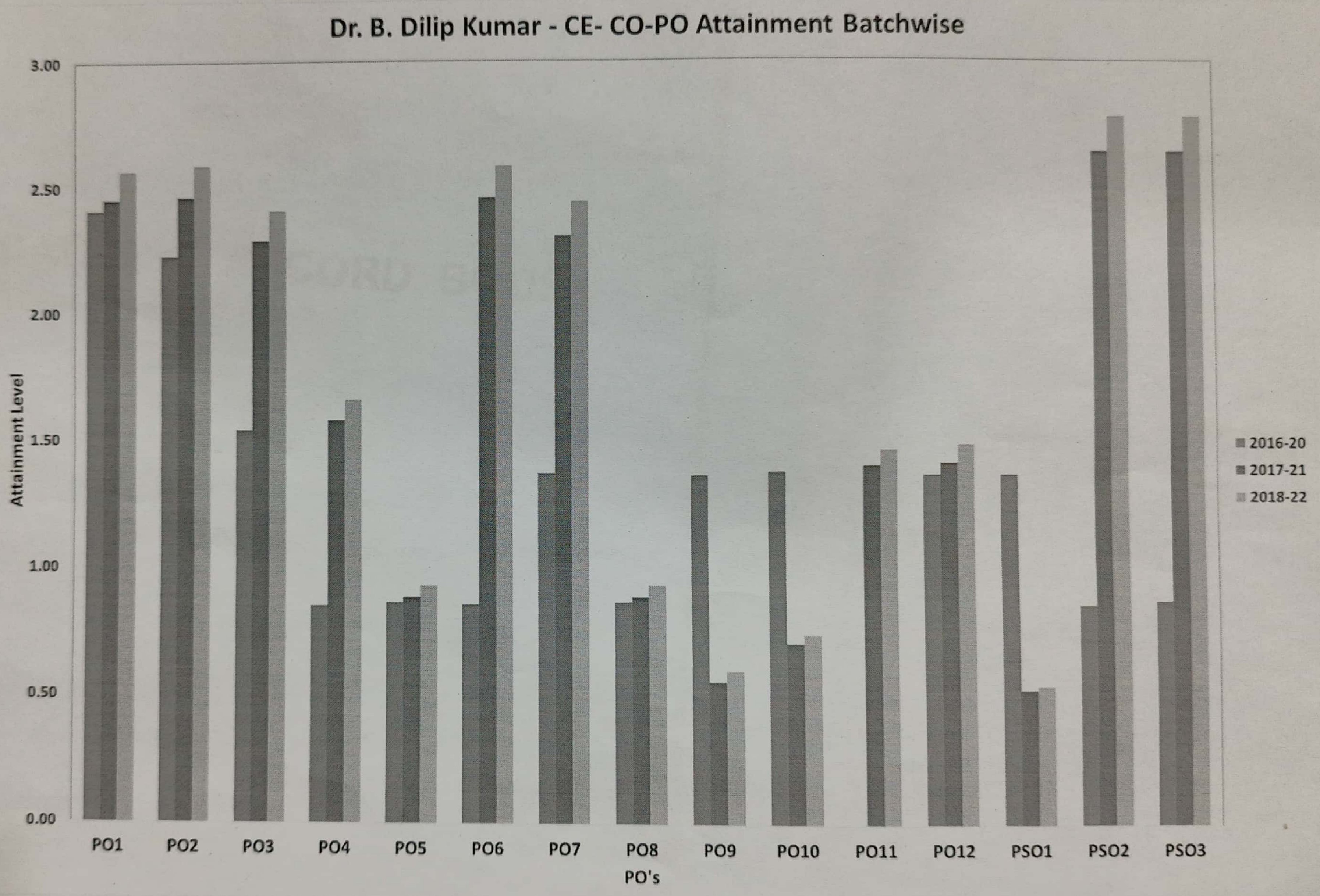
(E-IV) CE - 2017-21 Batch

B.Tech-(R-17)- 2017-21 Batch




Dr. B. Dilip Kumar - CE- CO-PO Attainment Batchwise
Attainment Level
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PO1
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PO8
PO9
PO10
PO11
PO12
PSO1
PSO2
PSO3
PO's
2016-20
2017-21
2018-22

Corrosion Engineering

by

Dr. Dilip Kumar Behara

Ph.D (IITK)

Assistant Professor of Chemical Engineering

& Deputy Controller of Examinations

JNTUA College of Engineering, Anantapuramu

Syllabus

❑ Unit-I:

- **Introduction** Definitions of Corrosion - Overall classification of types of corrosion-Basic electrochemistry –Galvanic and electrolytic cells – Potential measurements - EMF and Galvanic series – Galvanic corrosion and bimetallic contacts – Eh – pH diagrams, Cost of Corrosion, Metallurgical properties influencing corrosion

❑ Unit-II:

- **Forms of Corrosion:** Uniform attack, galvanic, crevice, pitting, Inter granular, selective leaching, erosion and stress corrosion – Mechanisms, testing procedures and their protection.

❑ Unit-III:

- **Electrode Kinetics and Polarization Phenomenon:** Electrode – solution interface – Electrode kinetics and polarization phenomena – Exchange current density – Polarization techniques to measure corrosion rates – Mixed potential theory – Activation and diffusion controlled mixed electrodes.

Unit-IV:

Methods of Corrosion prevention and control

Design, coatings and inhibition – Cathodic protection – Stray current corrosion – Passivity phenomena and development of corrosion resistant alloys – Anodic control.

Unit-V:

Industry Approach:

Selection for a given Chemical Engineering Service Environment- Materials for Chemical Engineering Industry to resist the given chemical Environment.- Ferritic, Austenitic steels and stainless steels- Copper and its alloys-Brasses, bronzes, Nickel and its alloys- Monel alloys materials for a petroleum refinery industry.

TEXT BOOKS:

1. M. G. Fontana, Corrosion Engineering (Third Edition) McGraw-Hill Book Company.
2. Corrosion Engineering Principles and Practice by Pierre R. Roberge

Objectives

❑ Be introduced to the principles of electrochemistry as well as the essential elements of electrochemical corrosion.

❑ Lay a foundation for understanding the forms of corrosion, the mechanism of corrosion, electrochemical methods.

❑ Develop the thermodynamic and kinetic aspects of electrochemistry, including potential-pH (Pourbaix) diagrams, mixed potential theory, and the theory and application of polarization.

❑ Design methods for combating corrosion, the principles and methods leading to mitigation of corrosion problems that might occur in engineering practice.

Iron + Oxygen + H_2O ⟶ Iron Oxide *(brown color)*

Copper + Carbon di-Oxide +Air ⟶ Copper Carbonate *(green color)*

Silver + Sulphur +Air ⟶ Silver Sulphide *(black color)*

Rust is also a disease that can harm your plants. But it isn’t just one disease; it’s actually a group of fungal diseases that attack many different kinds of plants, including—but not limited to—roses, daylilies, carnations, snapdragons, mums, tomatoes, beans, pines, spruce trees and cypress. It can even attack your grass.

Corrosion

Corrosion is defined as destruction or deterioration of a material due to the unwanted chemical or electrochemical reaction with its environment.

The main constituents are electrons and ions

☐ Will there be any cost incurred to overcome corrosion?

Cost of Corrosion

Estimates of the annual cost of corrosion in the United States vary between $ 8 Billion and $ 126 Billion. In any case, corrosion represents a tremendous economic loss And much can be done to reduce it. These dollar figures are not surprising When we consider that corrosion occurs, with varying degrees of severity, wherever Metals and other materials are used.

According to Wall Street Journal (Sept 11, 1981) cost to oil and gas producers is nearly $ 2 Billion.

Costs are increasing because of deeper wells and more hostile environments. Higher temperatures and corrosive sulfur gases

One large chemical company spent more than **$ 4000, 000 per year** for corrosion maintenance in its sulfuric acid plants.

Petroleum industry spends a million dollars per day to protect underground pipelines.

The paper industry estimates corrosion increases the cost of paper **$ 6 to $7 per ton.**

Coal conversion to gas and oil involves high temperatures, erosive particles, and corrosive gases, thus presenting severe problems that must be solved.

Corrosion costs of automobiles-fuel systems, radiators, exhaust systems and bodies are in billions. Cost of $ 500 in refurbishing an automobile fuel system in which water had been mixed with gasoline

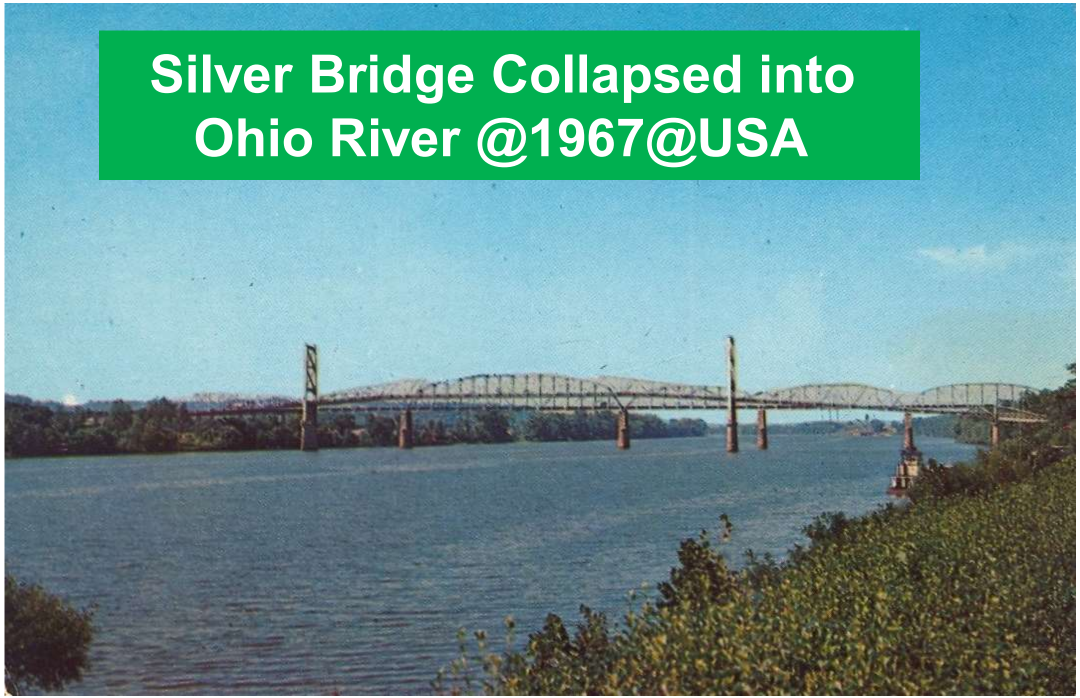
Corrosion touches all-inside and outside the home, on the road, on the sea, in the plant, and in aerospace vehicles

The total annual cost of floods, hurricanes, tornadoes, fires, lightening and earthquakes are less than the costs of corrosion

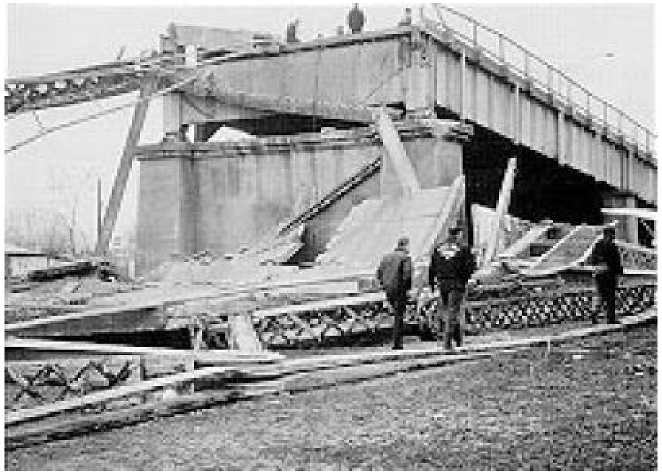
Costs of corrosion will escalate substantially during the next decade because of world wide shortages of construction materials, higher energy costs, aggressive corrosion environments in coal conversion processes, large increases in numbers and scope of plants and other factors

Political considerations are also a factor. We depend largely on foreign sources for some metals: 90% for Chromium and 100% for columbium (niobium)

Corrosion of bridges is a major problem as they age and require replacement, which costs billions. The collapse (because of stress corrosion) of the Silver Bridge into the Ohio River cost 40 lives and Millions of dollars.



Silver Bridge Collapsed into Ohio River @1967@USA



Guadalajara Sewer Explosions@1992@Mexico

LCS 2 USS Independence Naval Ship Engine Corrosion@2002@USA

Carlsbad Natural Gas Pipe line Explosion@2000@Mexico

Sinking of the Erika@1999@France

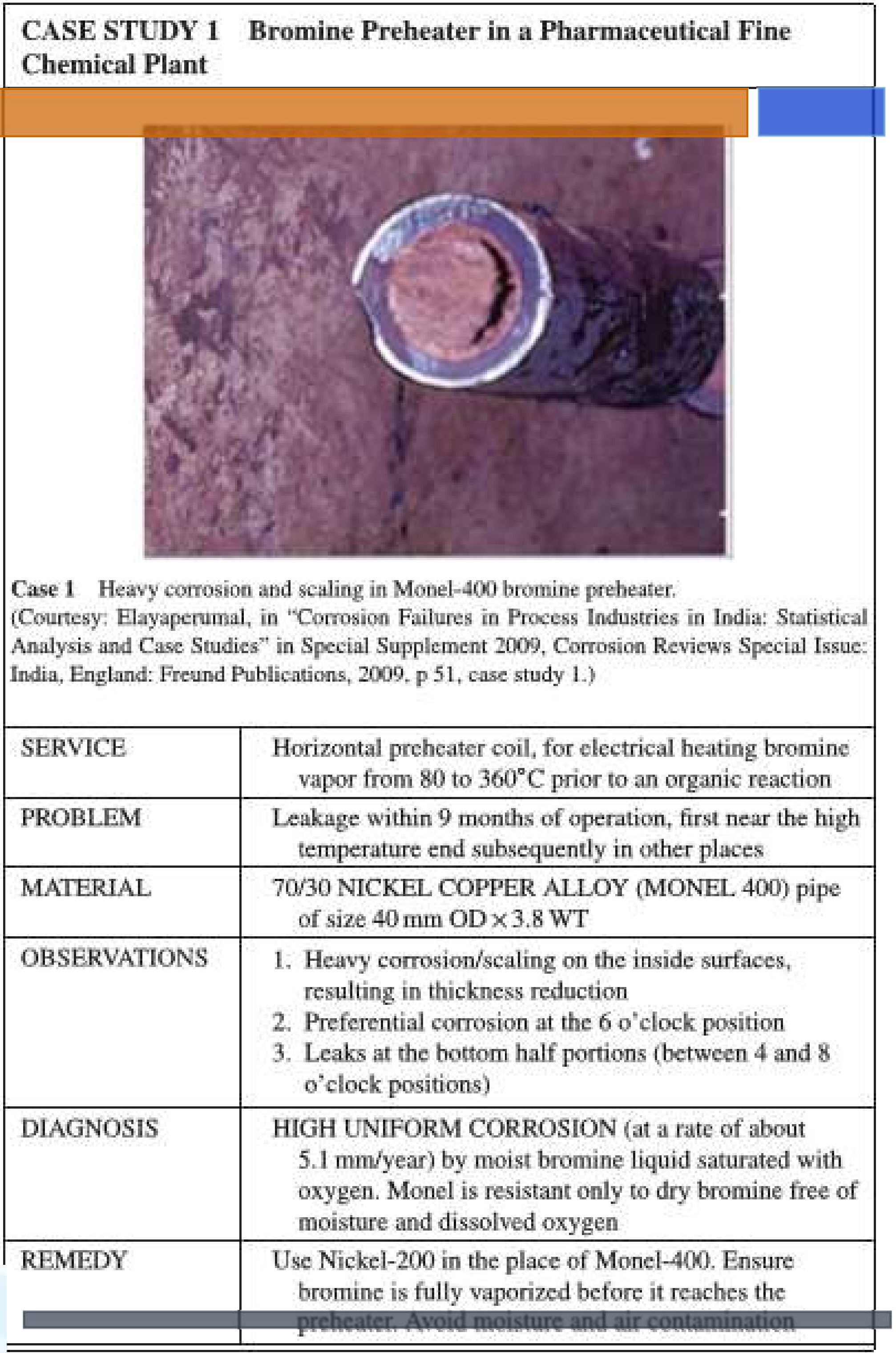
Lowe’s Motor Speedway Bridge Collapse@2000@USA

Flixborough Disaster@1974@England

Prudhoe Bay Oil Spill@2006@Alaska

Bhopal Gas Tragedy@1984@India

Aloha incident
Bhopal accident
Carlsbad pipeline explosion
Guadalajara sewer explosion
EL AL Boeing 747 crash
Explosion due to corrosion by process chemicals
F-16 fighter aircraft
Nuclear reactor with a hole in the head
Piping rupture caused by flow accelerated corrosion
Pitting corrosion accidents and incidents of aircraft and helicopters
Pollution by oil pipeline releases
Prudhoe Bay 2006 Oil Spill
Silver bridge
Sinking of the Erika
Stress corrosion cracking of chemical reactor, the Flixborough explosion
Swimming Pool Roof Collapse



CASE STUDY 1 Bromine Preheater in a Pharmaceutical Fine Chemical Plant

Case 1 Heavy corrosion and scaling in Monel-400 bromine preheater.
(Courtesy: Elayaperumal, in "Corrosion Failures in Process Industries in India: Statistical Analysis and Case Studies" in Special Supplement 2009, Corrosion Reviews Special Issue: India, England: Freund Publications, 2009, p 51, case study 1.)

SERVICE	Horizontal preheater coil, for electrical heating bromine vapor from 80 to 360°C prior to an organic reaction
PROBLEM	Leakage within 9 months of operation, first near the high temperature end subsequently in other places
MATERIAL	70/30 NICKEL COPPER ALLOY (MONEL 400) pipe of size 40 mm OD × 3.8 WT
OBSERVATIONS	1. Heavy corrosion/scaling on the inside surfaces, resulting in thickness reduction 2. Preferential corrosion at the 6 o'clock position 3. Leaks at the bottom half portions (between 4 and 8 o'clock positions)
DIAGNOSIS	HIGH UNIFORM CORROSION (at a rate of about 5.1 mm/year) by moist bromine liquid saturated with oxygen. Monel is resistant only to dry bromine free of moisture and dissolved oxygen
REMEDY	Use Nickel-200 in the place of Monel-400. Ensure bromine is fully vaporized before it reaches the preheater. Avoid moisture and air contamination

Table 3 Elements of cost of corrosion

Element of cost	Example
Replacement of equipment or buildings	Corroded pressure vessel
Loss of product	Corrosion leak
	Corrosion contamination of product
	Corrosion during storage
Maintenance and repair	Repair corroded corrugated metal roof
	Weld overlay of chemical reaction tank
	Repair pump handling corrosive slurry—erosion and corrosion
	Scheduled downtime for plant in continuous operation, for example, petroleum refinery
Redundant equipment	Installation of three large fans where two are required during operation
Corrosion control	
Inhibitors	Injection of oil wells
Organic coatings	Coal tar on exterior of underground pipeline
	Paint on wooden furniture
	Topcoat on automobile—aesthetics and corrosion
	Zinc-rich paint on automobile
	Galvanized steel siding
Metallic coatings	Chrome-plated faucets—aesthetics and corrosion
Cathodic protection	Cathodic protection of underground pipelines
Technical support	Corrosion-resistant alloy development
	Materials selection
	Corrosion monitoring and control
Design	
Material of construction for structural integrity	Stainless steel for corrosive applications
	Stainless steel for high-temperature mechanical properties
Material of construction	High alloy to prevent corrosion products contamination, for example, drug industry
Corrosion allowance	Thicker wall for corrosion
Special processing for corrosion resistance	Stress relief, shot peening, special heat treatment (e.g., Al alloys) for corrosion
Insurance	Portion of premiums on policy to protect against loss because of corrosion (to cover charge of writing and administering policy, not protection amount)
Parts and equipment inventory	Pumps kept on hand for maintenance, for example, chemical plant inventory

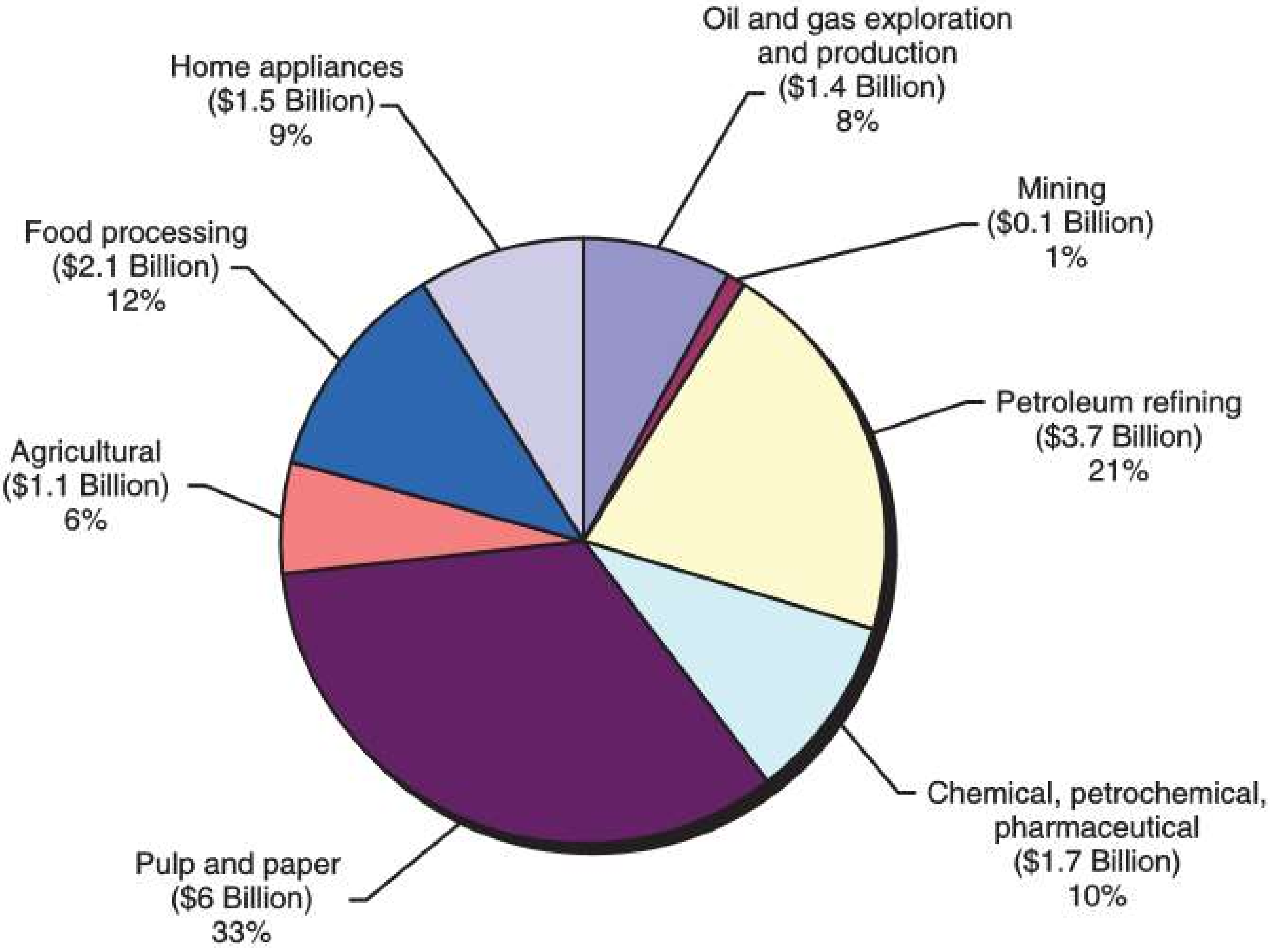


Figure 1.1 Annual cost of corrosion in the production and manufacturing category in US ($17.6 Billion). Koch et al. (2002) (courtesy Federal Highway Administration, USA.)

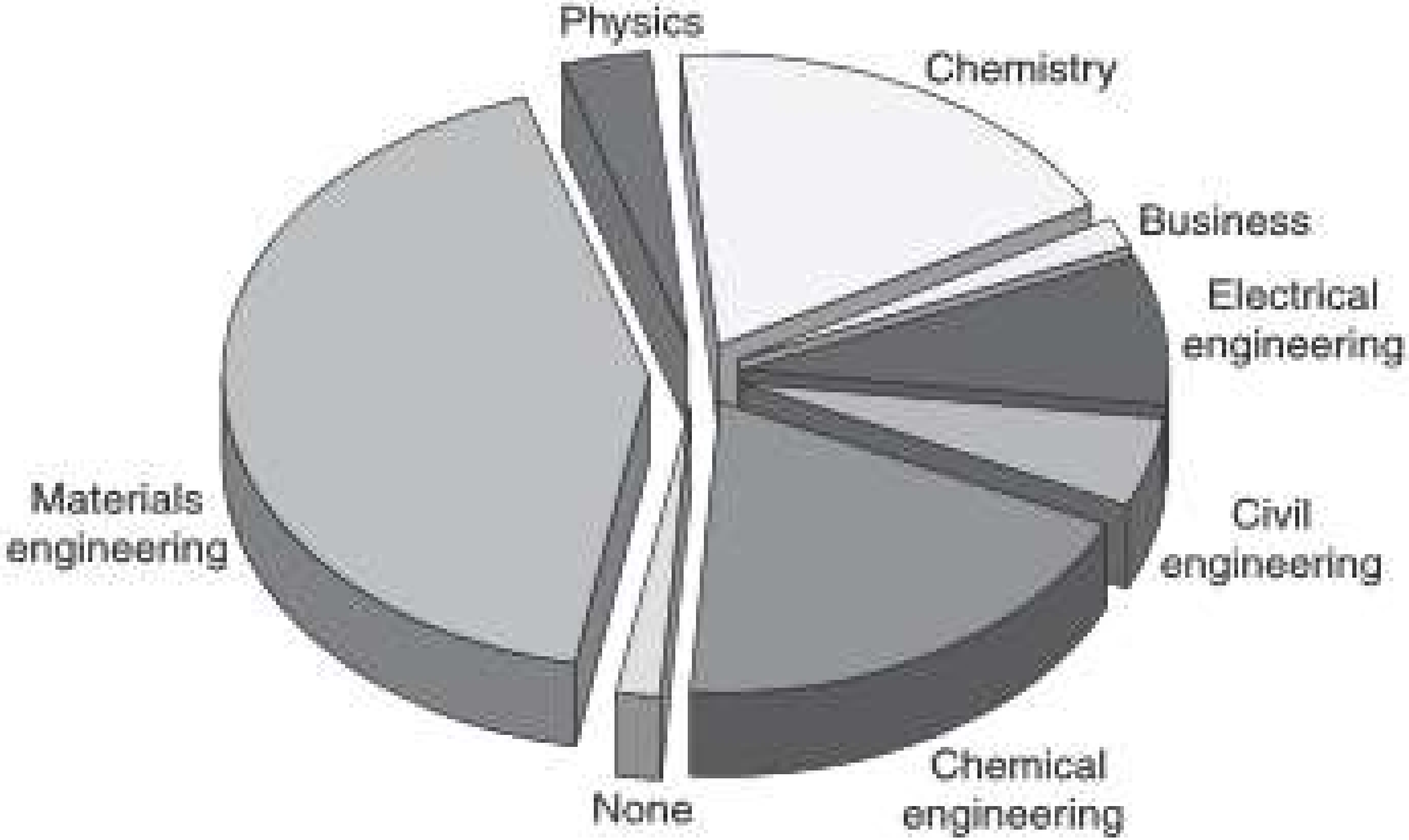
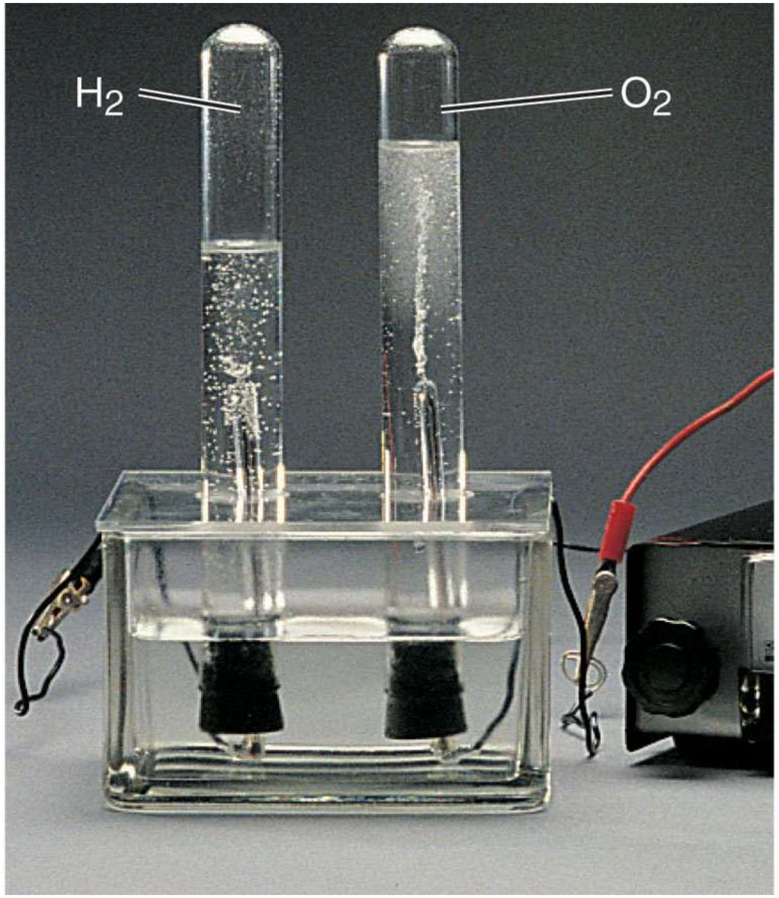


FIGURE 1.1 Distribution of disciplines in which active corrosion engineers have graduated.

The electrolysis of water

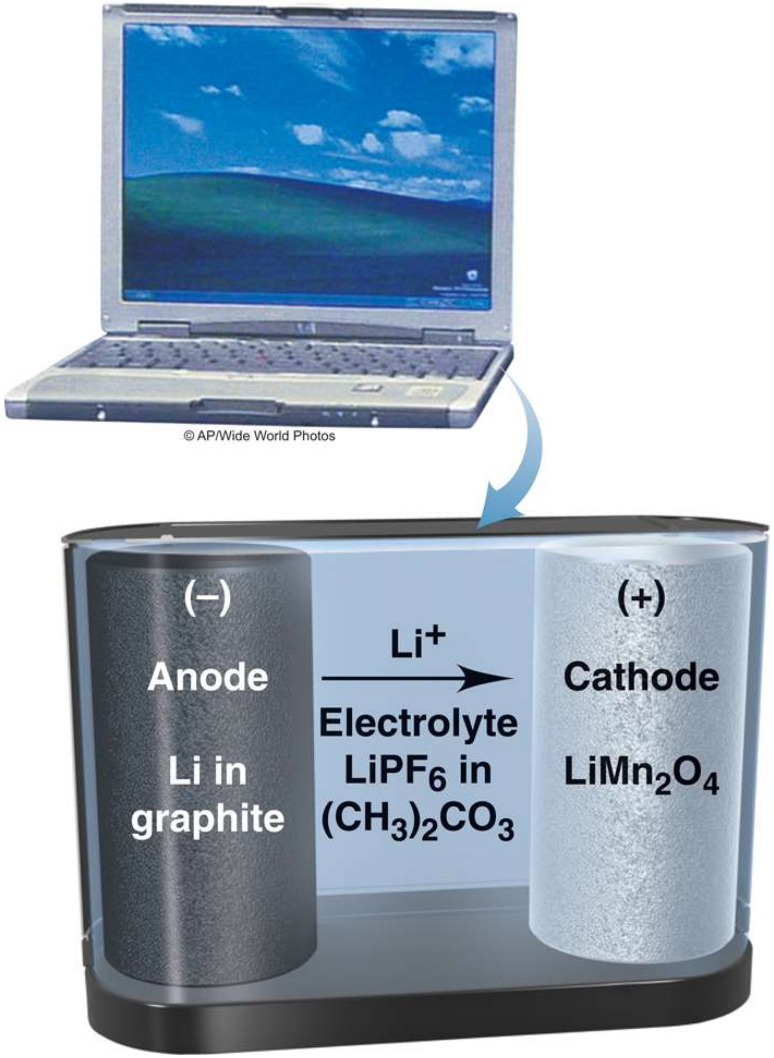


Overall (cell) reaction
$2H_2O(l) \rightarrow H_2(g) + O_2(g)$

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

Reduction half-reaction
$2H_2O(l) + 4e^- \rightarrow 2H_2(g) + 2OH^-(aq)$

Lithium-ion battery



© AP/Wide World Photos

Anode (oxidation):

$$Li_xC_6(s) \rightarrow xLi^+ + xe^- + C_6(s)$$

Cathode (reduction):

$$Li_{1-x}Mn_2O_4(s) + xLi^+ + xe^- \rightarrow LiMn_2O_4(s)$$

Overall (cell) reaction:

$$Li_xC_6(s) + Li_{1-x}Mn_2O_4(s) \rightarrow LiMn_2O_4(s)$$

$$E_{cell} = 3.7\ V$$

The secondary (rechargeable) lithium-ion battery is used to power laptop computers, cell phones, and camcorders.

Alkaline battery

© Jill Braaten

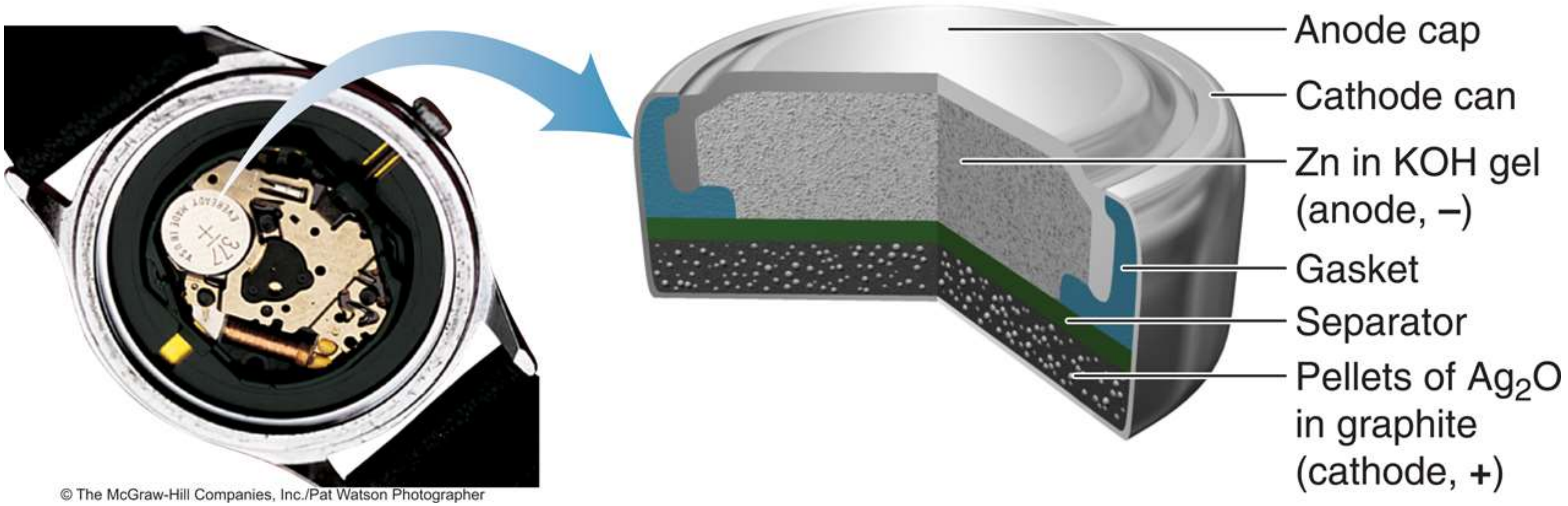
Anode (oxidation): $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode (reduction): $MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow Mn(OH)_2(s) + 2OH^-(aq)$

Overall (cell) reaction:

$$Zn(s) + MnO_2(s) + H_2O(l) \rightarrow ZnO(s) + Mn(OH)_2(s) \quad E_{cell} = 1.5\ V$$

Silver button battery.



© The McGraw-Hill Companies, Inc./Pat Watson Photographer

Anode (oxidation): $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

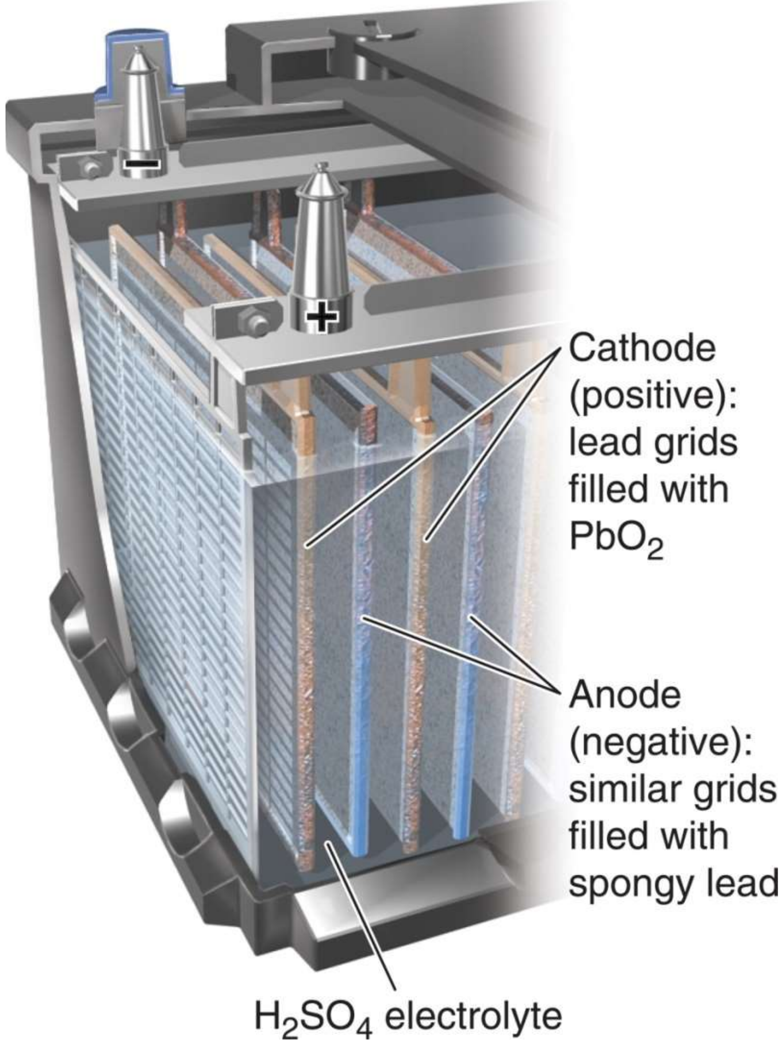
Cathode (reduction): $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Overall (cell) reaction: $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$

$E_{cell} = 1.6\ V$

The mercury battery uses HgO as the oxidizing agent instead of Ag_2O and has cell potential of 1.3 V.

Lead-acid battery



The reactions in a lead-acid battery:

The cell generates electrical energy when it discharges as a voltaic cell.

Anode (oxidation): $\mathrm{Pb}(s) + \mathrm{HSO_4^-}(aq) \rightarrow \mathrm{PbSO_4}(s) + \mathrm{H^+}(aq) + 2e^-$

Cathode (reduction):

$$\mathrm{PbO_2}(s) + 3\mathrm{H^+}(aq) + \mathrm{HSO_4^-}(aq) + 2e^- \rightarrow \mathrm{PbSO_4}(s) + 2\mathrm{H_2O}(l)$$

Overall (cell) reaction (discharge):

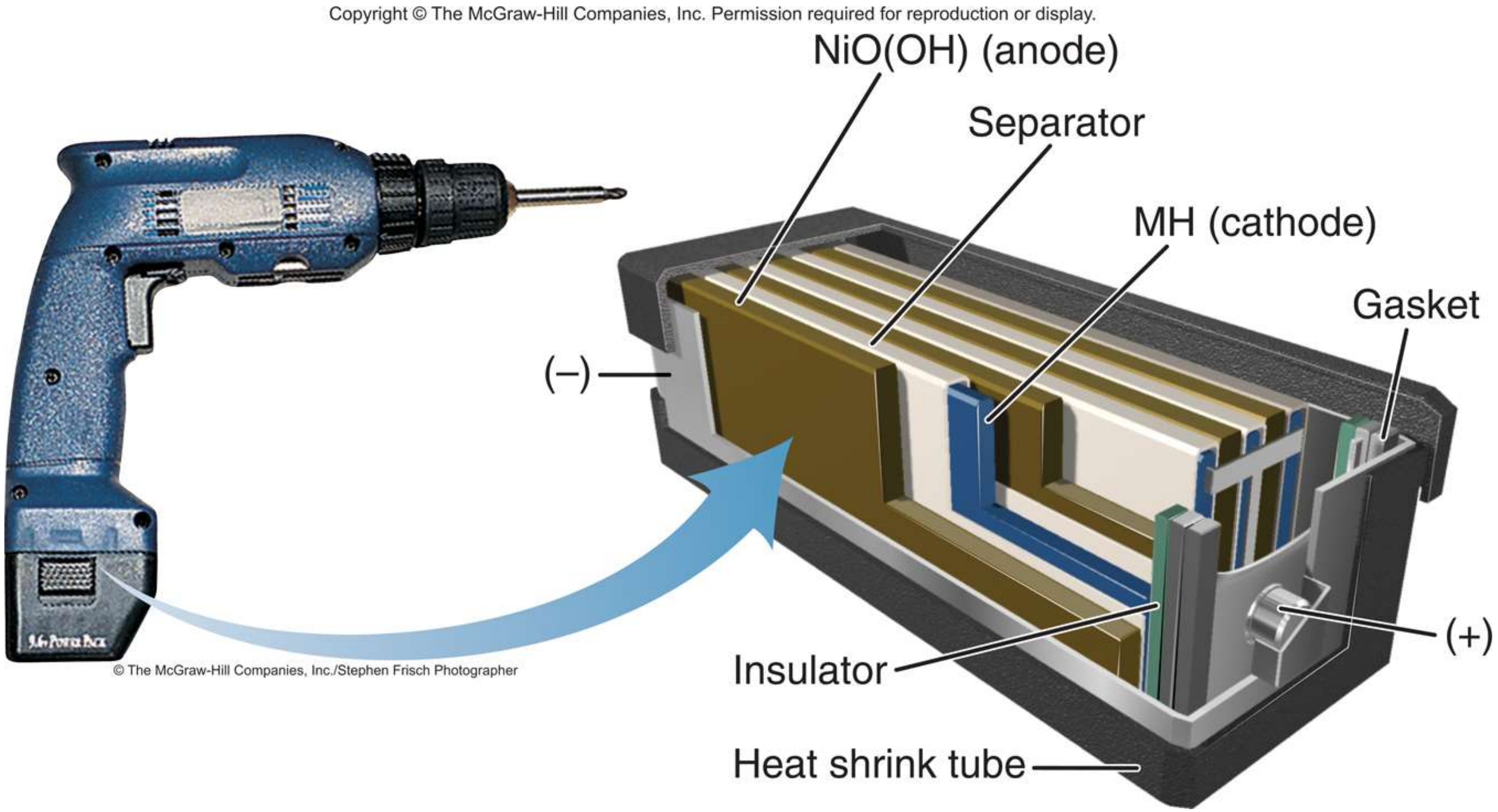
$$\mathrm{PbO_2}(s) + \mathrm{Pb}(s) + \mathrm{H_2SO_4}(aq) \rightarrow 2\mathrm{PbSO_4}(s) + 2\mathrm{H_2O}(l) \quad E_{\mathrm{cell}} = 2.1\ \mathrm{V}$$

Overall (cell) reaction (recharge):

$$2\mathrm{PbSO_4}(s) + 2\mathrm{H_2O}(l) \rightarrow \mathrm{PbO_2}(s) + \mathrm{Pb}(s) + \mathrm{H_2SO_4}(aq)$$

The lead-acid car battery is a secondary battery and is rechargeable.

Nickel-metal hydride battery



Anode (oxidation): $\mathrm{MH}(s) + \mathrm{OH}^-(aq) \rightarrow M(s) + \mathrm{H_2O}(l) + e^-$

Cathode (reduction): $\mathrm{NiO(OH)}(s) + \mathrm{H_2O}(l) + e^- \rightarrow \mathrm{Ni(OH)_2}(s) + \mathrm{OH}^-(aq)$

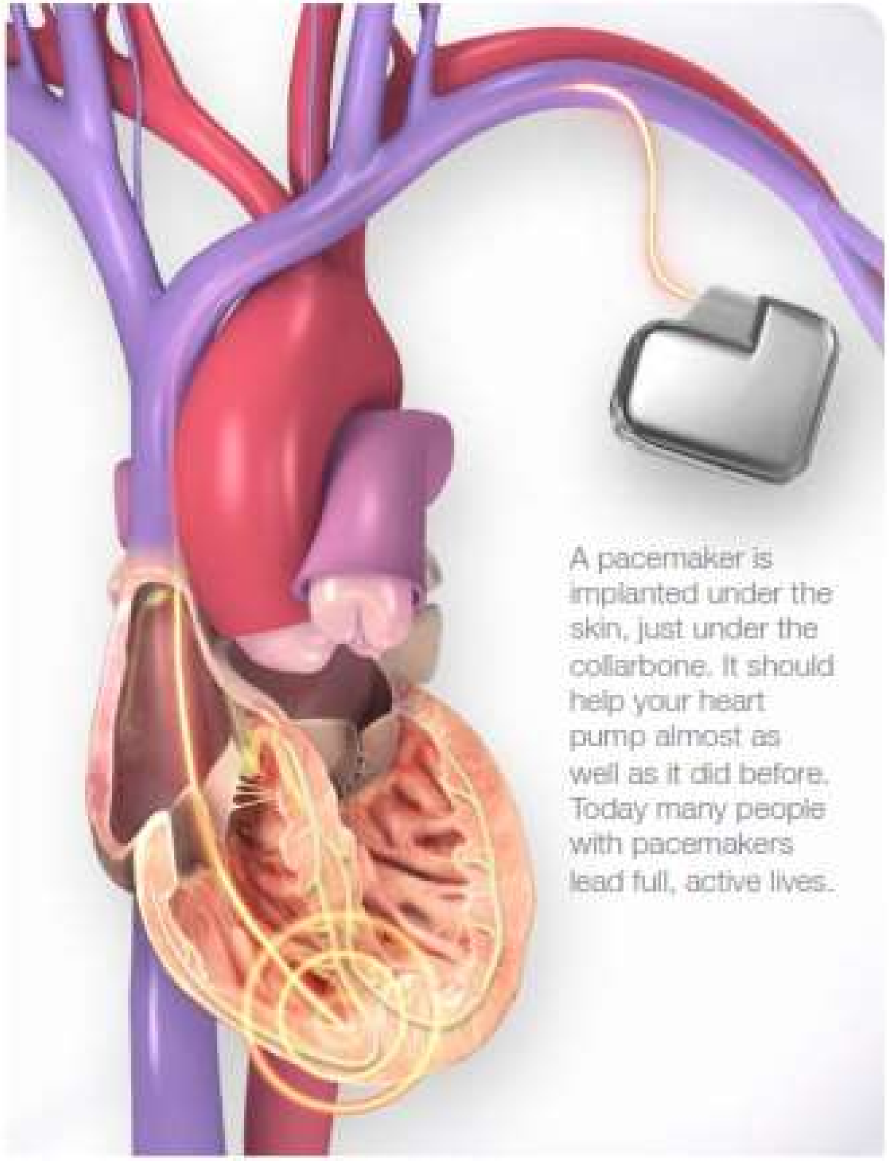
Overall (cell) reaction:

$$\mathrm{MH}(s) + \mathrm{NiO(OH)}(s) \rightarrow \mathrm{M}(s) + \mathrm{Ni(OH)_2}(s) \quad E_{\mathrm{cell}} = 1.4\ \mathrm{V}$$

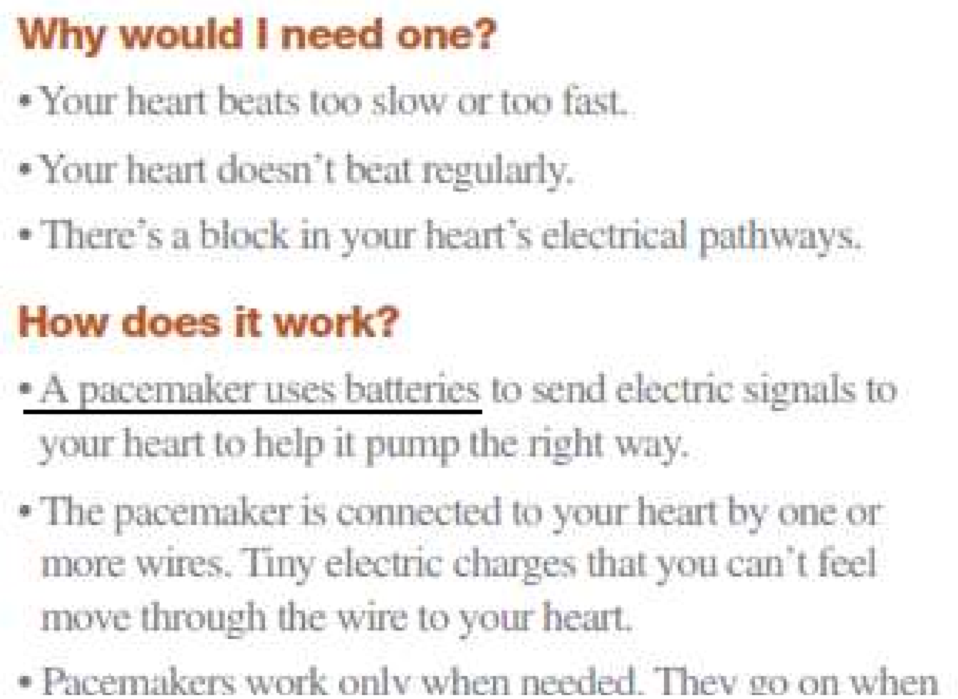
What Is a Pacemaker?

A pacemaker is a small device that helps your heart beat more regularly. It does this with a small electric stimulation that helps control your heartbeat. Your doctor puts the pacemaker under the skin on your chest, just under your collarbone. It's hooked up to your heart with tiny wires.

You may need a pacemaker to keep your heart beating properly. This helps your body get the blood and oxygen it needs. Some people just need a pacemaker for a short time (like after a heart attack) and may use a kind that's outside the skin. The battery unit for this type can be worn on a belt.



A pacemaker is implanted under the skin, just under the collarbone. It should help your heart pump almost as well as it did before. Today many people with pacemakers lead full, active lives.



Why would I need one?

- Your heart beats too slow or too fast.
- Your heart doesn't beat regularly.
- There's a block in your heart's electrical pathways.

How does it work?

- A pacemaker uses batteries to send electric signals to your heart to help it pump the right way.
- The pacemaker is connected to your heart by one or more wires. Tiny electric charges that you can't feel move through the wire to your heart.
- Pacemakers work only when needed. They go on when

Anode (oxidation):

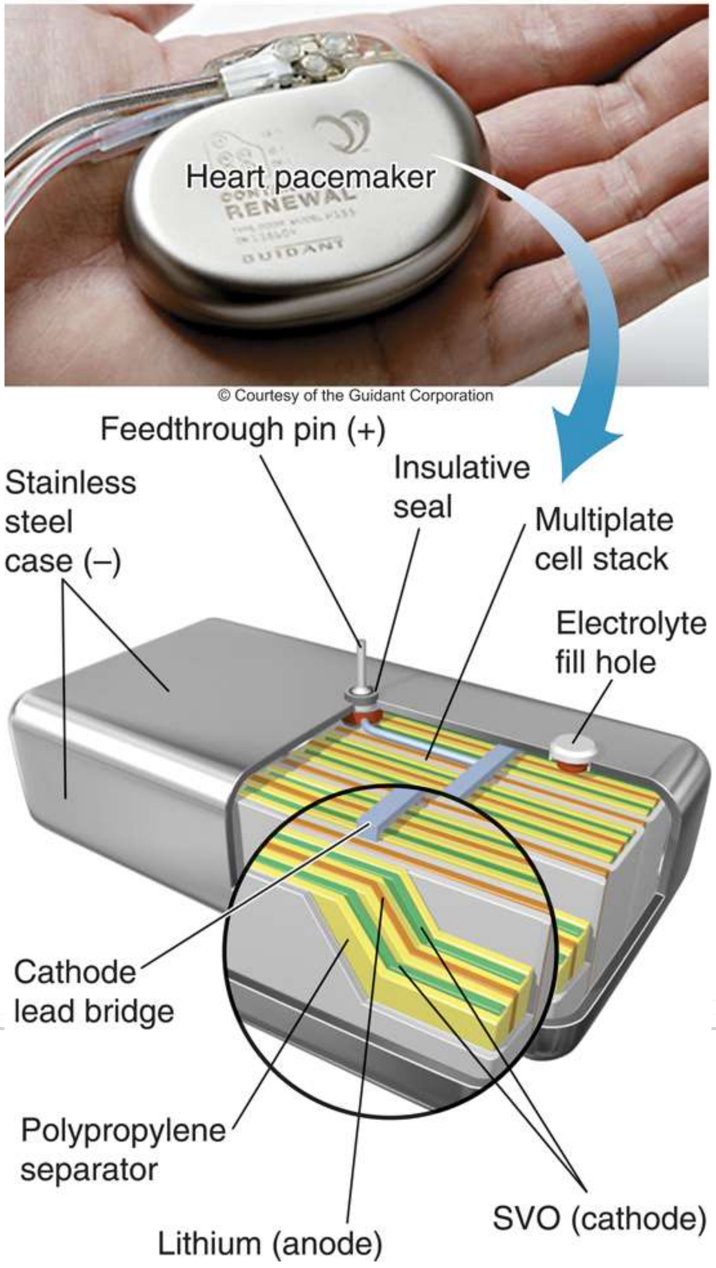
$$3.5Li(s) \rightarrow 3.5Li^{+} + 3.5e^{-}$$

Cathode (reduction):

$$AgV_2O_{5.5} + 3.5Li^{-} + 3.5e^{-} \rightarrow Li_{3.5}V_2O_{5.5}$$

Overall (cell) reaction:

$$AgV_2O_{5.5} + 3.5Li(s) \rightarrow Li_{3.5}V_2O_{5.5}$$



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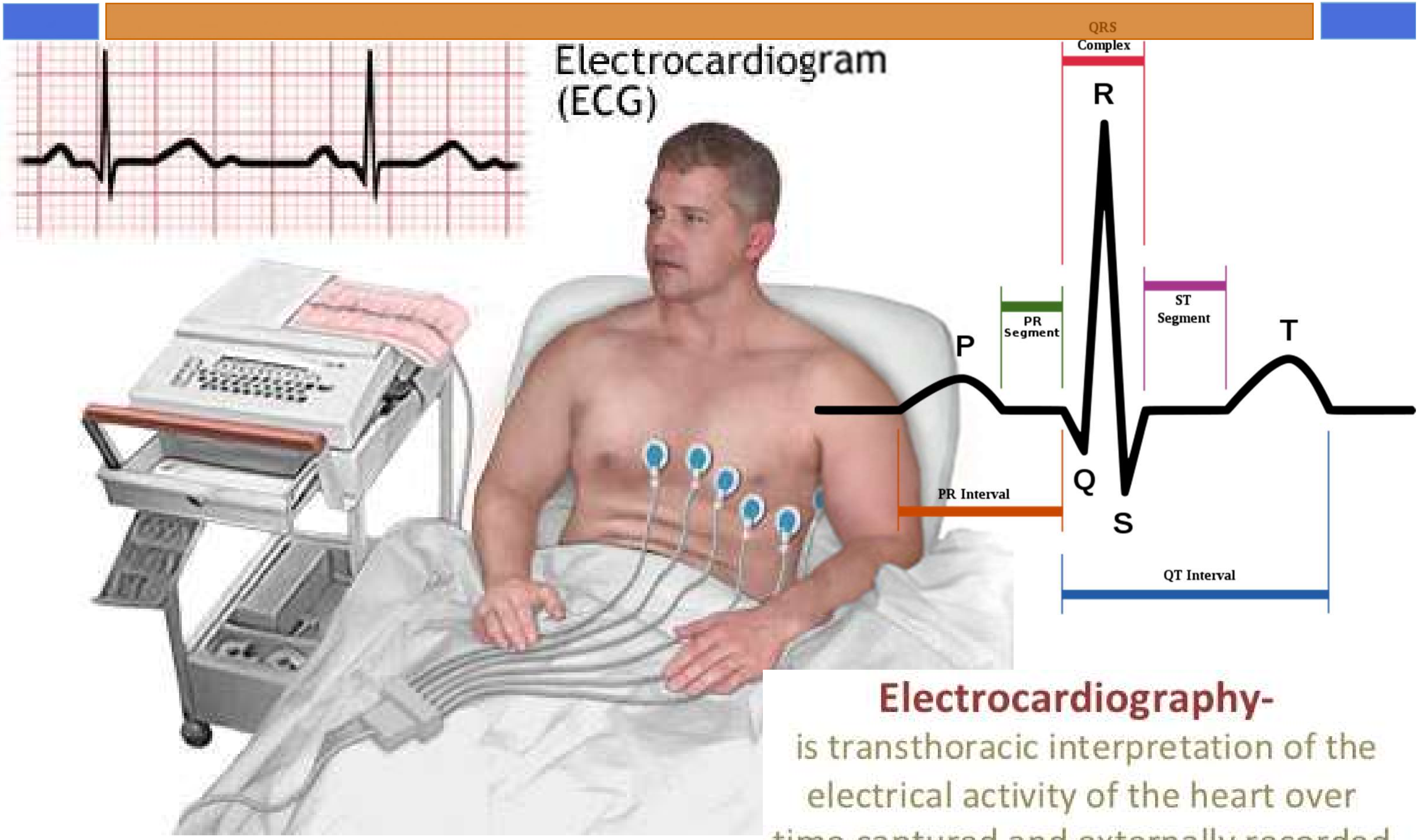
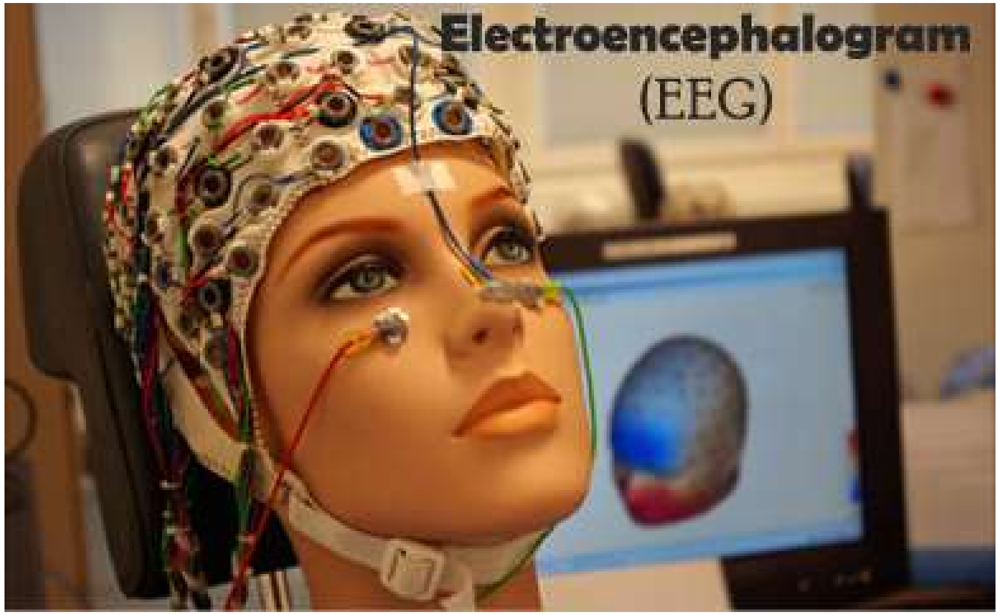
Electrocardiogram (ECG)

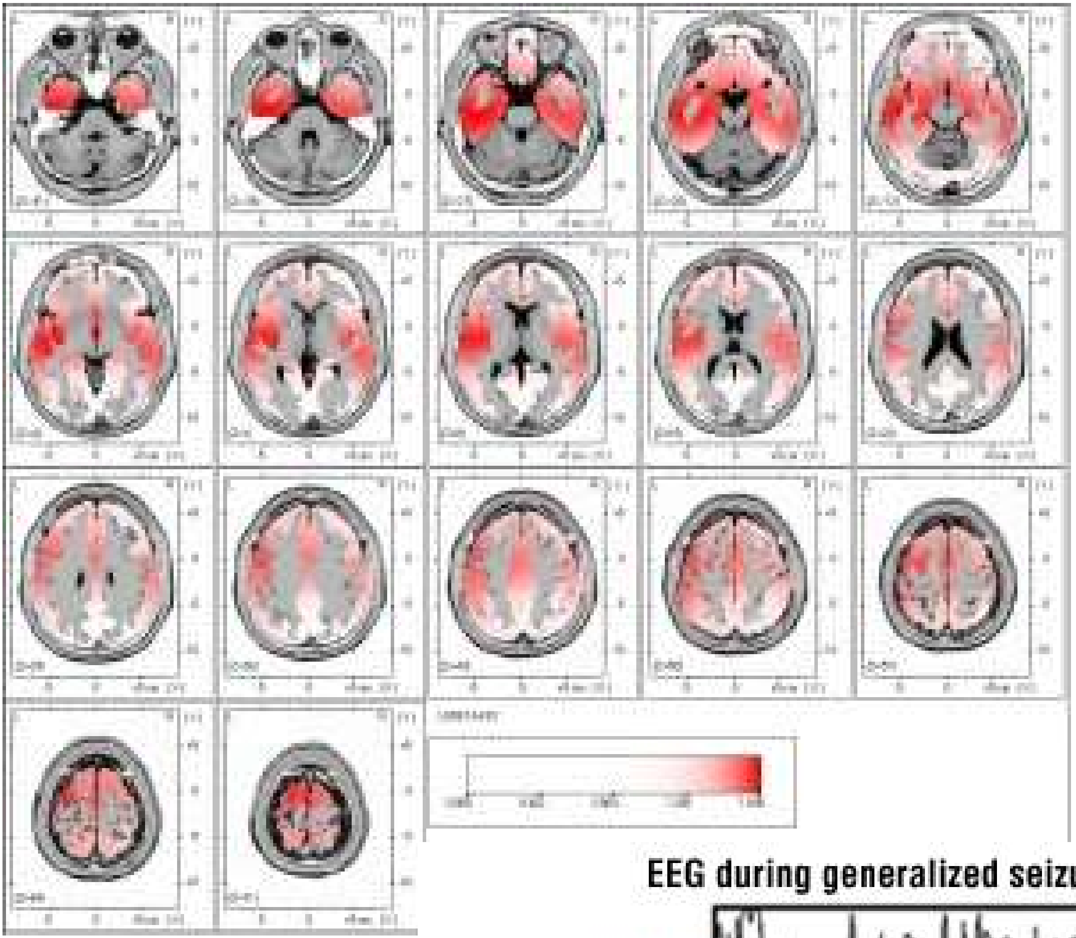


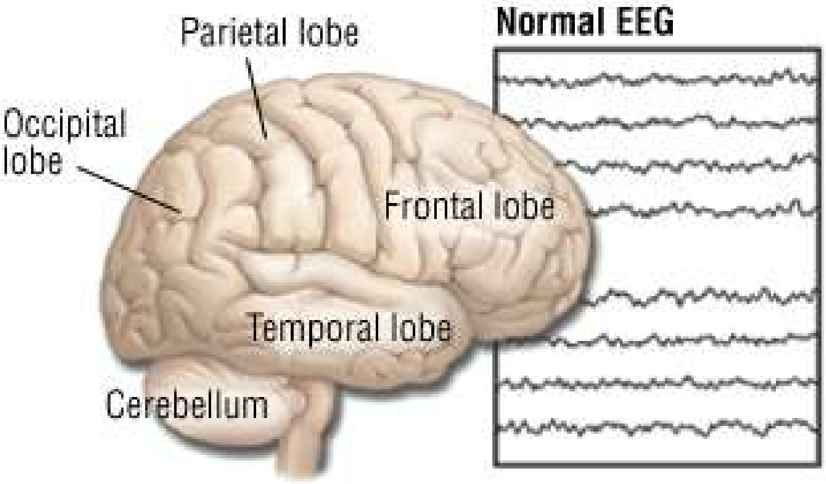
Electrocardiography- is transthoracic interpretation of the electrical activity of the heart over time captured and externally recorded by skin electrodes for diagnostic or research purposes on human hearts.

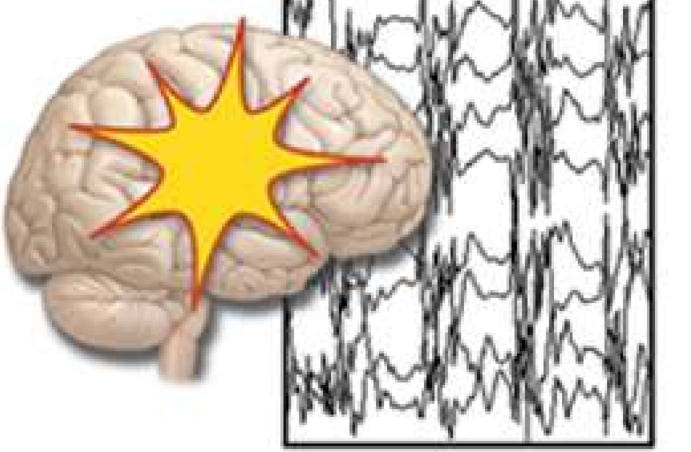
Diagnose heart abnormalities

Electroencephalogram



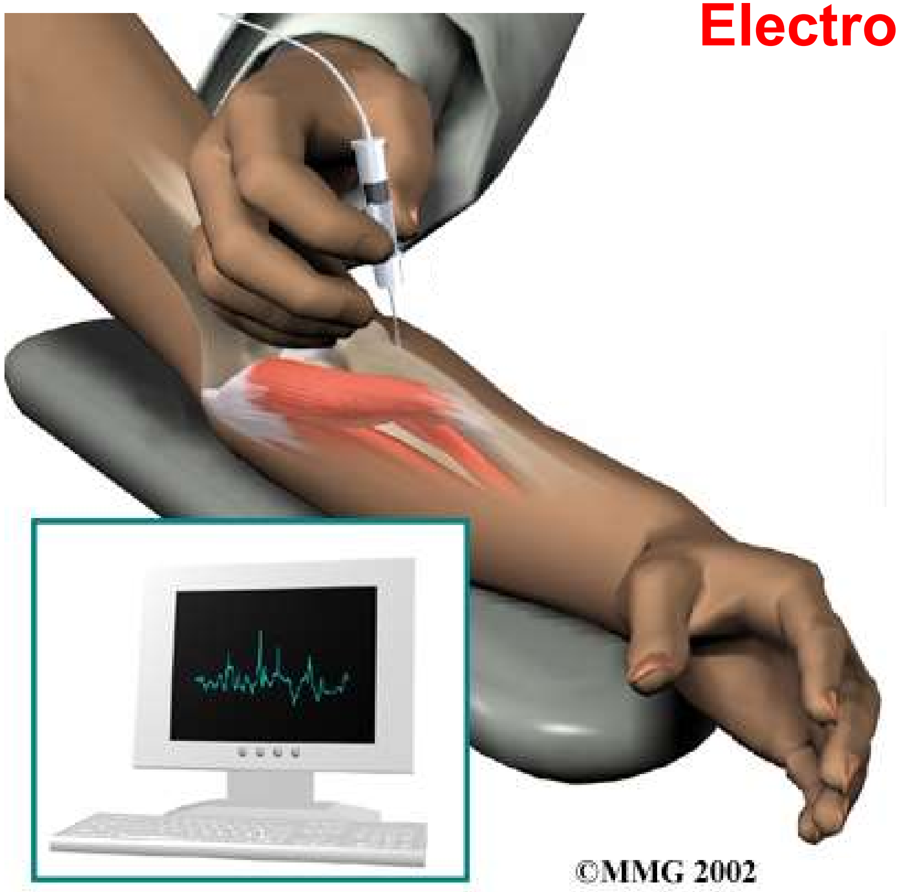


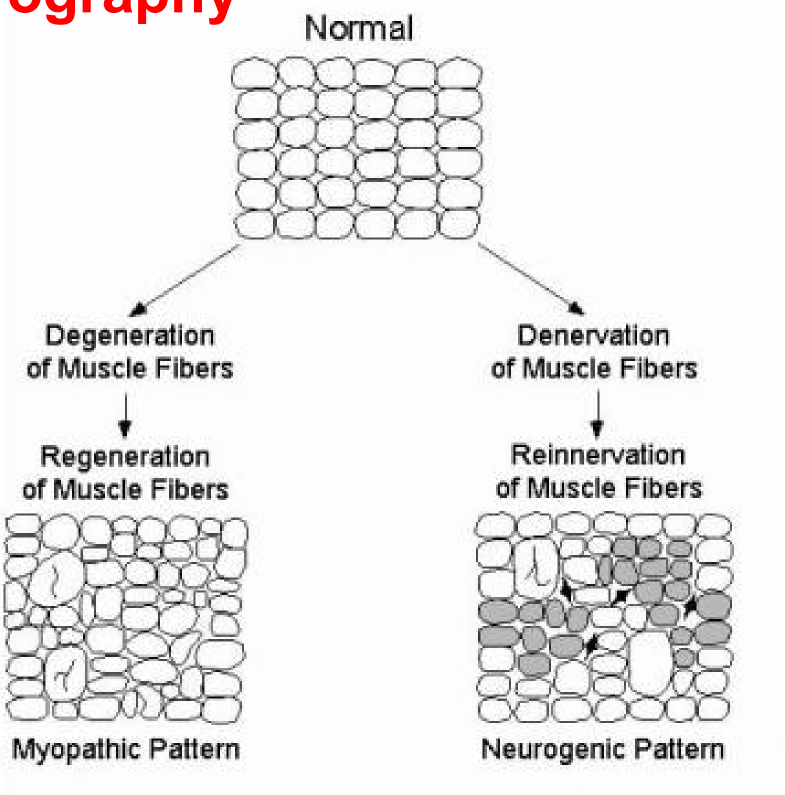




Brain disturbance with electroencephalograms (EEGs)

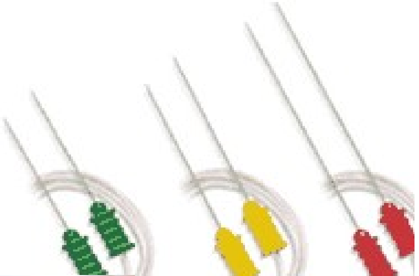
Electromyography





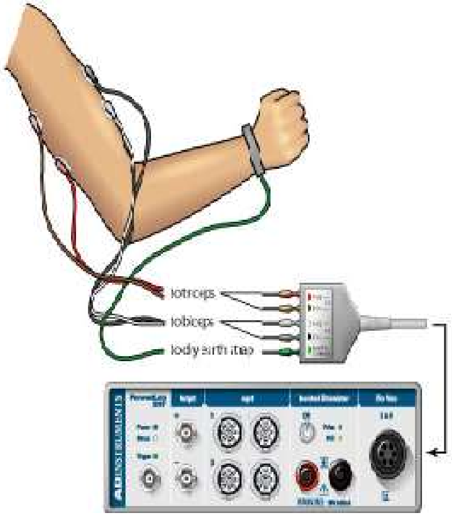
EMG Electrodes

Surface Electrodes

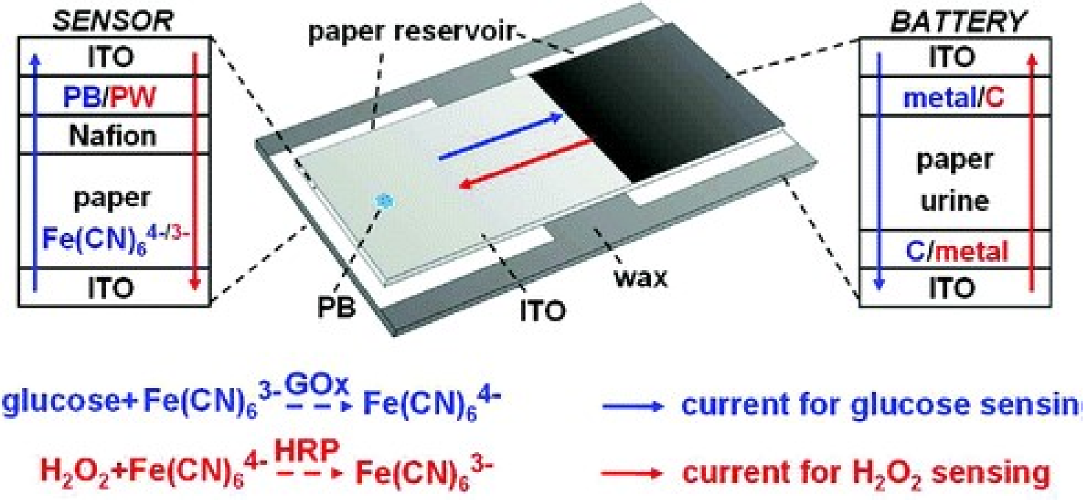


Fine wire

Needle electrode



loss of nerve function with electromyograms (EMGs)



Glucose Sensors

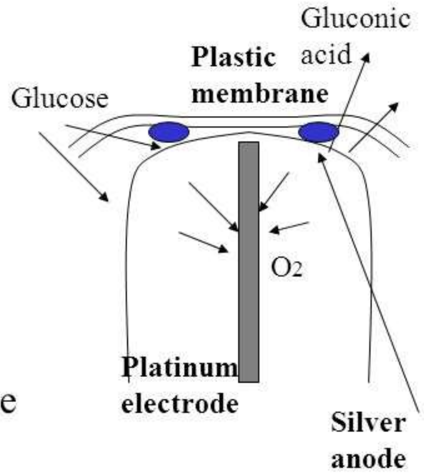
Enzymatic Approach

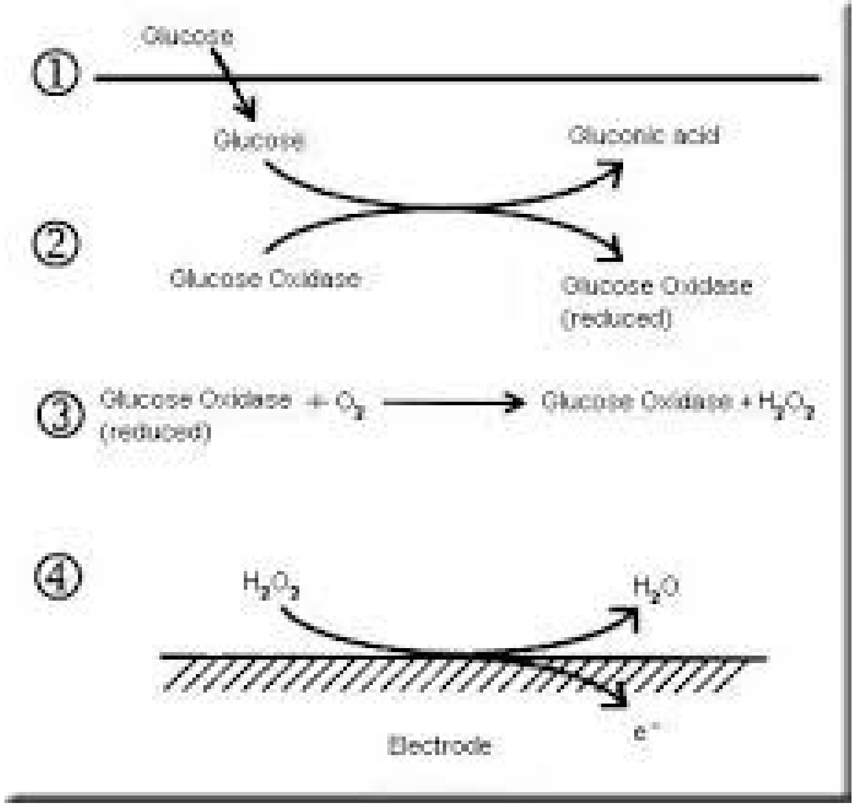
$$Glucose + O_2 \xrightarrow{GlucoseOxidase} GluconicAcid + H_2O_2$$

Makes use of catalytic (enzymatic) oxidation of glucose

The setup contains an enzyme electrode and an oxygen electrode and the difference in the readings indicates the glucose level.

The enzyme electrode has glucose oxidase immobilized on a membrane or a gel matrix.

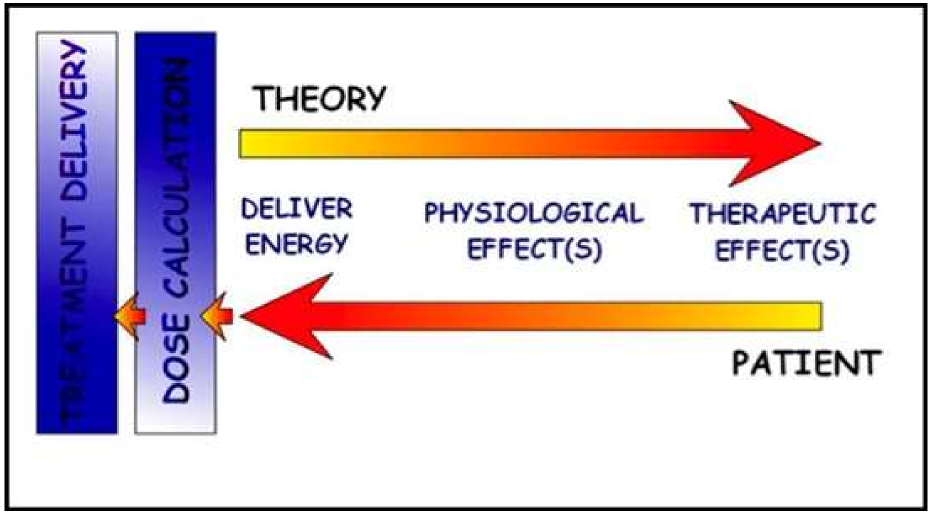




Avoiding the Knife

The destructive effect of passing an electrical current though human tissue (electrolysis) also has therapeutic uses. In the nineteenth century surgery was a very dangerous and painful affair. Rather than surgically removing a tumor, a physician could use electrolysis — which was unlikely to result in death from infection or shock — to slow or even stop its growth. With improvements in surgical technique, electrolysis has ceased to be a common treatment for cancer, but it is still frequently used (under the name of electrocautery) to stop the bleeding of small blood vessels. Dermatologists also continue to use it to remove warts, moles, and hair.

Electrotherapy: Shocks to the system



Electrotherapy: Shocks to the system

During the eighteenth and early nineteenth centuries, electricity was all the rage. Doctors, scientists, and quacks — not always easily distinguished from one another — used electrochemical shocks to treat almost every malady imaginable. They succeeded most often when treating certain kinds of paralysis by stimulating the muscles, and by the mid-nineteenth century Guillaume Benjamin Duchenne de Boulogne had systematized this technique. Physical therapists today still use electrotherapy for paralysis and other physical problems.

The most important muscle treated with electricity is the heart. Normally, regular pulses of electricity keep it beating at a constant pace. If something goes wrong with the natural electrical pulse, artificial pacemakers, available since the 1950s, can keep a patient’s heart beating steadily. Emergency treatment for irregular heartbeat can be delivered by a cardioverter or defibrillator. In some cases a single jolt of electricity through the chest is enough to restore normal rhythms.

While electrotherapy, heart packing, and cardioversion all use electricity to stimulate muscles, electroconvulsion (electroshock treatment) delivers it to the brain. Some psychiatrists still use this treatment, which was first used in Italy in 1938, to treat depression and other mental illness. It is extremely controversial, for it can cause brain damage and sometimes even death.

UPS

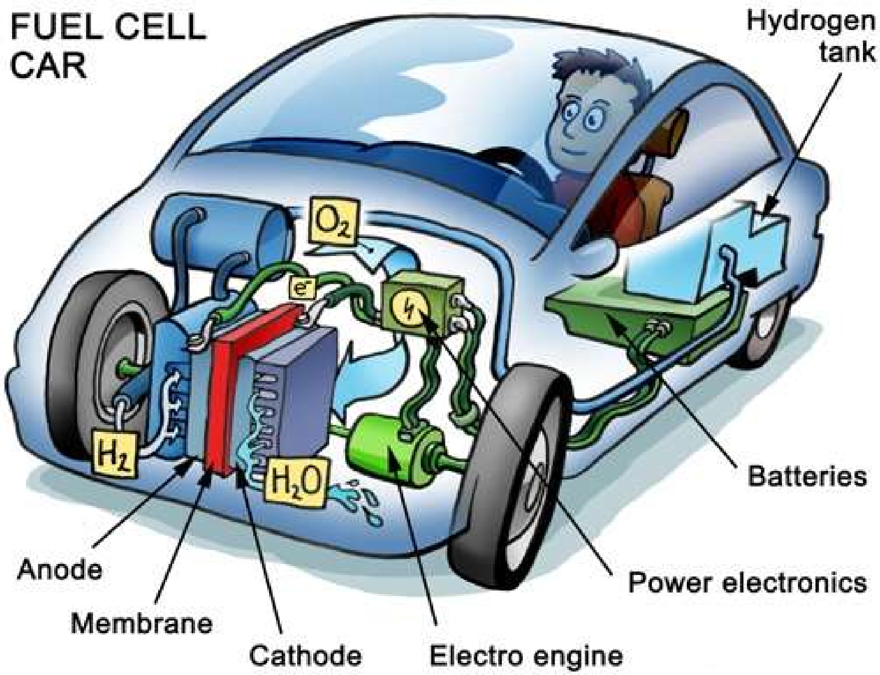
Inverter

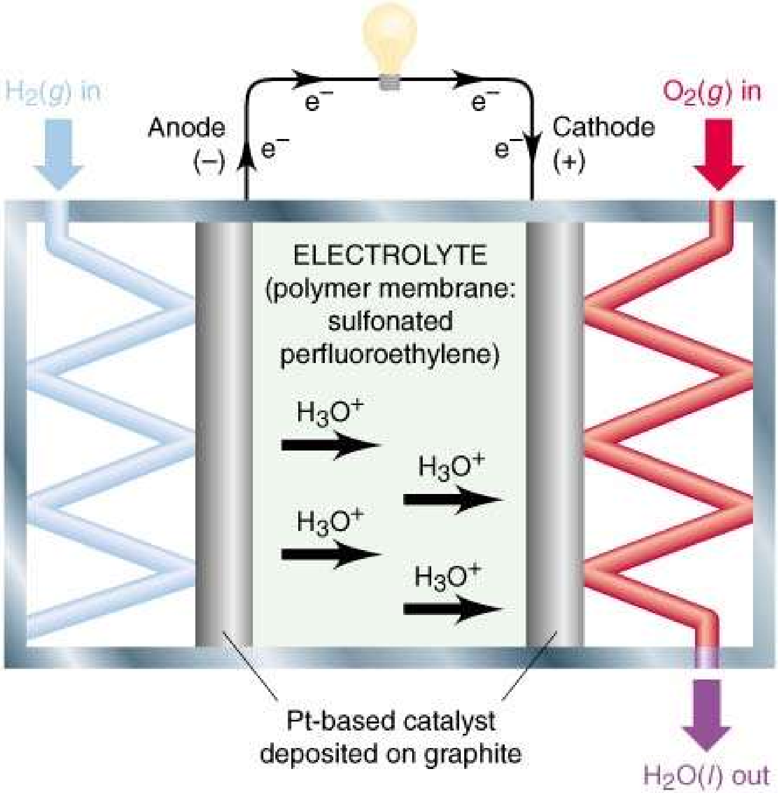
Fuel Cells

In a ***fuel cell***, also called a ***flow cell***, reactants enter the cell and products leave, generating electricity through controlled combustion.

Reaction rates are lower in fuel cells than in other batteries, so an ***electrocatalyst*** is used to decrease the activation energy.

Hydrogen fuel cell.





Anode (oxidation): $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$

Cathode (reduction): $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(g)$

Overall (cell) reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad E_{cell} = 1.2\ V$

The role of Metal Ions Biological Systems and Medicine

❑Metals play crucial roles in life processes. It is increasingly recognized that metals are involved in cellular and subcellular functions. With the application of new and sophisticated machines to study biological and biochemical systems the true role of inorganic salts in living systems can be revealed.
Inorganic chemistry is not the "Dead Chemistry" that some people may think. **Today, it is known that metals are important ingredients in life, just as the organic molecules.** For instance, the **divalent magnesium and calcium ions** play important regulatory roles in cells. Metallothionins are proteins rich in metal ions found in living systems. **The divalent cations Zn^{2+}, Ca^{2+} and Mg^{2+} prevent cytotoxicity** and *in vivo* antagonize Cd-induced carcinogenesis. **Lack of body iron is common in cancer patients** and it is associated with complications in surgery and in animal experiments.
The transport of iron and other metal ions by the blood plasma is achieved through the formation of protein complexes. Copper is recognized as an essential metalloelement and is primarily associated with copper-dependent cellular enzymes. **Metals are also used as inorganic drugs for many diseases**.
The cisplatin (*cis*-$Pt(NH_3)_2Cl_2$) is the first member of a new class of potent antitumor drugs belonging to metal coordination complexes which are being introduced in Medicine.

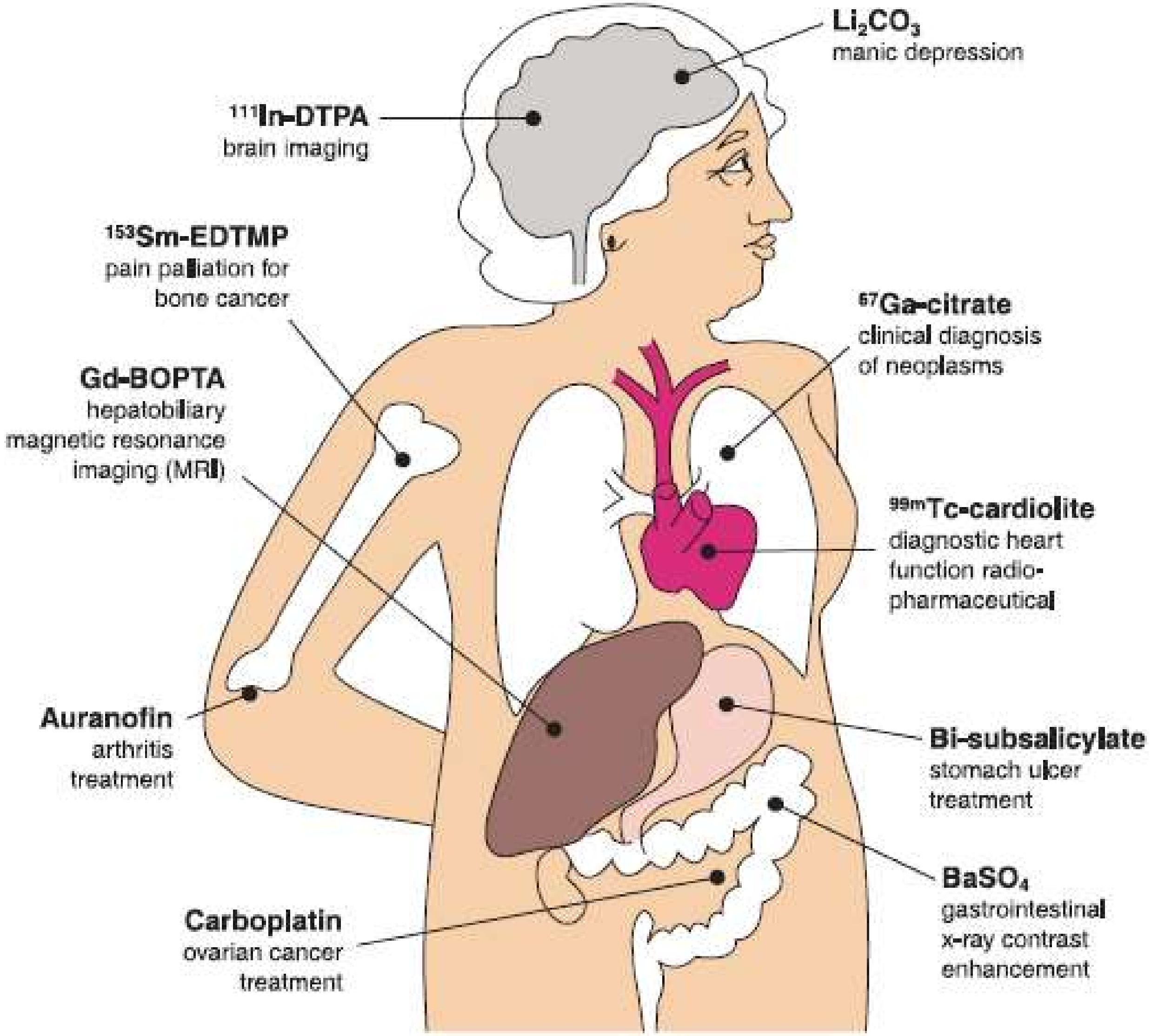


Fig. 1. Metal ions are important in diagnosis and therapy of a host of different human pathologies. Gd, ^{111}In, and ^{99m}Tc are used in medical imaging; ^{153}Sm and Au to relieve pain in bone cancer and arthritis, respectively; Bi to soothe upset stomach; and Li to calm bipolar psychosis. ^{67}Ga-citrate is used in clinical diagnosis of neoplasms (by SPECT imaging), and Pt is used for cancer treatment.

SCIENCE VOL 300 9 MAY 2003

soda ash
windows
glassware
fiberglass
detergents

cobalt
paints
magnets
engines
tools

tungsten
lights blubs
light fixtures
stained glass
paints

iron
faucets
tools
magnets

silica
abrasive and blasting sand
ceramics
plastics
glass

aluminum
refrigerators
automobiles
cans

gypsum
concrete
wallboard

coal tar
shampoos
asphalt

fluorite
toothpaste
paint pigments

feldspar
plates
glassware
paper

vermiculite
fire-protection boards
wallboard
fertilizers
ceramics

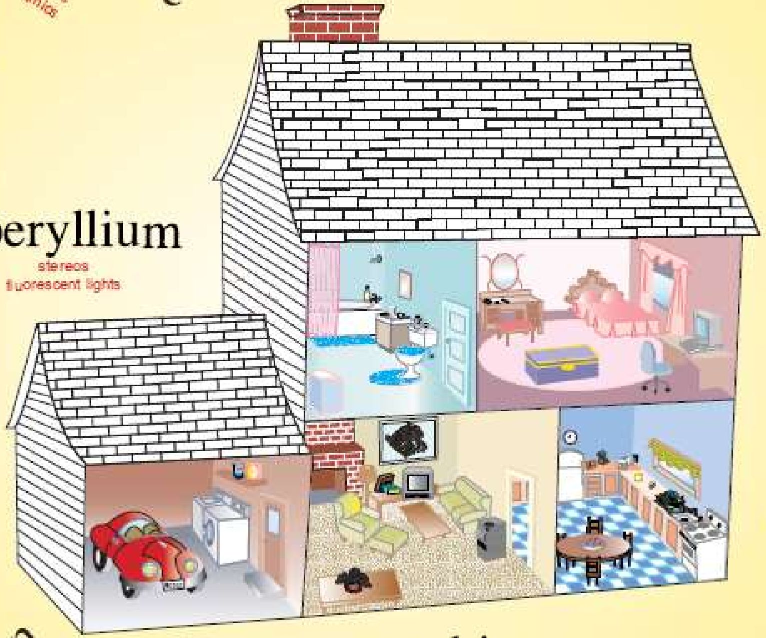
sand & gravel
concrete products
fill material
bricks
asphalt

sulfur
paints
fertilizers
rubber products

silver
photographic materials
mirrors
wiring
jewelry

zeolites
soil additives
water softeners
cat litter

gold
stereo components
jewelry
telephones
electronic components



titanium
white paints
toothpaste
enamel finishes

beryllium
stereos
fluorescent lights

petroleum products
plastics
automotive parts
natural gas
gasoline for cars

micas
lipstick
bricks
insulation for electrical motors
paints

halite
salts
ceramics
de-icing agents

boron
glass
insulation
soaps and detergents

chromium
toasters
car bumpers
stainless steel

zinc
washing machines
galvanized steel
cameras
coins

calcium carbonate
wallboard
concrete products
toothpaste
glass
paper and paints

coal
steel production
electricity
synthetic fabrics

graphite
pencils
refractory bricks
lubricants
fuel cells/batteries

molybdenum
lamps and fixtures
alloy wheels

copper
stoves
wiring
brass fixtures
plumbing
coins

lithium
ceramics
lubricants
batteries

clays
porcelain
sinks
bricks
paper

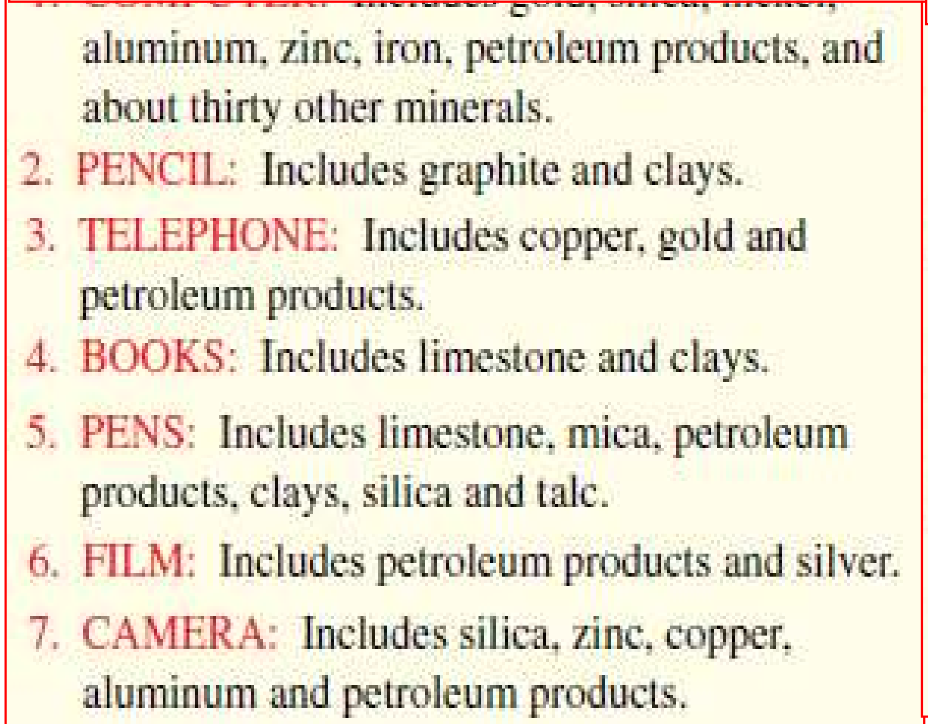
lead
electronic components
television screens
batteries

nickel
clocks
stainless steel
copper-nickel alloys

barium
spark plugs
rubber products
glass and plastics

1. DEODORANT: Includes aluminum and the container is made of petroleum products.
2. TOOTH PASTE: Includes fluorite, barite and calcite. The container is made of petroleum products or aluminum.
3. DRINKING GLASSES: Includes feldspar, silica and soda ash.
4. ABRASIVE CLEANSER: Includes silica or calcite.
5. LIPSTICK AND MAKEUP: Includes clay, mica, talc, limestone and petroleum products.
6. PLUMBING: Made of copper, clay and petroleum products.
7. RUGS: Includes limestone, petroleum products and selenium.

8. PLASTIC SHOWER CURTAINS: Contains petroleum products.
9. FLOWER POT: Made of clays and metallic minerals for pigments in glaze.
10. TALCUM POWDER: Contains talc and mica.
11. DANDRUFF SHAMPOO: Includes coal tar, lithium clays and selenium. The container is made of petroleum products.
12. MIRROR: Includes feldspar, silica and silver.
13. FAUCETS: Includes iron, nickel and chromium.
14. TILES: Made of clay, feldspar, wollastonite or talc, mineral pigments.
15. TOILET: Includes clays, silica, copper, zinc, petroleum products and borates.



aluminum, zinc, iron, petroleum products, and about thirty other minerals.

2. PENCIL: Includes graphite and clays.
3. TELEPHONE: Includes copper, gold and petroleum products.
4. BOOKS: Includes limestone and clays.
5. PENS: Includes limestone, mica, petroleum products, clays, silica and talc.
6. FILM: Includes petroleum products and silver.
7. CAMERA: Includes silica, zinc, copper, aluminum and petroleum products.

products.

9. TELEVISION: Includes aluminum, copper, iron, nickel, silica, rare earths, and strontium.
10. STEREO: Includes gold, iron, nickel, beryllium and petroleum products.
11. COMPACT DISC: Includes aluminum and petroleum products.
12. METAL CHEST: Includes iron and nickel. The brass trim is made of copper and zinc.
13. CARPET: Includes limestone, petroleum products and selenium.

MINERAL COMMODITIES

CONSTRUCTION AND MANUFACTURING MATERIALS

CONSTRUCTION MATERIALS

- concrete products
- crushed stone
- sand and gravel

DIMENSION STONE

- granite
- limestone
- marble
- sandstone
- slate

FILLERS, EXTENDERS, PIGMENTS, AND FILTERS

- asbestos
- barium
- calcium carbonate
- clays
- fluorite
- gypsum
- micas
- talc
- vermiculite
- zeolites

ABRASIVE AND REFRACTORY MATERIALS

- clays
- graphite
- silica sand

RAW MATERIALS FOR MAKING GLASS

- boron
- feldspar
- lithium
- silica
- soda ash

PRECIOUS METALS AND ELEMENTS

- gold
- platinum-group elements
- silver

NONFERROUS METALS

LIGHT METALS

- aluminum
- beryllium
- magnesium
- titanium

BASE METALS

- copper
- lead
- zinc

ENERGY RESOURCES (FOSSIL FUELS)

- coal
- coal tar
- natural gas
- oil shale
- petroleum and its products
- tar sand

IRON AND FERROALLOYS

- chromium
- cobalt
- ferroalloy metals
- iron
- manganese
- molybdenum
- nickel
- tungsten

FERTILIZER AND CHEMICAL INDUSTRIAL MATERIALS

- limestone, dolomite, and lime
- lithium
- nitrogen compounds and nitrate
- phosphate
- potash
- salts
- sulfur

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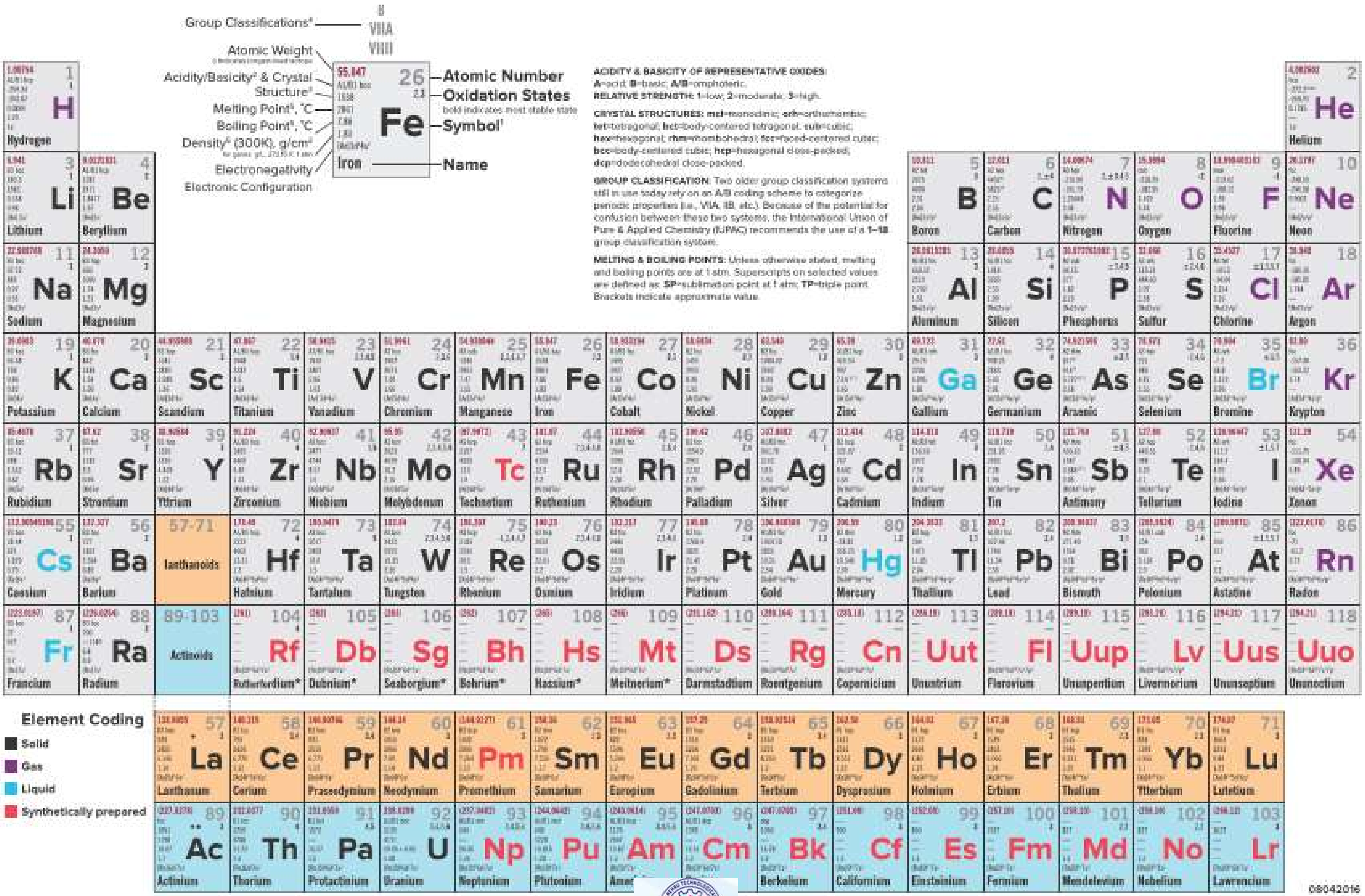
[1] Kesler, S.E., 1994, Mineral resources, economics, and the environment: New York, Macmillian College Publishing Company, Inc., 391 p.



Group Classifications* — 8 / VIIIA / VIIII

Atomic Weight

Acidity/Basicity & Crystal Structure

Melting Point, °C

Boiling Point, °C

Density (300K), g/cm³

Electronegativity

Electronic Configuration

Atomic Number

Oxidation States
bold indicates most stable state

Symbol

Name

ACIDITY & BASICITY OF REPRESENTATIVE OXIDES: **A**=acid; **B**=basic; **A/B**=amphoteric.
RELATIVE STRENGTH: **1**=low; **2**=moderate; **3**=high.

CRYSTAL STRUCTURES: **mcl**=monoclinic; **orh**=orthorhombic; **tet**=tetragonal; **bct**=body-centered tetragonal; **cub**=cubic; **hex**=hexagonal; **rhm**=rhombohedral; **fcc**=faced-centered cubic; **bcc**=body-centered cubic; **hcp**=hexagonal close-packed; **dcp**=dodecahedral close-packed.

GROUP CLASSIFICATION: Two older group classification systems still in use today rely on an A/B coding scheme to categorize periodic properties (i.e., VIIA, IB, etc.). Because of the potential for confusion between these two systems, the International Union of Pure & Applied Chemistry (IUPAC) recommends the use of a **1–18** group classification system.

MELTING & BOILING POINTS: Unless otherwise stated, melting and boiling points are at 1 atm. Superscripts on selected values are defined as: **SP**=sublimation point at 1 atm; **TP**=triple point. Brackets indicate approximate value.

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57-71 lanthanoids	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89-103 Actinoids	104 Rf Rutherfordium*	105 Db Dubnium*	106 Sg Seaborgium*	107 Bh Bohrium*	108 Hs Hassium*	109 Mt Meitnerium*	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium

57 La * Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
89 Ac ** Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Amer	96 Cm	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

Element Coding

- ■ Solid
- ■ Gas
- ■ Liquid
- ■ Synthetically prepared

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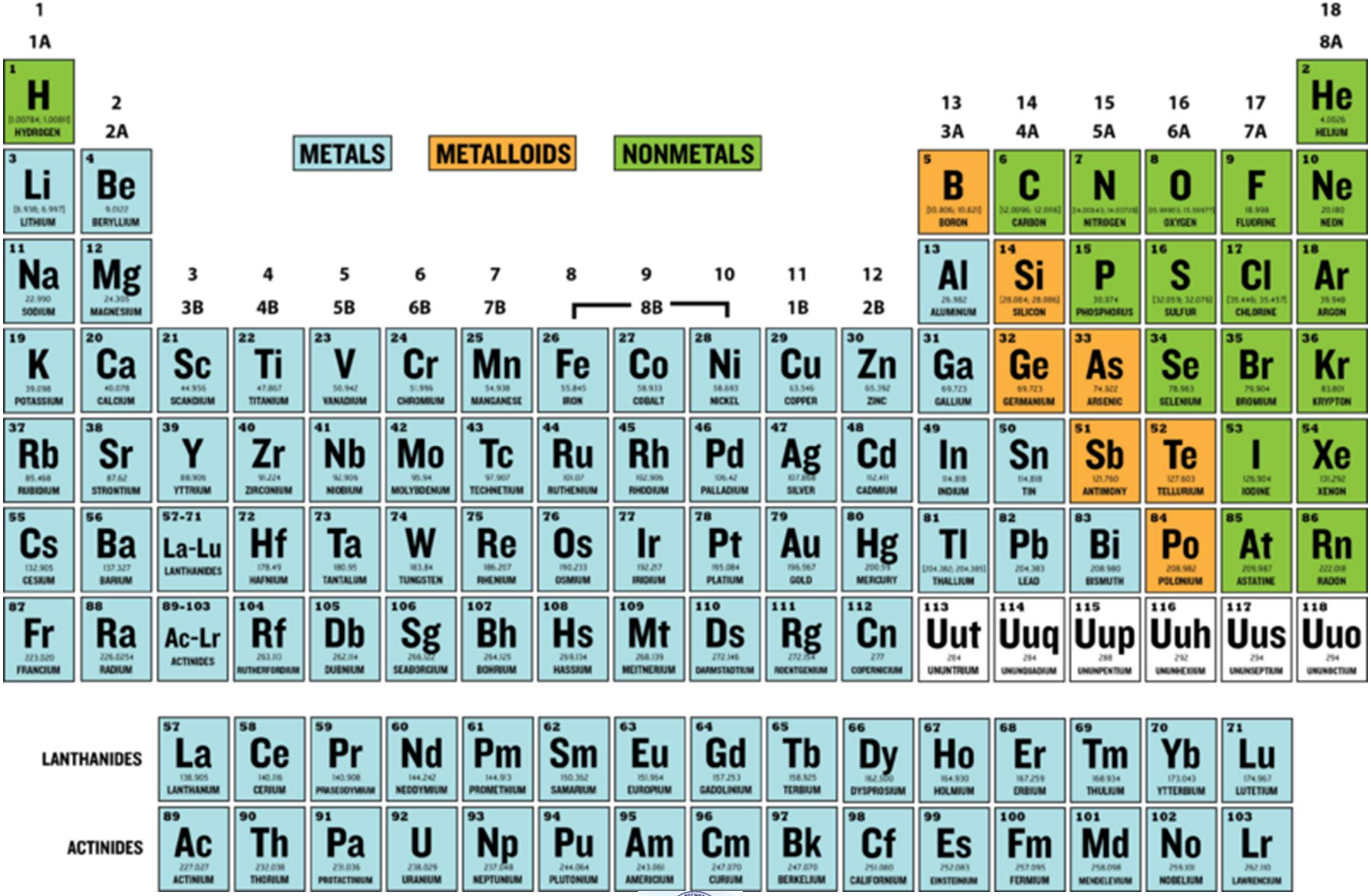
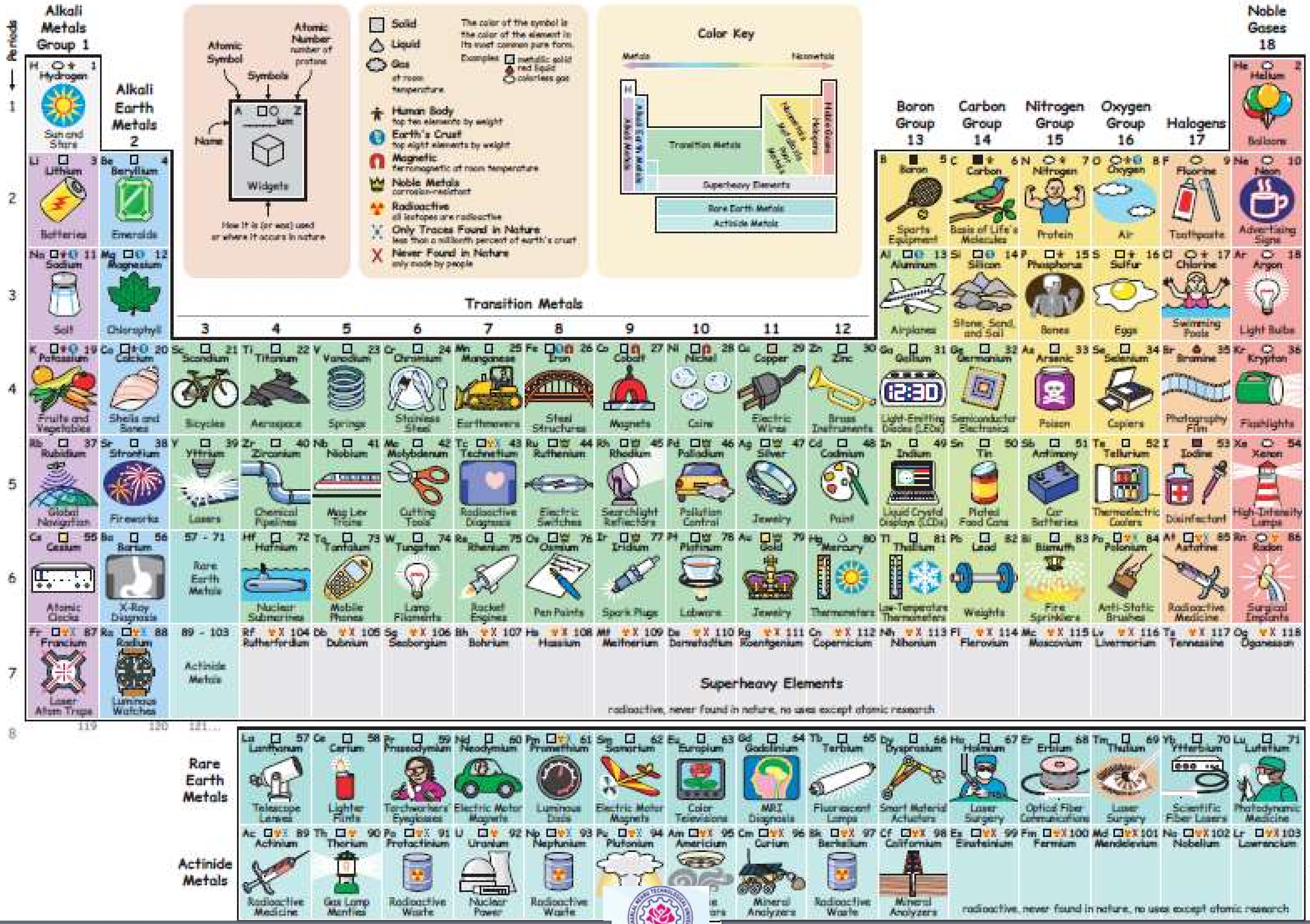


METALS METALLOIDS NONMETALS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H [1.00784; 1.00811] HYDROGEN																	2 He 4.0026 HELIUM
3 Li [6.938; 6.997] LITHIUM	4 Be 9.0122 BERYLLIUM											5 B [10.806; 10.821] BORON	6 C [12.0096; 12.0116] CARBON	7 N [14.00643; 14.00728] NITROGEN	8 O [15.99903; 15.99977] OXYGEN	9 F 18.998 FLUORINE	10 Ne 20.180 NEON
11 Na 22.990 SODIUM	12 Mg 24.305 MAGNESIUM											13 Al 26.982 ALUMINUM	14 Si [28.084; 28.086] SILICON	15 P 30.974 PHOSPHORUS	16 S [32.059; 32.076] SULFUR	17 Cl [35.446; 35.457] CHLORINE	18 Ar 39.948 ARGON
19 K 39.098 POTASSIUM	20 Ca 40.078 CALCIUM	21 Sc 44.956 SCANDIUM	22 Ti 47.867 TITANIUM	23 V 50.942 VANADIUM	24 Cr 51.996 CHROMIUM	25 Mn 54.938 MANGANESE	26 Fe 55.845 IRON	27 Co 58.933 COBALT	28 Ni 58.693 NICKEL	29 Cu 63.546 COPPER	30 Zn 65.392 ZINC	31 Ga 69.723 GALLIUM	32 Ge 69.723 GERMANIUM	33 As 74.922 ARSENIC	34 Se 78.963 SELENIUM	35 Br 79.904 BROMIUM	36 Kr 83.801 KRYPTON
37 Rb 85.468 RUBIDIUM	38 Sr 87.62 STRONTIUM	39 Y 88.906 YTTRIUM	40 Zr 91.224 ZIRCONIUM	41 Nb 92.906 NIOBIUM	42 Mo 95.94 MOLYBDENUM	43 Tc 97.907 TECHNETIUM	44 Ru 101.07 RUTHENIUM	45 Rh 102.906 RHODIUM	46 Pd 106.42 PALLADIUM	47 Ag 107.868 SILVER	48 Cd 112.411 CADMIUM	49 In 114.818 INDIUM	50 Sn 114.818 TIN	51 Sb 121.760 ANTIMONY	52 Te 127.603 TELLURIUM	53 I 126.904 IODINE	54 Xe 131.292 XENON
55 Cs 132.905 CESIUM	56 Ba 137.327 BARIUM	57-71 La-Lu LANTHANIDES	72 Hf 178.49 HAFNIUM	73 Ta 180.95 TANTALUM	74 W 183.84 TUNGSTEN	75 Re 186.207 RHENIUM	76 Os 190.233 OSMIUM	77 Ir 192.217 IRIDIUM	78 Pt 195.084 PLATIUM	79 Au 196.967 GOLD	80 Hg 200.59 MERCURY	81 Tl [204.382; 204.385] THALLIUM	82 Pb 204.383 LEAD	83 Bi 208.980 BISMUTH	84 Po 208.982 POLONIUM	85 At 209.987 ASTATINE	86 Rn 222.018 RADON
87 Fr 223.020 FRANCIUM	88 Ra 226.0254 RADIUM	89-103 Ac-Lr ACTINIDES	104 Rf 263.113 RUTHERFORDIUM	105 Db 262.114 DUBNIUM	106 Sg 266.122 SEABORGIUM	107 Bh 264.125 BOHRIUM	108 Hs 269.134 HASSIUM	109 Mt 268.139 MEITNERIUM	110 Ds 272.146 DARMSTADTIUM	111 Rg 272.154 ROENTGENIUM	112 Cn 277 COPERNICIUM	113 Uut 284 UNUNTRIUM	114 Uuq 284 UNUNQUADIUM	115 Uup 288 UNUNPENTIUM	116 Uuh 292 UNUNHEXIUM	117 Uus 294 UNUNSEPTIUM	118 Uuo 294 UNUNOCTIUM
LANTHANIDES		57 La 138.905 LANTHANUM	58 Ce 140.116 CERIUM	59 Pr 140.908 PRASEODYMIUM	60 Nd 144.242 NEODYMIUM	61 Pm 144.913 PROMETHIUM	62 Sm 150.362 SAMARIUM	63 Eu 151.964 EUROPIUM	64 Gd 157.253 GADOLINIUM	65 Tb 158.925 TERBIUM	66 Dy 162.500 DYSPROSIUM	67 Ho 164.930 HOLMIUM	68 Er 167.259 ERBIUM	69 Tm 168.934 THULIUM	70 Yb 173.043 YTTERBIUM	71 Lu 174.967 LUTETIUM	
ACTINIDES		89 Ac 227.027 ACTINIUM	90 Th 232.038 THORIUM	91 Pa 231.036 PROTACTINIUM	92 U 238.029 URANIUM	93 Np 237.048 NEPTUNIUM	94 Pu 244.064 PLUTONIUM	95 Am 243.061 AMERICIUM	96 Cm 247.070 CURIUM	97 Bk 247.070 BERKELIUM	98 Cf 251.080 CALIFORNIUM	99 Es 252.083 EINSTEINIUM	100 Fm 257.095 FERMIUM	101 Md 258.098 MENDELEVIUM	102 No 259.101 NOBELIUM	103 Lr 262.110 LAWRENCIUM	



Periods	Alkali Metals Group 1	Alkali Earth Metals 2	3	4	5	6	7	8	9	10	11	12	Boron Group 13	Carbon Group 14	Nitrogen Group 15	Oxygen Group 16	Halogens 17	Noble Gases 18	
1	H 1 Hydrogen Sun and Stars																	He 2 Helium Balloons	1
2	Li 3 Lithium Batteries	Be 4 Beryllium Emeralds											B 5 Boron Sports Equipment	C 6 Carbon Basis of Life's Molecules	N 7 Nitrogen Protein	O 8 Oxygen Air	F 9 Fluorine Toothpaste	Ne 10 Neon Advertising Signs	2
3	Na 11 Sodium Salt	Mg 12 Magnesium Chlorophyll											Al 13 Aluminum Airplanes	Si 14 Silicon Stone, Sand, and Soil	P 15 Phosphorus Bones	S 16 Sulfur Eggs	Cl 17 Chlorine Swimming Pools	Ar 18 Argon Light Bulbs	3
4	K 19 Potassium Fruits and Vegetables	Ca 20 Calcium Shells and Bones	Sc 21 Scandium Bicycles	Ti 22 Titanium Aerospace	V 23 Vanadium Springs	Cr 24 Chromium Stainless Steel	Mn 25 Manganese Earthmovers	Fe 26 Iron Steel Structures	Co 27 Cobalt Magnets	Ni 28 Nickel Coins	Cu 29 Copper Electric Wires	Zn 30 Zinc Brass Instruments	Ga 31 Gallium Light-Emitting Diodes (LEDs)	Ge 32 Germanium Semiconductor Electronics	As 33 Arsenic Poison	Se 34 Selenium Copiers	Br 35 Bromine Photography Film	Kr 36 Krypton Flashlights	4
5	Rb 37 Rubidium Global Navigation	Sr 38 Strontium Fireworks	Y 39 Yttrium Lasers	Zr 40 Zirconium Chemical Pipelines	Nb 41 Niobium Mag Lev Trains	Mo 42 Molybdenum Cutting Tools	Tc 43 Technetium Radioactive Diagnosis	Ru 44 Ruthenium Electric Switches	Rh 45 Rhodium Searchlight Reflectors	Pd 46 Palladium Pollution Control	Ag 47 Silver Jewelry	Cd 48 Cadmium Paint	In 49 Indium Liquid Crystal Displays (LCDs)	Sn 50 Tin Plated Food Cans	Sb 51 Antimony Car Batteries	Te 52 Tellurium Thermoelectric Coolers	I 53 Iodine Disinfectant	Xe 54 Xenon High-Intensity Lamps	5
6	Cs 55 Cesium Atomic Clocks	Ba 56 Barium X-Ray Diagnosis	57 - 71 Rare Earth Metals	Hf 72 Hafnium Nuclear Submarines	Ta 73 Tantalum Mobile Phones	W 74 Tungsten Lamp Filaments	Re 75 Rhenium Rocket Engines	Os 76 Osmium Pen Points	Ir 77 Iridium Spark Plugs	Pt 78 Platinum Labware	Au 79 Gold Jewelry	Hg 80 Mercury Thermometers	Tl 81 Thallium Low-Temperature Thermometers	Pb 82 Lead Weights	Bi 83 Bismuth Fire Sprinklers	Po 84 Polonium Anti-Static Brushes	At 85 Astatine Radioactive Medicine	Rn 86 Radon Surgical Implants	6
7	Fr 87 Francium Laser Atom Traps	Ra 88 Radium Luminous Watches	89 - 103 Actinide Metals	Rf 104 Rutherfordium	Db 105 Dubnium	Sg 106 Seaborgium	Bh 107 Bohrium	Hs 108 Hassium	Mt 109 Meitnerium	Ds 110 Darmstadtium	Rg 111 Roentgenium	Cn 112 Copernicium	Nh 113 Nihonium	Fl 114 Flerovium	Mc 115 Moscovium	Lv 116 Livermorium	Ts 117 Tennessine	Og 118 Oganesson	7
8	119	120	121...																

Rare Earth Metals	La 57 Lanthanum Telescope Lenses	Ce 58 Cerium Lighter Flints	Pr 59 Praseodymium Torchworkers' Eyeglasses	Nd 60 Neodymium Electric Motor Magnets	Pm 61 Promethium Luminous Dials	Sm 62 Samarium Electric Motor Magnets	Eu 63 Europium Color Televisions	Gd 64 Gadolinium MRI Diagnosis	Tb 65 Terbium Fluorescent Lamps	Dy 66 Dysprosium Smart Material Actuators	Ho 67 Holmium Laser Surgery	Er 68 Erbium Optical Fiber Communications	Tm 69 Thulium Laser Surgery	Yb 70 Ytterbium Scientific Fiber Lasers	Lu 71 Lutetium Photodynamic Medicine	6
Actinide Metals	Ac 89 Actinium Radioactive Medicine	Th 90 Thorium Gas Lamp Mantles	Pa 91 Protactinium Radioactive Waste	U 92 Uranium Nuclear Power	Np 93 Neptunium Radioactive Waste	Pu 94 Plutonium	Am 95 Americium e ars	Cm 96 Curium Mineral Analyzers	Bk 97 Berkelium Radioactive Waste	Cf 98 Californium Mineral Analyzers	Es 99 Einsteinium	Fm 100 Fermium	Md 101 Mendelevium	No 102 Nobelium	Lr 103 Lawrencium	7

radioactive, never found in nature, no uses except atomic research

Thermodynamics and Kinetics are two important key role playing in corrosion

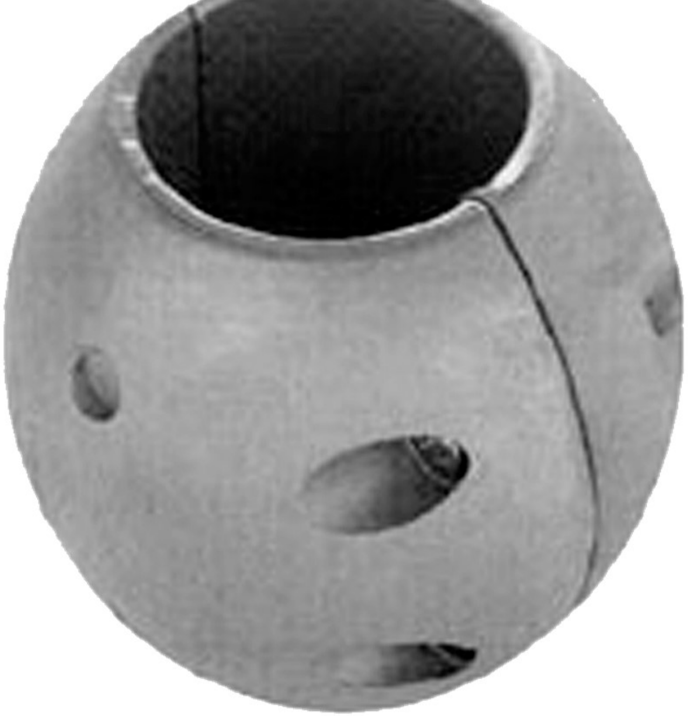
. Thermodynamics : which reactions will occur ?

. Kinetics : how fast these reactions will occur ?

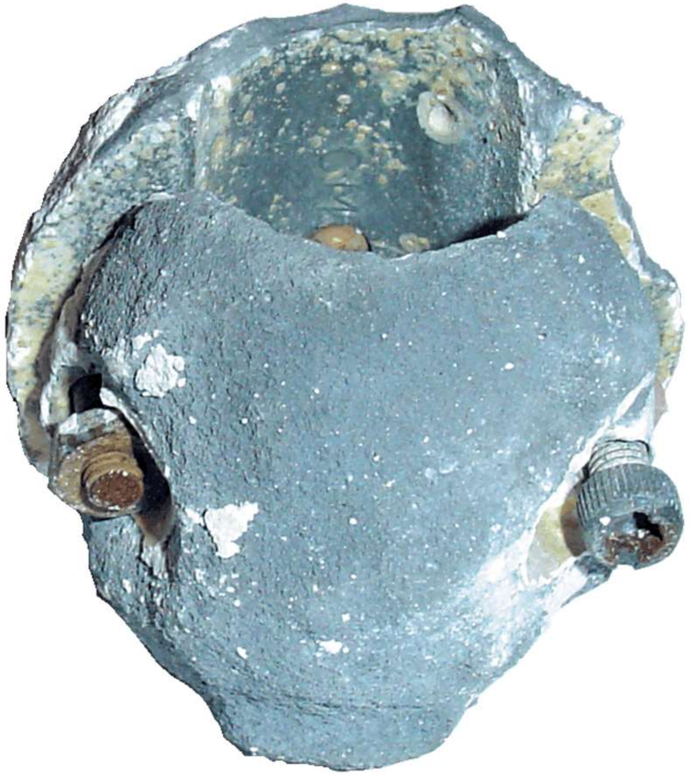
Iron + Oxygen + H_2O → Iron Oxide ***(brown color)***

Copper + Carbon di-Oxide +Air → Copper Carbonate ***(green color)***

Silver + Sulphur +Air → Silver Sulphide ***(black color)***



New Zinc
(for 1″ diameter shaft)



Old Zinc after 8 months
(for 1″ diameter shaft)

Aluminium Corrosion

The current trend for aluminium vehicles is not without problems. This aluminium alloy chassis member shows very advanced corrosion due to contact with road salt from gritting operations or use in coastal / beach regions.

"Corrosion" of Plastics

This dished end of a vessel is made of glass fibre reinforced PVC. Due to internal stresses and an aggressive environment it has suffered "environmental stress cracking".

S. NO	Material Type	Deterioration	Remarks
1	**Metals**	**Corrosion**	**More often we see in day to day life**
2	Polymers	Degradation/ Dissolution	Exposed to solvents
3	Ceramics	Swelling/Dissolution	Only at elevated temperatures or extreme environments
4	Glasses	Degradation/ Dissolution	Chemical Attack rather than electrochemical attack
5	Plastics	Degradation	Attack by solvents
6	Rubber	Corrosion	Attack by solid material (liquid metal corrosion)
7	Paint	Corrosion	

Attack of Environment on Materials

- Metals get oxidized
- Polymers react with oxygen and degrade
- Ceramic refractories may dissolved in contact with molten materials
- Materials may undergo irradiation damage

The degradation of Polymers

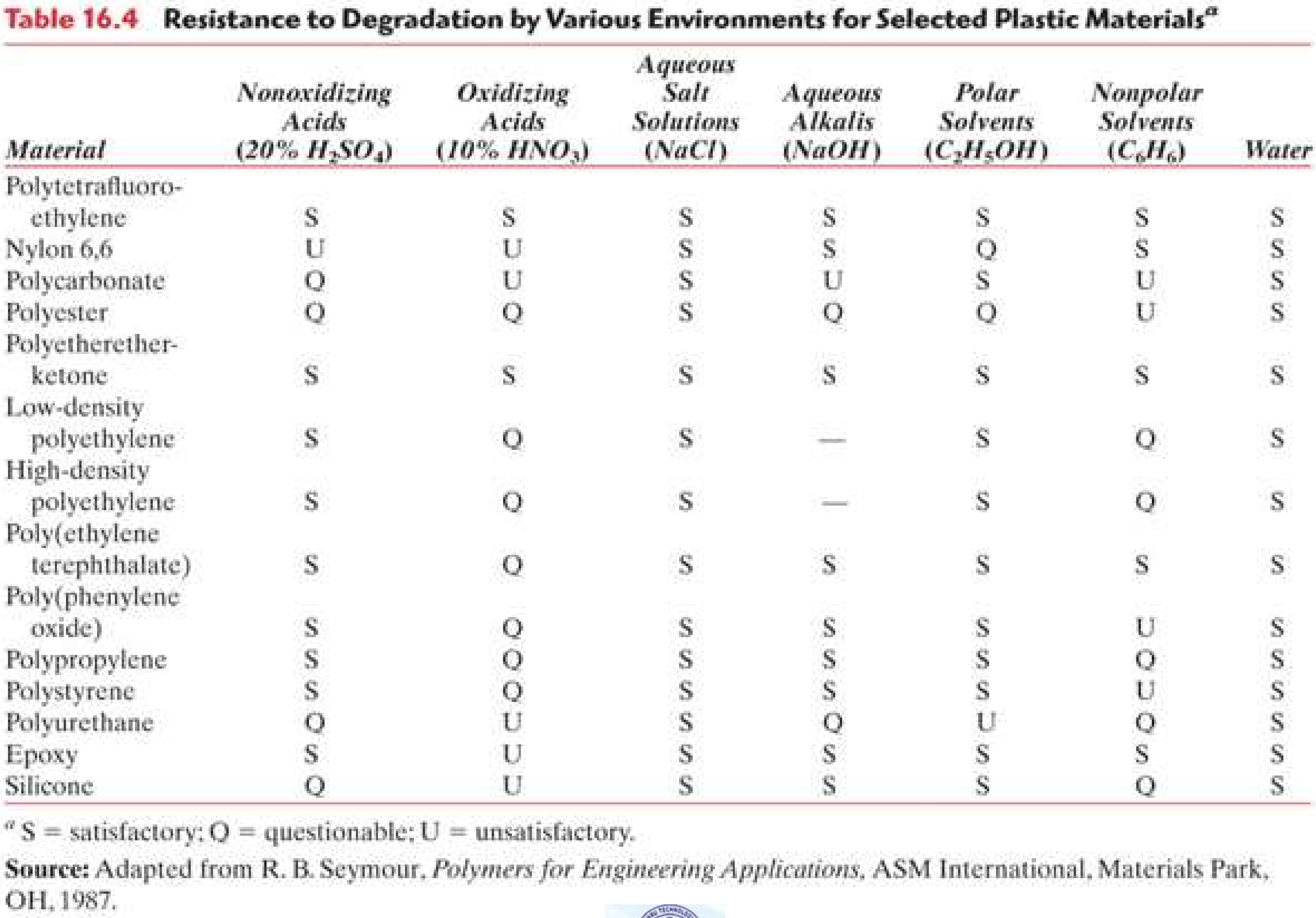


Table 16.4 **Resistance to Degradation by Various Environments for Selected Plastic Materials**[a]

Material	*Nonoxidizing Acids ($20\%\ H_2SO_4$)*	*Oxidizing Acids ($10\%\ HNO_3$)*	*Aqueous Salt Solutions ($NaCl$)*	*Aqueous Alkalis ($NaOH$)*	*Polar Solvents (C_2H_5OH)*	*Nonpolar Solvents (C_6H_6)*	*Water*
Polytetrafluoroethylene	S	S	S	S	S	S	S
Nylon 6,6	U	U	S	S	Q	S	S
Polycarbonate	Q	U	S	U	S	U	S
Polyester	Q	Q	S	Q	Q	U	S
Polyetheretherketone	S	S	S	S	S	S	S
Low-density polyethylene	S	Q	S	—	S	Q	S
High-density polyethylene	S	Q	S	—	S	Q	S
Poly(ethylene terephthalate)	S	Q	S	S	S	S	S
Poly(phenylene oxide)	S	Q	S	S	S	U	S
Polypropylene	S	Q	S	S	S	Q	S
Polystyrene	S	Q	S	S	S	U	S
Polyurethane	Q	U	S	Q	U	Q	S
Epoxy	S	U	S	S	S	S	S
Silicone	Q	U	S	S	S	Q	S

[a] S = satisfactory; Q = questionable; U = unsatisfactory.

Source: Adapted from R. B. Seymour, *Polymers for Engineering Applications*, ASM International, Materials Park, OH, 1987.

The degradation of Elastomers

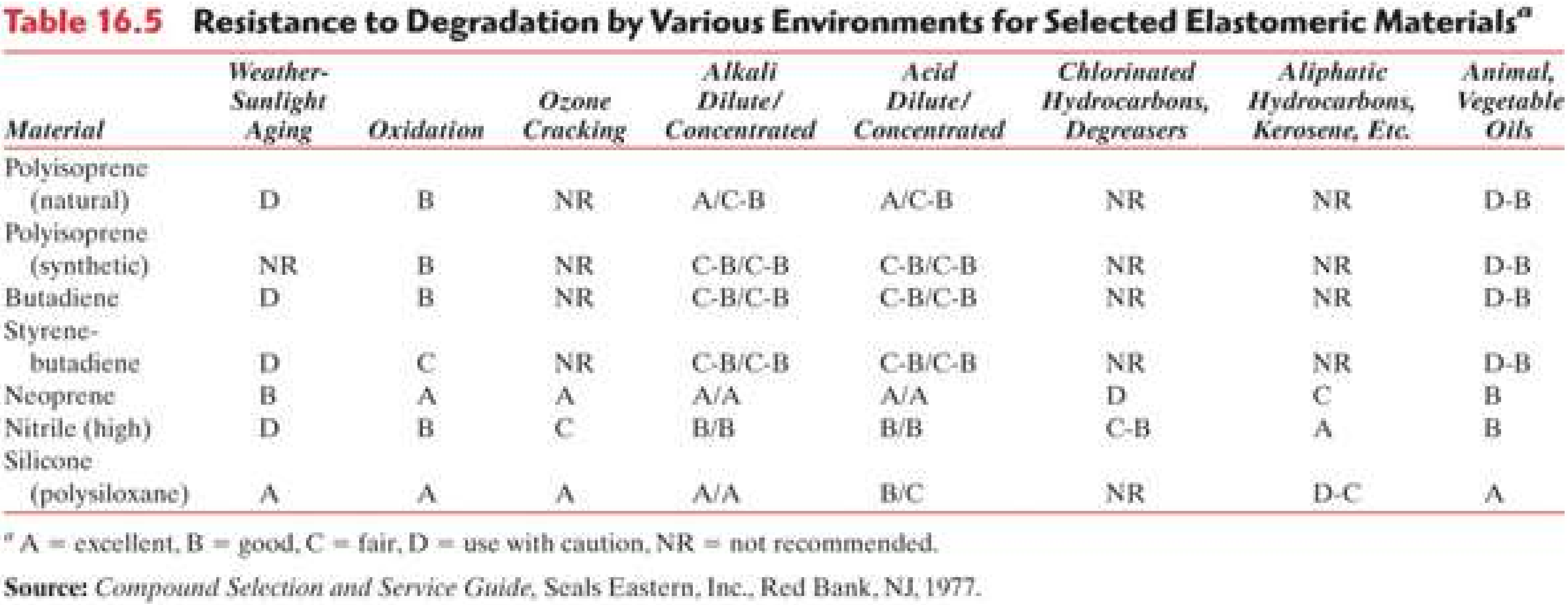


Table 16.5 **Resistance to Degradation by Various Environments for Selected Elastomeric Materials**[a]

Material	*Weather-Sunlight Aging*	*Oxidation*	*Ozone Cracking*	*Alkali Dilute/Concentrated*	*Acid Dilute/Concentrated*	*Chlorinated Hydrocarbons, Degreasers*	*Aliphatic Hydrocarbons, Kerosene, Etc.*	*Animal, Vegetable Oils*
Polyisoprene (natural)	D	B	NR	A/C-B	A/C-B	NR	NR	D-B
Polyisoprene (synthetic)	NR	B	NR	C-B/C-B	C-B/C-B	NR	NR	D-B
Butadiene	D	B	NR	C-B/C-B	C-B/C-B	NR	NR	D-B
Styrene-butadiene	D	C	NR	C-B/C-B	C-B/C-B	NR	NR	D-B
Neoprene	B	A	A	A/A	A/A	D	C	B
Nitrile (high)	D	B	C	B/B	B/B	C-B	A	B
Silicone (polysiloxane)	A	A	A	A/A	B/C	NR	D-C	A

[a] A = excellent, B = good, C = fair, D = use with caution, NR = not recommended.

Source: *Compound Selection and Service Guide*, Seals Eastern, Inc., Red Bank, NJ, 1977.

Cause of Corrosion

Barring a few metals, such as gold and platinum, much of them are found in nature as ores (oxide, sulfdes, etc.). So, considerable amount of energy is expended to convert these ores into respective metals. As a result, they remain at higher energy levels than their corresponding ores. Therefore, it is not surprising that most of these metals tend to go back to their low energy state (oxides, chlorides, sulfates, etc.) on exposure to chemical environments. Taking iron—a metal commonly used—as an example the above concept is illustrated in below Figure

At 500 °C

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

At 850 °C

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

At 1000 °C

$FeO + CO \rightarrow Fe + CO_2$

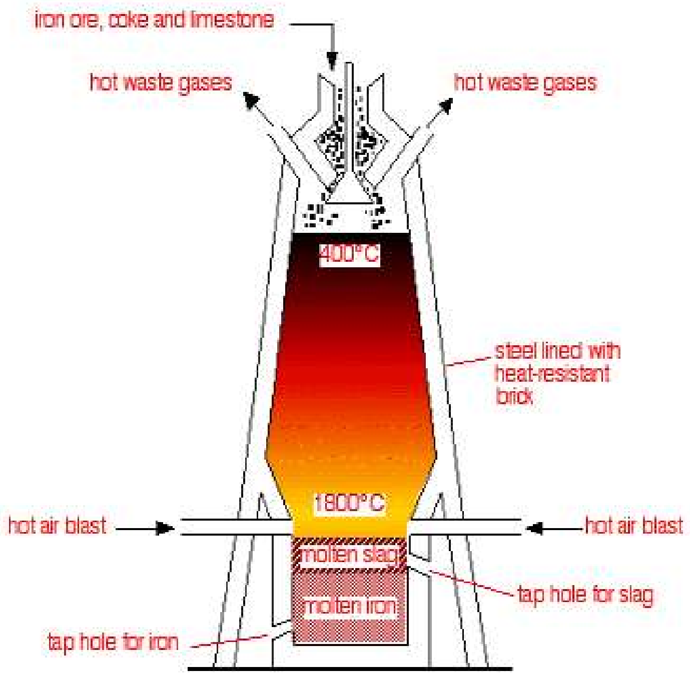
At 1300 °C

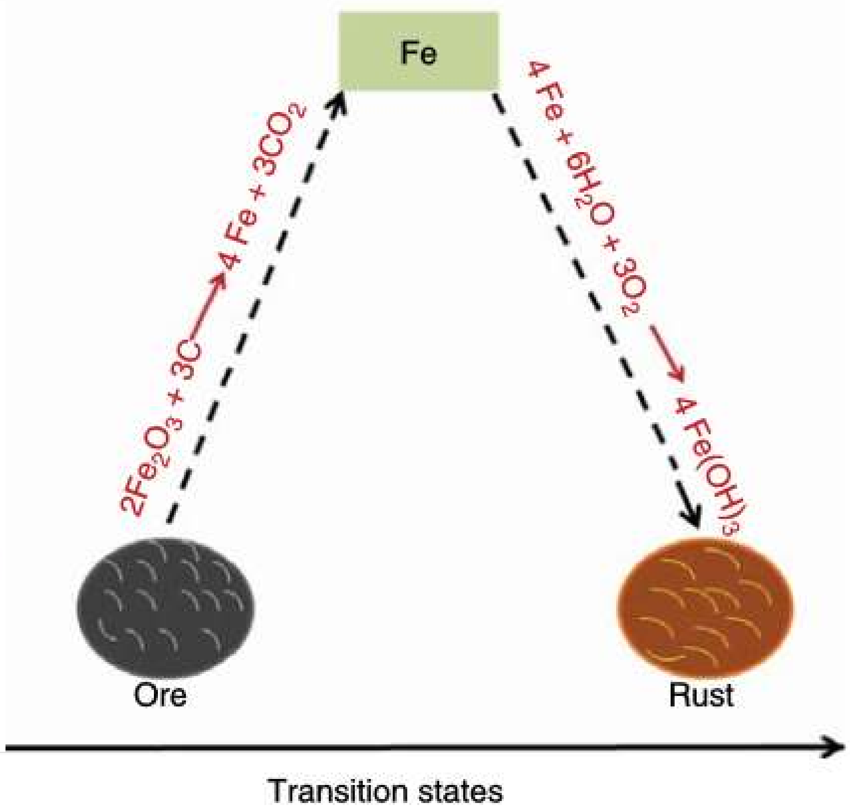
$CO_2 + C \rightarrow 2CO$

At 1900 °C

$C + O_2 \rightarrow CO_2$

$FeO + C \rightarrow Fe + CO$





$$\text{Ore of Metal} \xrightarrow[+\text{ Energy}]{\text{Metallurgical Process}} \text{Pure Metal} \xrightarrow{\text{Environment}} \text{Corroded Metal}$$

(Thermo dynamically stable state) (Thermodynamically unstable state) (More stable than Pure metal)

Corrosion Failures-VS Raja et.al

Oxidation - Reduction

- Anodic metal gives up electrons (oxidation or anodic reaction)

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

Increase in valence or a production of electrons

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

- Cathodic metal accepts electrons (reduction or cathodic reaction)

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

Decrease in valence or consumption of electrons

$$2H^{+} + 2e^{-} \rightarrow H_2(gas)$$

Usual Oxidation Reactions

$$\mathrm{Ag} \rightarrow \mathrm{Ag}^{+} + e$$

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

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

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

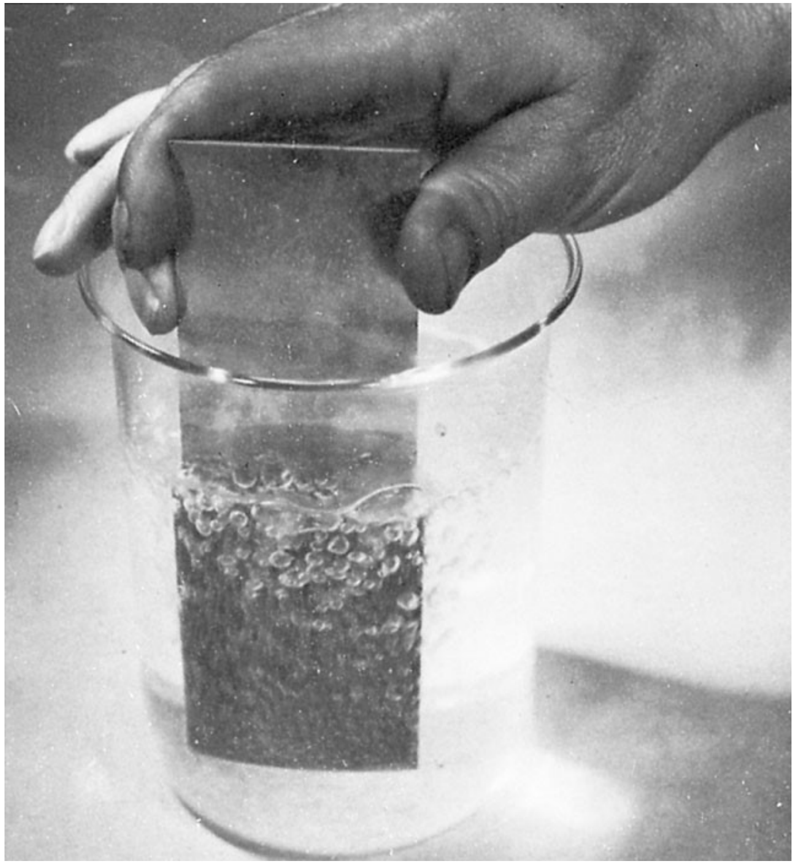
Usual Reduction Reactions

There are several different cathodic reactions that are frequently encountered in metallic corrosion. The most common are:

Hydrogen evolution	$2\mathrm{H}^{+} + 2e \rightarrow \mathrm{H}_2$	(2.4)
Oxygen reduction (acid solutions)	$\mathrm{O}_2 + 4\mathrm{H}^{+} + 4e \rightarrow 2\mathrm{H}_2\mathrm{O}$	(2.11)
Oxygen reduction (neutral or basic solutions)	$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4e \rightarrow 4\mathrm{OH}^{-}$	(2.12)
Metal ion reduction	$M^{3+} + e \rightarrow M^{2+}$	(2.13)
Metal deposition	$M^{+} + e \rightarrow M$	(2.14)

The electrochemical nature of corrosion can be illustrated by the attack on zinc by hydrochloric acid. When zinc is placed in dilute hydrochloric acid, a vigorous reaction occurs; hydrogen gas is evolved and the zinc dissolves, forming a solution of zinc chloride. The reaction is:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \qquad (2.1)$$



Oxidation (anodic reaction)* $\quad Zn \rightarrow Zn^{2+} + 2e \qquad (2.3)$
Reduction (cathodic reaction) $\quad 2H^+ + 2e \rightarrow H_2 \qquad (2.4)$

Noting that the chloride ion is not involved in the reaction, this equation can be written in the simplified form:

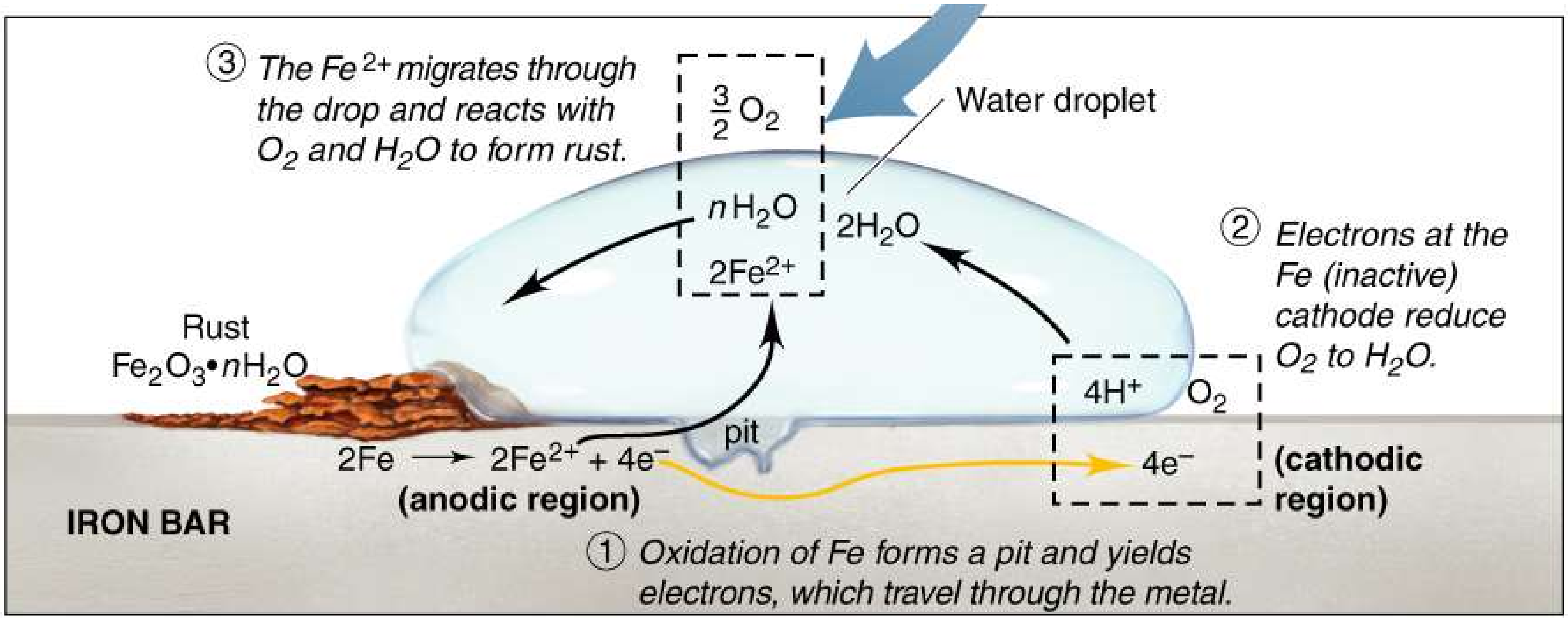
$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \qquad (2.2)$$

Hence, zinc reacts with the hydrogen ions of the acid solution to form zinc ions and hydrogen gas. Examining the above equation, it can be seen that during the reaction, zinc is oxidized to zinc ions and hydrogen ions are reduced to hydrogen. Thus Eq. (2.2) can be conveniently divided into two reactions, the oxidation of zinc and the reduction of hydrogen ions:

Oxidation (anodic reaction)* $Zn \rightarrow Zn^{2+} + 2e$ (2.3)
Reduction (cathodic reaction) $2H^+ + 2e \rightarrow H_2$ (2.4)

Oxidation and reduction must occur simultaneously and at the same rate on the metal surface. If this were not true, the metal would spontaneously become electrically charged, which is clearly impossible. This leads to one of the most important basic principles of corrosion: *during metallic corrosion, the rate of oxidation equals the rate of reduction* (in terms of electron production and consumption).

The mechanism of Iron (Fe) corrosion



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

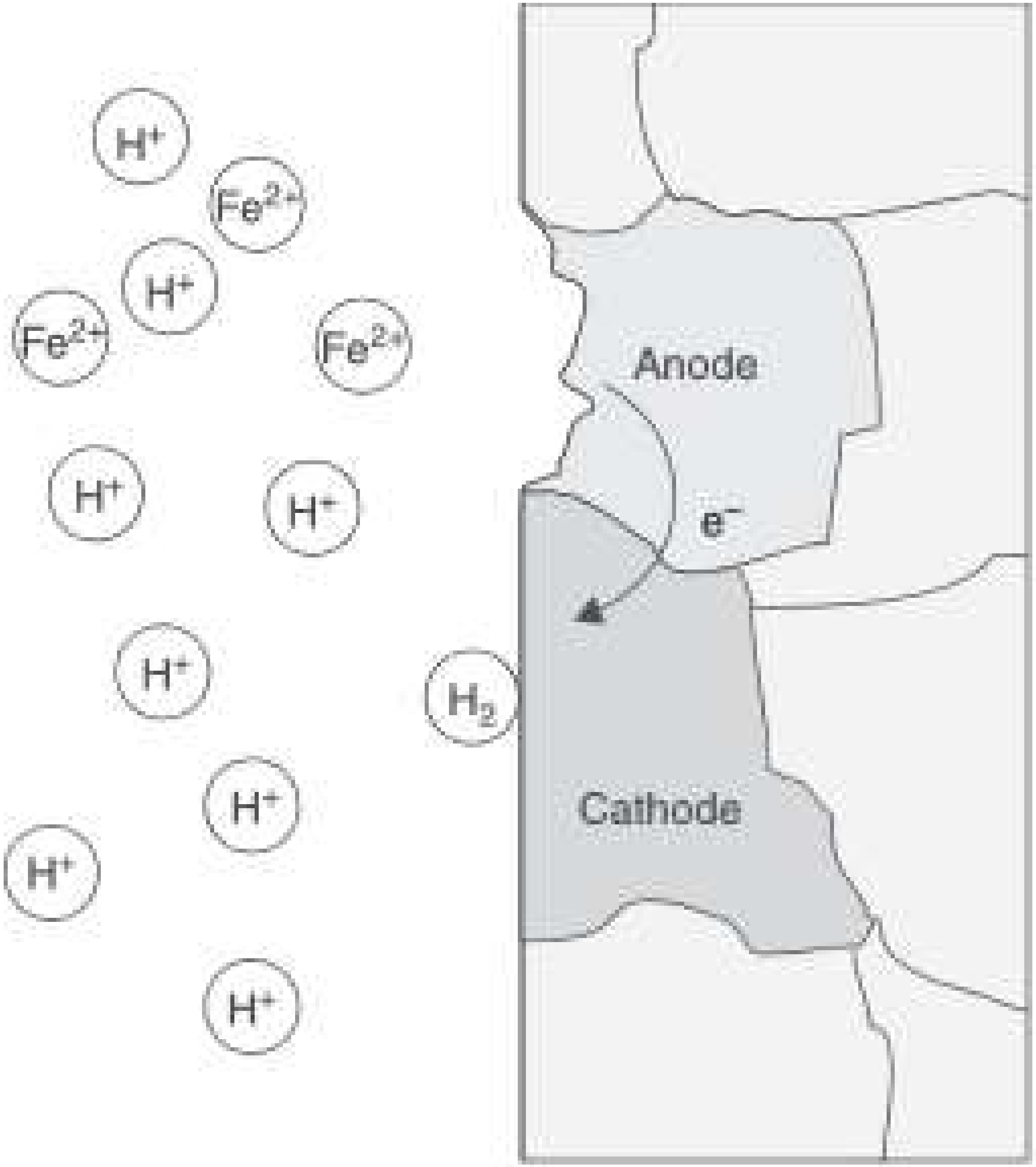
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$2Fe + O_2 + 2H_2O \rightarrow 4OH^- \rightarrow 2Fe(OH)_2 \downarrow$$

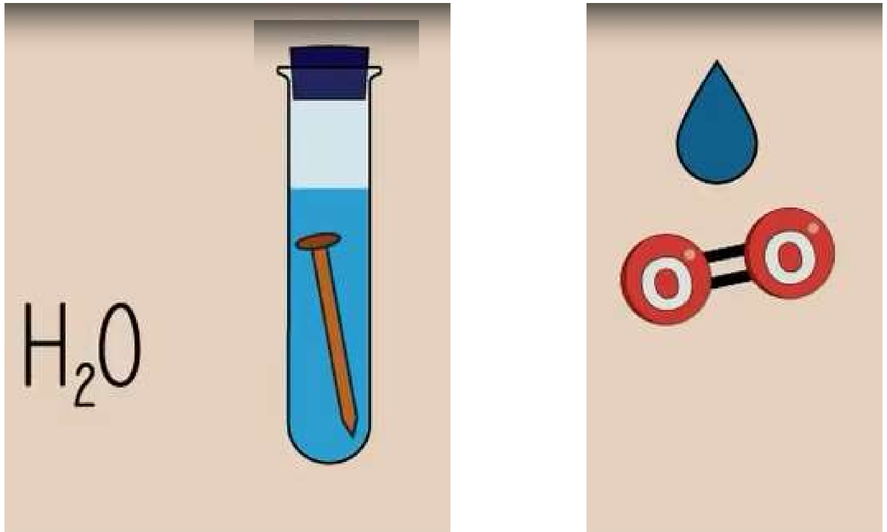
Ferrous hydroxide precipitates from solution. However, this compound is unstable in oxygenated solutions and is oxidized to the ferric salt:

$$2\,Fe\,(OH)_2 + H_2O + \frac{1}{2}O_2 \rightarrow 2\,Fe\,(OH)_3$$

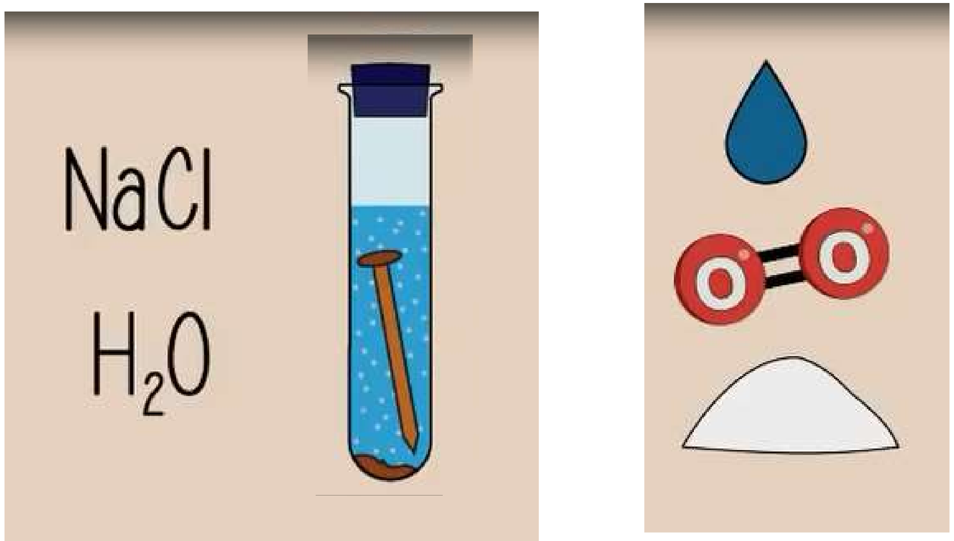
FIGURE 3.7
Formation of ions at an anodic area and release of hydrogen at a cathodic area in a local cell on an iron surface.



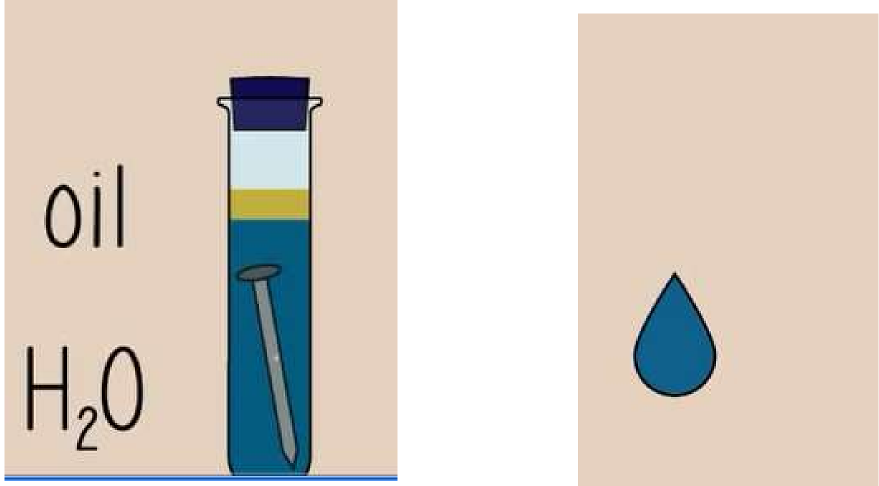
Small experiment to confirm the need of H_2O and O_2 for rusting of iron



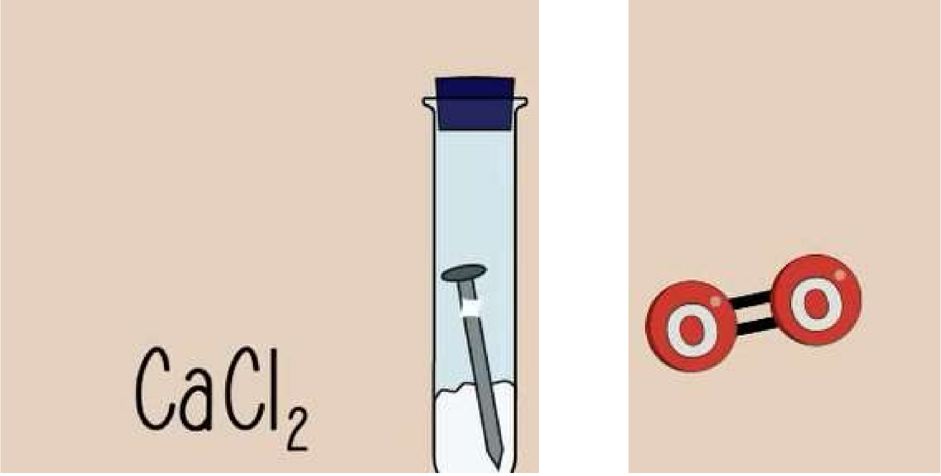
Case-I



Case-II



Case-III



Case-IV

Resistance of Common Electrolytes

Soils – High resistivity water reduces the corrosion rate, while low resistivity water increases the corrosion rate.

CLASSIFICATION	ELECTROLYTE RESISTIVITY (ohm-cm)	ANTICIPATED CORROSIVITY
Low Resistance	0 to 2,000	Severe
Medium	2,000 to 10,000	Moderate
High	10,000 to 30,000	Mild
Very High	Above 30,000	Increasingly Less

Water – Approximate resistivity values

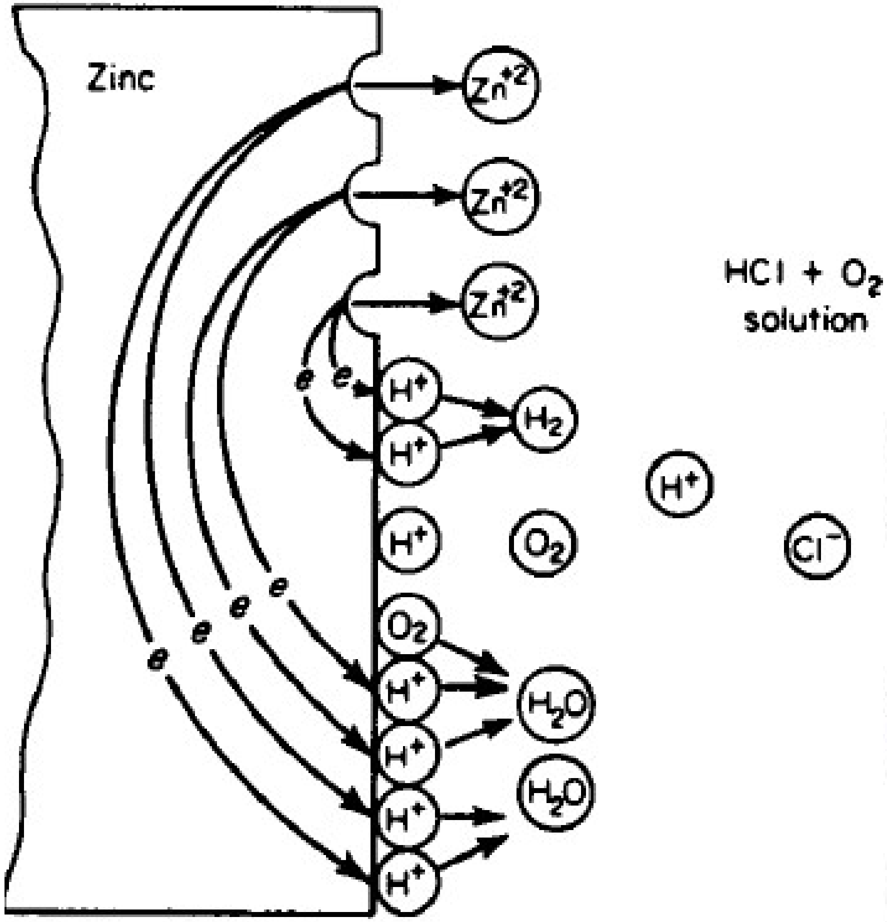
Water resistivity	Ohms-cm
open sea	20-25
seawater (coastal)	30-40
river water	500-10,000
tap water	1,000-10,000
rain water	20,000
distilled water	500,000
pure water	20,000,000

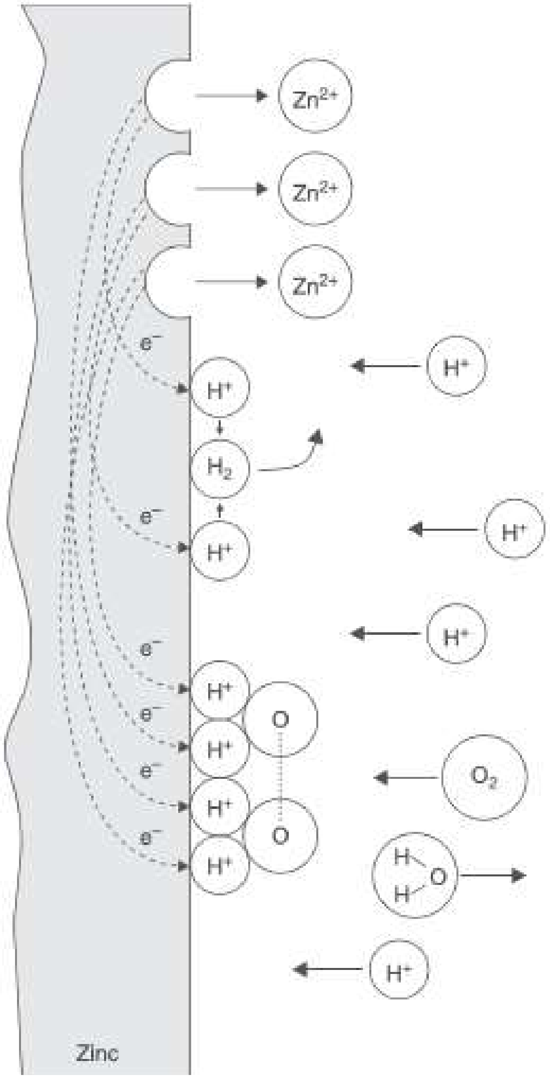
Weather also has a large effect on the rate of galvanic corrosion. In "harsher" environments (typically outdoors; highly humid; salty environments) a potential difference of ~0.15V is sufficient enough to cause galvanic corrosion. In what is considered to be a "normal" environment (storage places; warehouses; humidity-controlled areas) there should not be a potential difference of more than ~0.25V, otherwise galvanic corrosion can occur.

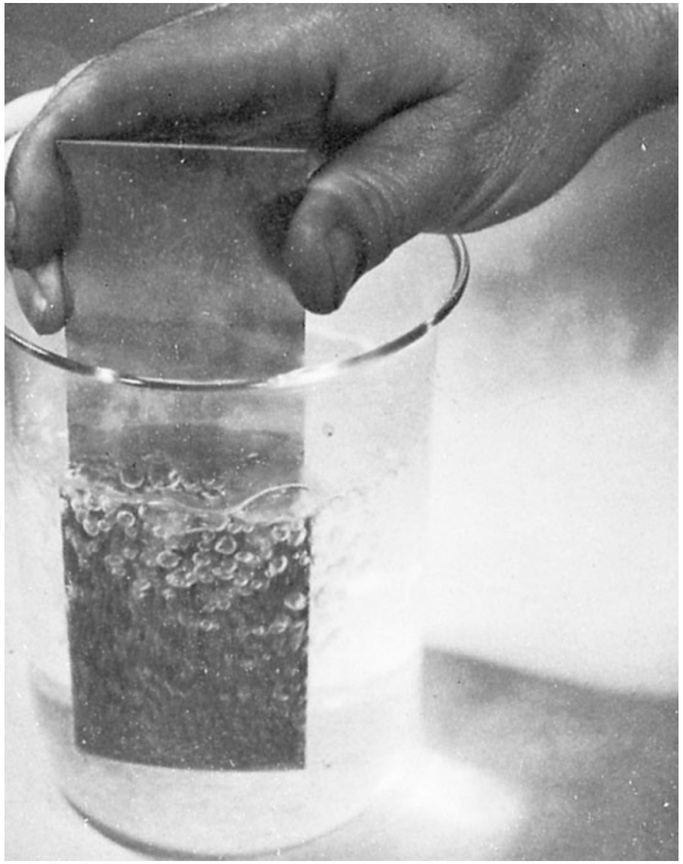
- ❑ Alloys used in service are complex and so are the electrolytes (difficult to define in terms of M^+) *(the environment provides the electrolyte*

Environment	Corrosion rate of mild steel (mm / year)
Dry	0.001
Marine	0.02
Humid with other agents	0.2

The mechanism of corrosion of Zinc (Zn) in aerated HCl





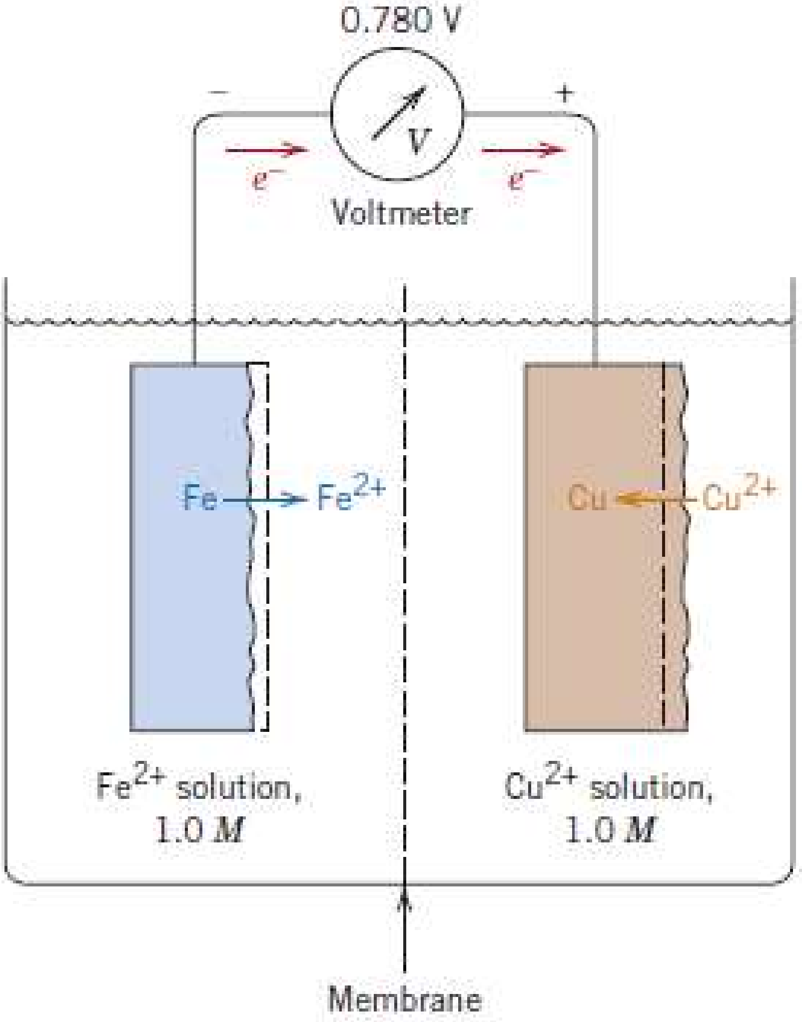


$Zn + 2HCl \rightarrow ZnCl_2 + H_2$

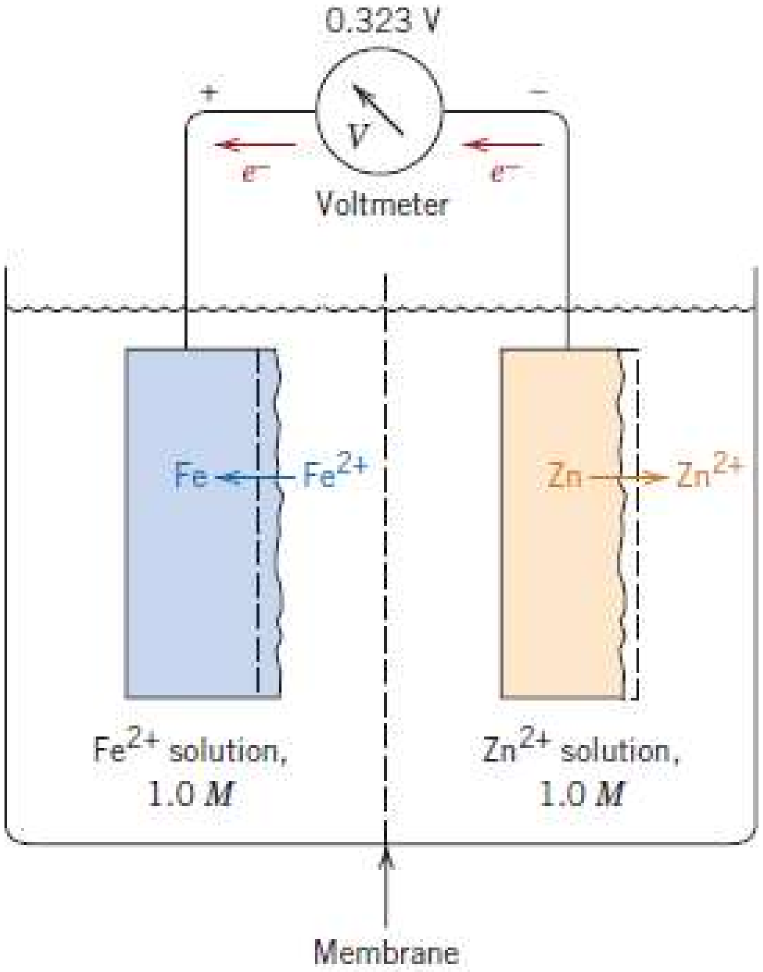
Hydrogen evolution $2H^+ + 2e \rightarrow H_2$

Oxygen reduction (acid solutions) $O_2 + 4H^+ + 4e \rightarrow 2H_2O$

Two cathodic reactions are possible during electrochemical corrosion reactions



An electrochemical cell consisting of iron and copper electrodes, each of which is immersed in a 1*M solution of its* ion. Iron corrodes while copper electrodeposits.



An electrochemical cell consisting of iron and zinc electrodes, each of which is immersed in a 1*M solution of its ion.* The iron electrodeposits while the zinc corrodes.

Electrode Potentials

Not all metallic materials oxidize to form ions with the same degree of ease. Consider the electrochemical cell shown in Figure 17.2. On the left-hand side is a piece of pure iron immersed in a solution containing Fe^{2+} ions of 1*M* concentration.[1] The other side of the cell consists of a pure copper electrode in a 1*M* solution of Cu^{2+} ions. The cell halves are separated by a membrane, which limits the mixing of the two solutions. If the iron and copper electrodes are connected electrically, reduction will occur for copper at the expense of the oxidation of iron, as follows:

$$Cu^{2+} + Fe \longrightarrow Cu + Fe^{2+} \tag{17.13}$$

or Cu^{2+} ions will deposit (electrodeposit) as metallic copper on the copper electrode, while iron dissolves (corrodes) on the other side of the cell and goes into solution as Fe^{2+} ions. Thus, the two half-cell reactions are represented by the relations

$$Fe \longrightarrow Fe^{2+} + 2e^- \tag{17.14a}$$

$$Cu^{2+} + 2e^- \longrightarrow Cu \tag{17.14b}$$

When a current passes through the external circuit, electrons generated from the oxidation of iron flow to the copper cell in order that Cu^{2+} be reduced. In addition, there will be some net ion motion from each cell to the other across the membrane. This is called a *galvanic couple*—two metals electrically connected in a liquid **electrolyte** wherein one metal becomes an anode and corrodes, while the other acts as a cathode.

An electric potential or voltage will exist between the two cell halves, and its magnitude can be determined if a voltmeter is connected in the external circuit. A potential of 0.780 V results for a copper–iron galvanic cell when the temperature is 25°C (77°F).

Now consider another galvanic couple consisting of the same iron half-cell connected to a metal zinc electrode that is immersed in a 1M solution of Zn^{2+} ions (Figure 17.3). In this case the zinc is the anode and corrodes, whereas the Fe now becomes the cathode. The electrochemical reaction is thus

$$Fe^{2+} + Zn \longrightarrow Fe + Zn^{2+} \tag{17.15}$$

The potential associated with this cell reaction is 0.323 V.

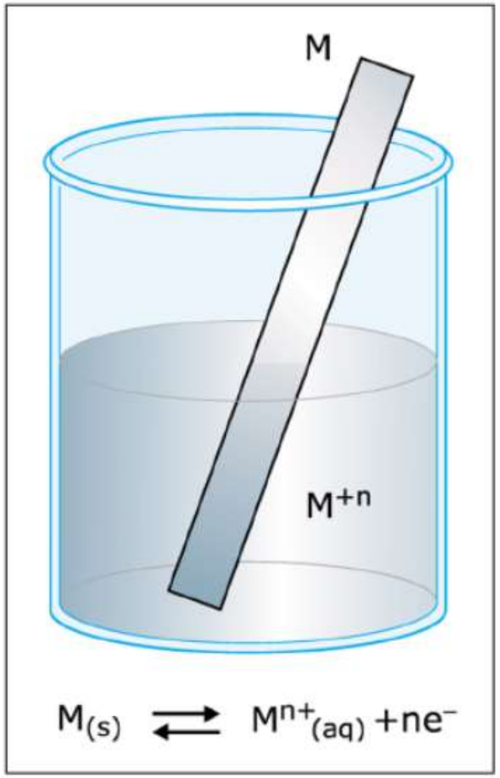
Thus, various electrode pairs have different voltages; the magnitude of such a voltage may be thought of as representing the driving force for the electrochemical oxidation–reduction reaction. Consequently, metallic materials may be rated as to their tendency to experience oxidation when coupled to other metals in solutions of their respective ions. A half-cell similar to those described above [i.e., a pure metal electrode immersed in a 1M solution of its ions and at 25°C (77°F)] is termed a **standard half-cell.**

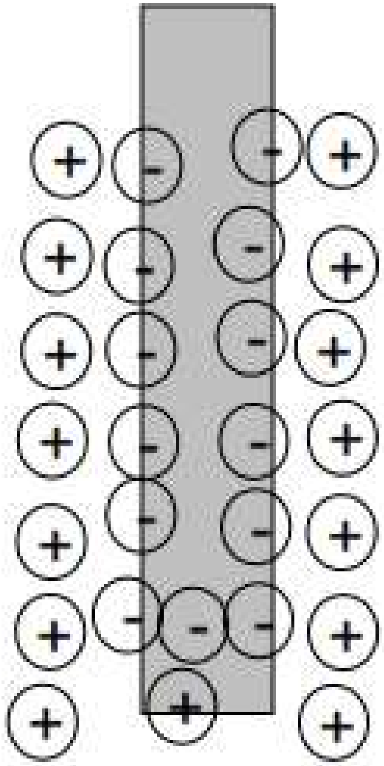
Electrode processes

The metallic electrode is dipped into a solution containing a salt of the metal. Some atoms of the metal can leave the electrode and form the cation in solution, leaving electrons in the metal. This form a double layer of opposite charges to the electrode surface. The electrochemical potential of the metal and its ion should be the same at the equilibrium.

$$M_{(s)} \leftrightarrows M^{n+}_{(aq)} + ne^-$$

There is the formation of an electric potential proportional at the ion concentration in solution





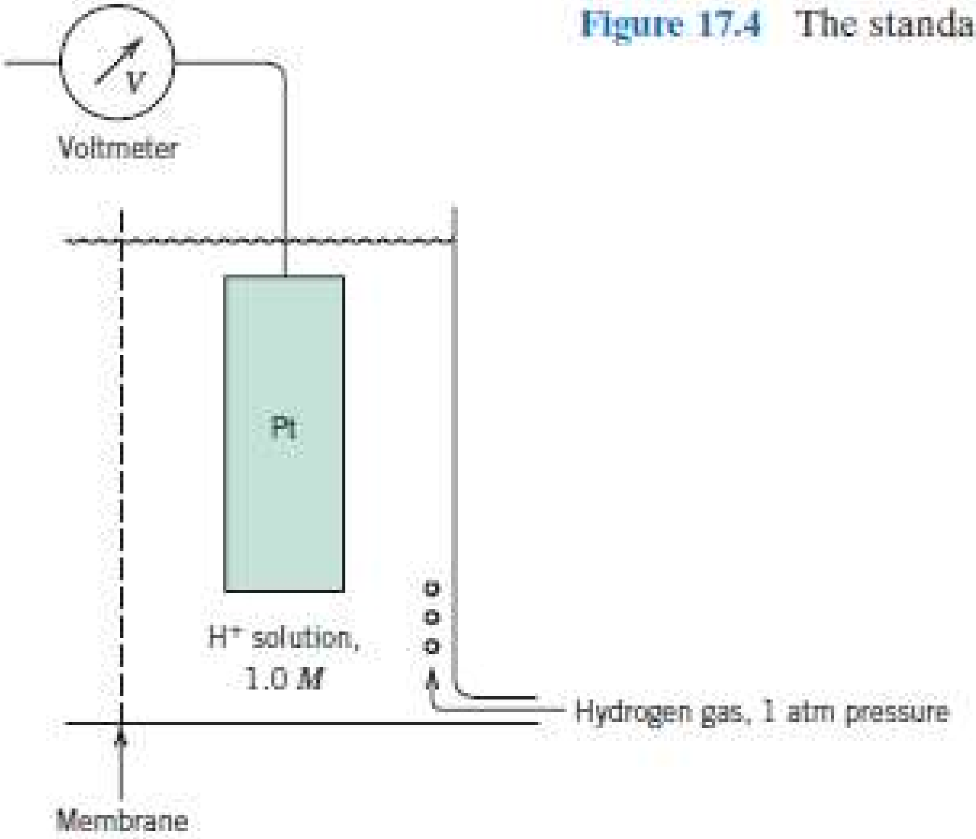


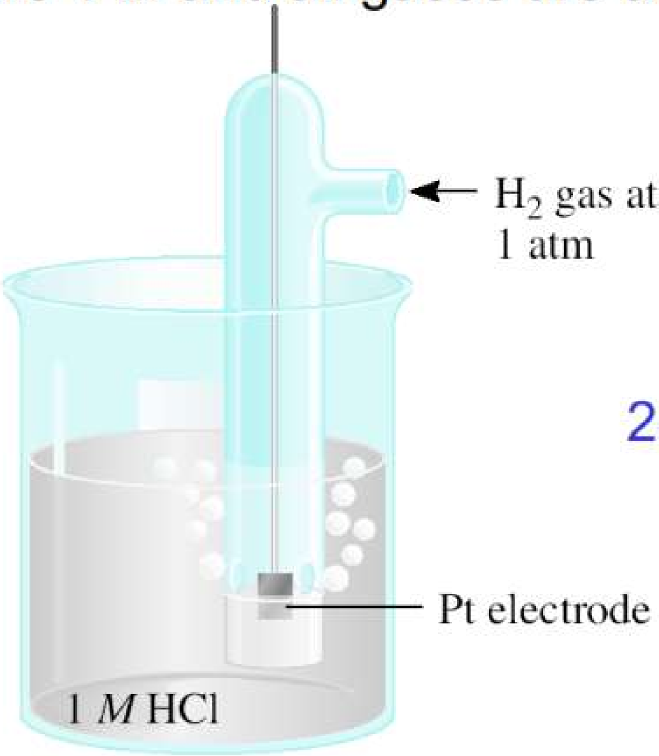
Figure 17.4 The standard hydrogen reference half-cell.

standard half-cells for various metals and ranking them according to measured voltage. Table 17.1 represents the corrosion tendencies for the several metals; those at the top (i.e., gold and platinum) are noble, or chemically inert. Moving down the table, the metals become increasingly more active, that is, more susceptible to oxidation. Sodium and potassium have the highest reactivities.

The voltages in Table 17.1 are for the half-reactions as *reduction reactions*, with the electrons on the left-hand side of the chemical equation; for oxidation, the direction of the reaction is reversed and the sign of the voltage changed.

Standard Reduction Potentials

Standard reduction potential (E°) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.



Standard hydrogen electrode (SHE)

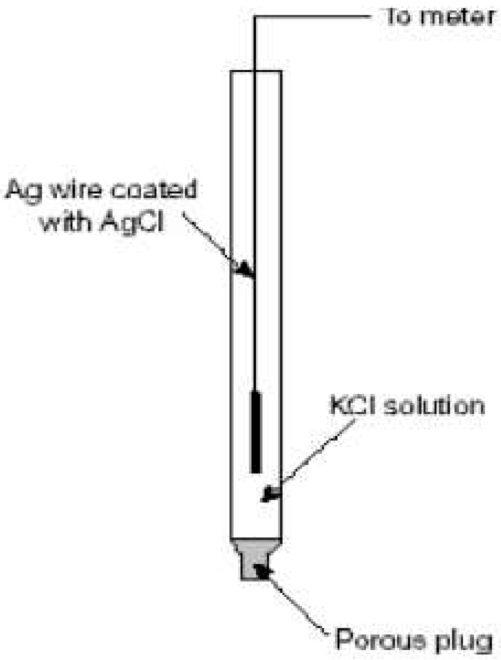
Reduction Reaction

$$2e^- + 2H^+ \,(1\ M) \longrightarrow H_2\,(1\ atm)$$

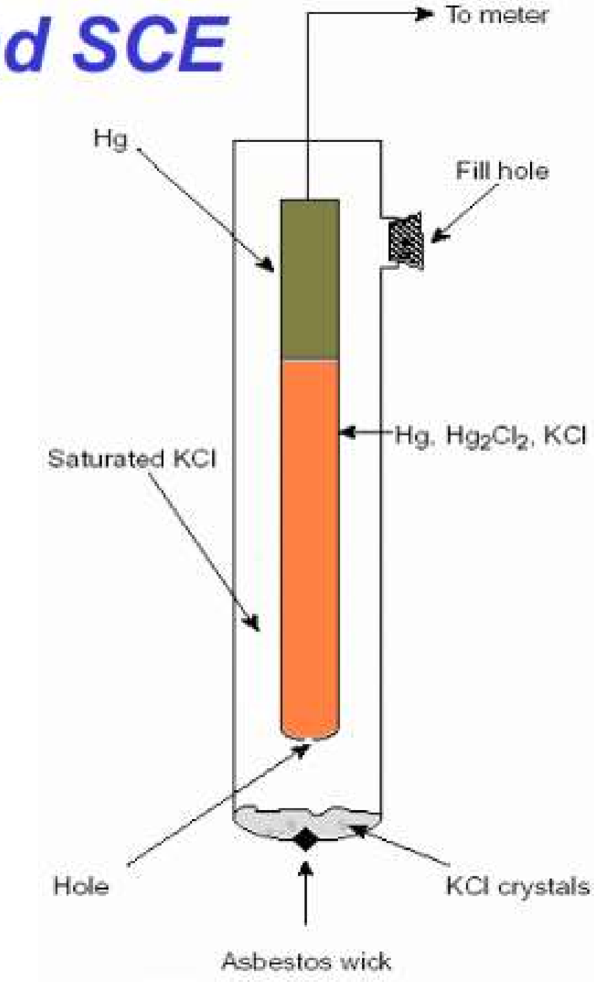
$$E^\circ = 0\ \text{V}$$

This reference is taken to be the hydrogen reaction, , for which both ΔG° and E° are assumed to be zero. The activity of all solid phases is defined as unity, and the Gibbs free energy of all pure elements in their standard states is set to zero.

Reference electrodes: Ag/AgCl and SCE



Ag/AgCl electrode E = 222 mV, t = 25C



Saturated calomel electrode (SCE) E = 244 mV, t=25C

silver/silver chloride electrode
Reference electrode based on the reduction of AgCl to Ag; that is, $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$.

$$E + E^\circ_{AgCl/Ag} - 0.05916 \log[Cl^-] = +0.2223 - 0.05916 \log[Cl^-]$$

saturated calomel electrode
Reference electrode based on the reduction of Hg_2Cl_2 to Hg in an aqueous solution saturated with KCl; that is, $Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(\ell) + 2Cl^-(aq)$.

$$E = E^\circ_{Hg_2Cl_2/Hg} - \frac{0.05916}{2}\log[Cl^-]^2 = +0.2682 - \frac{0.05916}{2}\log[Cl^-]^2$$

Single Electrode Potential

It is defined as the potential developed at the interface between the electrode and the solution and is denoted by ‘E’.

The individual electrode potential cannot be measured. We can measure only the difference in the potential between the two half cells (electrodes), that gives the EMF of the cell. If we arbitrarily choose the potential of one electrode, then that of the other can be determined with respect to this electrode. According to convention, the half cell (electrode) called standard hydrogen electrode (SHE) is assigned a zero potential at all temperatures.

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect to this.

The Standard emf Series

These measured cell voltages represent only differences in electrical potential, and thus it is convenient to establish a reference point, or reference cell, to which other cell halves may be compared. This reference cell, arbitrarily chosen, is the standard hydrogen electrode (Figure 17.4). It consists of an inert platinum electrode in a $1M$ solution of H^+ ions, saturated with hydrogen gas that is bubbled through the solution at a pressure of 1 atm and a temperature of 25°C (77°F). The platinum itself does not take part in the electrochemical reaction; it acts only as a surface on which hydrogen atoms may be oxidized or hydrogen ions may be reduced. The **electromotive force (emf) series** (Table 17.1) is generated by coupling to the standard hydrogen electrode,

- The standard electrode potentials are very important and we can extract a lot of useful information from them. The values of standard electrode potentials for some selected half-cell reduction reactions are given in Table 3.1.

- If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species.

- It can be seen that the standard electrode potential for fluorine is the highest in the Table indicating that fluorine gas (F2) has the maximum tendency to get reduced to fluoride ions (F–) and therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent. Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution.

- It may be seen that as we go from top to bottom in Table 3.1 the standard electrode potential decreases and with this, decreases the oxidising power of the species on the left and increases the reducing power of the species on the right hand side of the reaction.

- Electrochemical cells are extensively used for determining the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties and for potentiometric titrations.

Reaction (Oxidised form + ne$^-$	→ Reduced form)	E$^\ominus$/V
$F_2(g) + 2e^-$	→ $2F^-$	2.87
$Co^{3+} + e^-$	→ Co^{2+}	1.81
$H_2O_2 + 2H^+ + 2e^-$	→ $2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	→ $Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	→ $Au(s)$	1.40
$Cl_2(g) + 2e^-$	→ $2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	→ $2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	→ $2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	→ $Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	→ $2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	→ $NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	→ Hg_2^{2+}	0.92
$Ag^+ + e^-$	→ $Ag(s)$	0.80
$Fe^{3+} + e^-$	→ Fe^{2+}	0.77
$O_2(g) + 2H^+ + 2e^-$	→ H_2O_2	0.68
$I_2 + 2e^-$	→ $2I^-$	0.54
$Cu^+ + e^-$	→ $Cu(s)$	0.52
$Cu^{2+} + 2e^-$	→ $Cu(s)$	0.34
$AgCl(s) + e^-$	→ $Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	→ $Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	→ $H_2(g)$	0.00
$Pb^{2+} + 2e^-$	→ $Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	→ $Sn(s)$	–0.14
$Ni^{2+} + 2e^-$	→ $Ni(s)$	–0.25
$Fe^{2+} + 2e^-$	→ $Fe(s)$	–0.44
$Cr^{3+} + 3e^-$	→ $Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	→ $Zn(s)$	–0.76
$2H_2O + 2e^-$	→ $H_2(g) + 2OH^-(aq)$	–0.83
$Al^{3+} + 3e^-$	→ $Al(s)$	–1.66
$Mg^{2+} + 2e^-$	→ $Mg(s)$	–2.36
$Na^+ + e^-$	→ $Na(s)$	–2.71
$Ca^{2+} + 2e^-$	→ $Ca(s)$	–2.87
$K^+ + e^-$	→ $K(s)$	–2.93
$Li^+ + e^-$	→ $Li(s)$	–3.05

Increasing strength of oxidising agent ↑

Increasing strength of reducing agent ↓

Electron Affinities of Some Elements

(Values are given in eV and kJ mol^{-1})

For one electron

H							He
0.7							0
68							0
Li	Be	B	C	N	O	F	Ne
0.54	0	0.54	1.13	0.2	1.48	3.62	0
52	0	52	109	19	143	349	0
Na	Mg	Al	Si	P	S	Cl	Ar
0.74	0	0.4	1.90	0.80	2.07	3.82	0
71	0	39	183	77	200	369	0
						Br	Kr
						3.54	0
						342	0
						I	Xe
						3.24	0
						313	0


PRONAMEL
PRO-HEALTH
Colgate
Colgate Sensitive
PRO-SYS
Tom's
Crest PRO-HEALTH

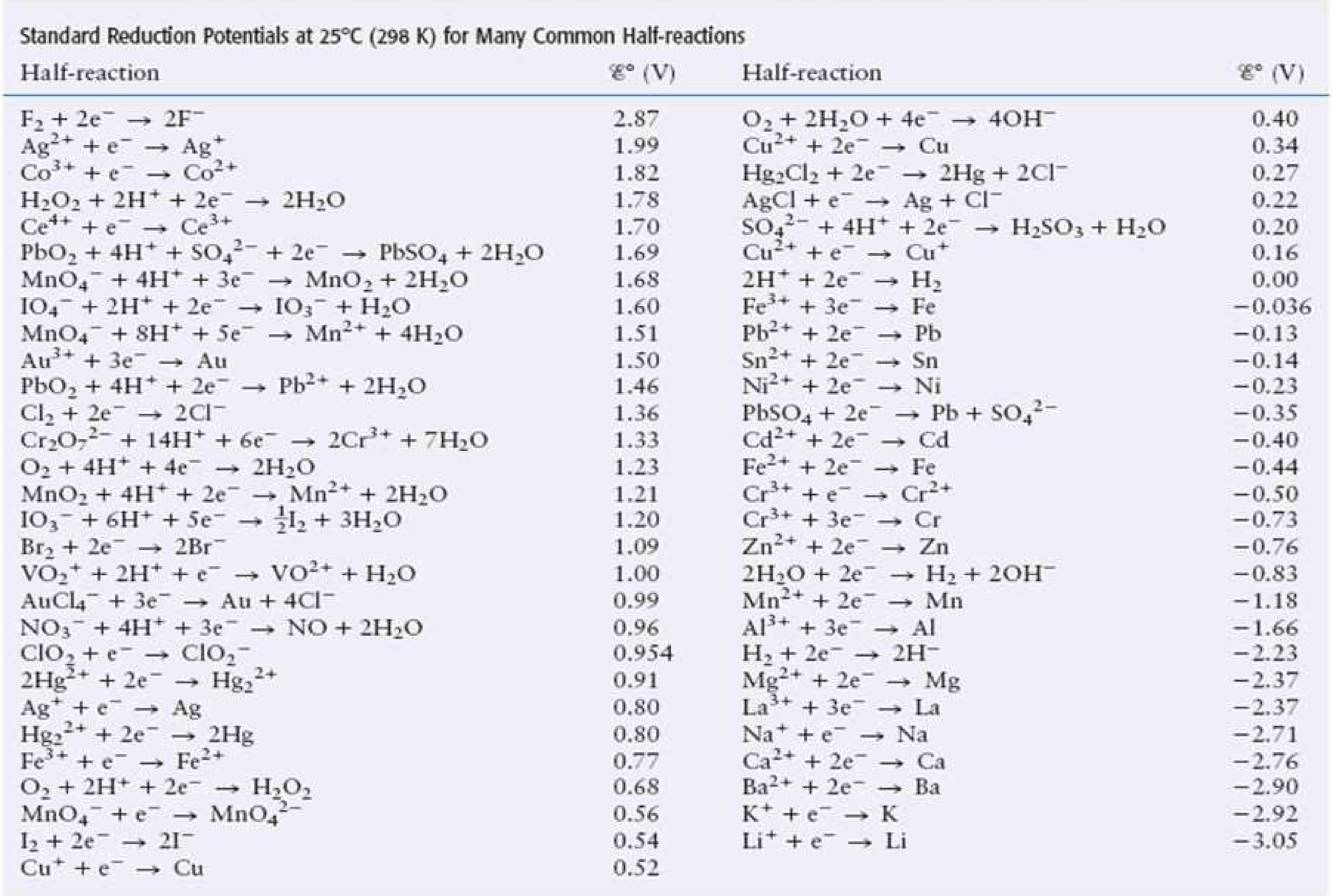

PURE
STABLE
BLEACHING POWDER


IODINE TINCTURE 2.0%
Antiseptic/Disinfectant
For Animal Use Only
Keep Out of Reach of Children
NET CONTENTS: 1 GALLON (3.785 Liters)
AgriLabs
IODINE TINCTURE 2.0%
Antiseptic/Disinfectant
For Animal Use Only
Keep Out of Reach of Children
NET CONTENTS: 16 fl oz (473 mL)
AgriLabs


10g
Povidone-Iodine Powder 5% w/w
बीटाडीन
Betadine®
MICROBICIDAL SPRINKLING POWDER
Win-Medicare
MICROBICIDAL POWDER
practo
FOR EXTERNAL USE ONLY


Betadine
Zalf
50 g

The Electrochemical Series

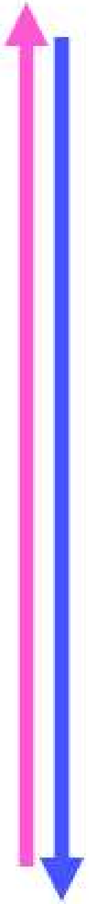


Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathscr{E}^\circ$ (V)	Half-reaction	$\mathscr{E}^\circ$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Table 21.2 Selected Standard Electrode Potentials (298 K)

Half-Reaction	E^0 (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	−0.23
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05



Increase oxidizing power

Increase reducing power

Table 17.1 The Standard emf Series

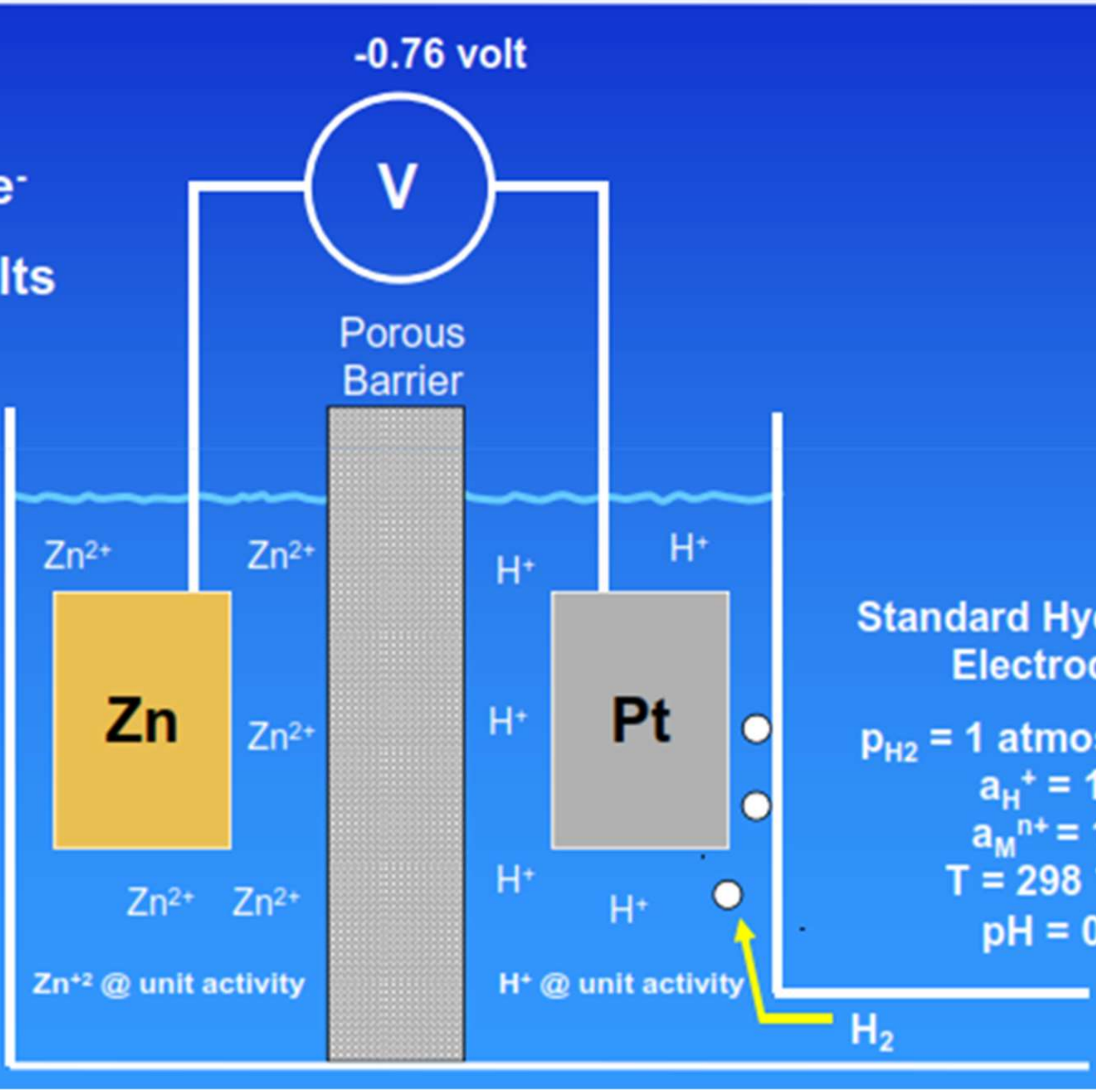
	Electrode Reaction	*Standard Electrode Potential, V^0(V)*
	$Au^{3+} + 3e^- \longrightarrow Au$	+1.420
↑	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^- \longrightarrow Pt$	~+1.2
	$Ag^+ + e^- \longrightarrow Ag$	+0.800
Increasingly inert	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
(cathodic)	$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.340
	$2H^+ + 2e^- \longrightarrow H_2$	0.000
	$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.126
	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.136
	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.250
	$Co^{2+} + 2e^- \longrightarrow Co$	−0.277
	$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.403
	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.440
Increasingly active	$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.744
(anodic)	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.763
	$Al^{3+} + 3e^- \longrightarrow Al$	−1.662
	$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.363
↓	$Na^+ + e^- \longrightarrow Na$	−2.714
	$K^+ \longrightarrow K$	−2.924

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

Table 17.2 The Galvanic Series

	Platinum
	Gold
	Graphite
	Titanium
	Silver
	316 Stainless steel (passive)
	304 Stainless steel (passive)
↑	Inconel (80Ni–13Cr–7Fe) (passive)
	Nickel (passive)
	Monel (70Ni–30Cu)
Increasingly inert (cathodic)	Copper–nickel alloys
	Bronzes (Cu–Sn alloys)
	Copper
	Brasses (Cu–Zn alloys)
	Inconel (active)
	Nickel (active)
	Tin
	Lead
Increasingly active (anodic)	316 Stainless steel (active)
↓	304 Stainless steel (active)
	Cast iron
	Iron and steel
	Aluminum alloys
	Cadmium
	Commercially pure aluminum
	Zinc
	Magnesium and magnesium alloys

Source: M. G. Fontana, *Corrosion* *ring*, 3rd edition. Copyright 1986 by McGraw-Hill Book Com printed with permission.

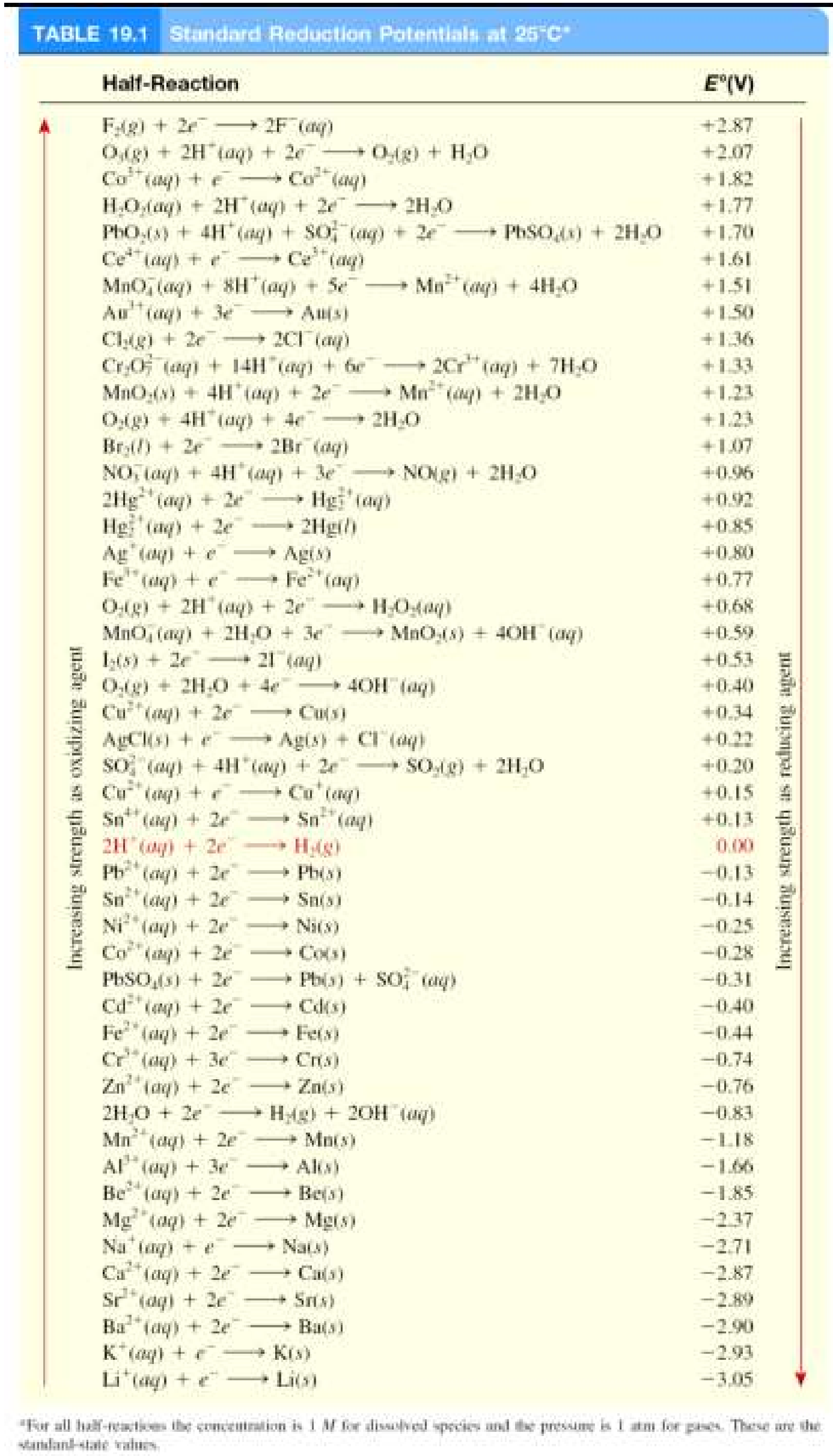


TABLE 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	E°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

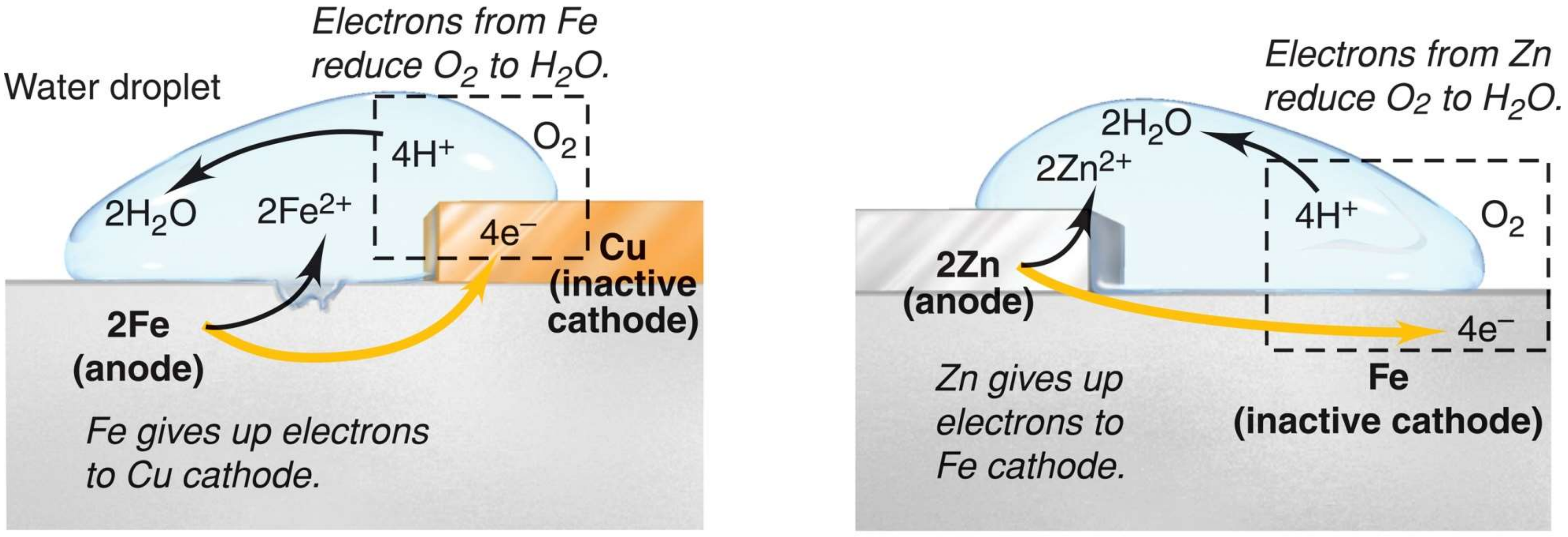
*For all half-reactions the concentration is 1 *M* for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

- E° is for the reaction as written $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
- The more positive E° the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of E° changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of E°

When two metals are electrically in contact with each other and exposed to the environment, they develop two different potential, called galvanic potential, with respect to the environment; therefore an electrical current starts flowing between the two metals. The metal having higher potential becomes cathodic, while the other is rendered anodic.

Carbon steel when comes into contact with alloys like stainless steel or brass it corrodes much faster than its normal rate in aqueous solutions. Carbon steel is active to stainless steel/brass and the latter is relatively noble to the former. On the other hand, when zinc comes into contact with steel the latter becomes relatively nobler than the former. In fact, this is the principle behind cathodic protection of steel with zinc anodes, zinc coatings, and zinc-rich paints.

The effect of metal-metal contact on the corrosion of iron



Electrons from Fe reduce O_2 to H_2O.

Fe gives up electrons to Cu cathode.

Electrons from Zn reduce O_2 to H_2O.

Zn gives up electrons to Fe cathode.

A Enhanced corrosion

B Cathodic protection

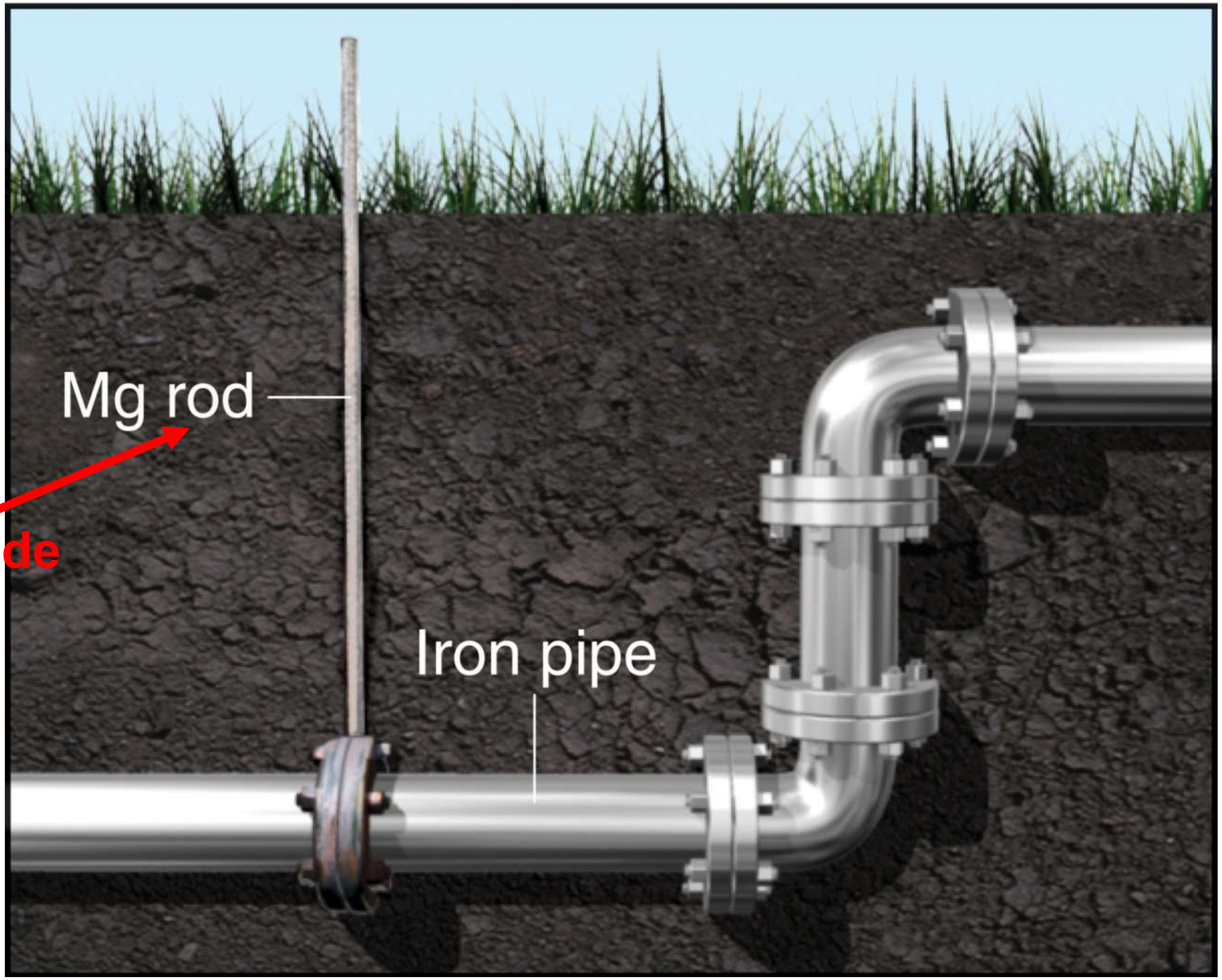
Fe in contact with Cu

Fe in contact with Zn

Fe corrodes faster.

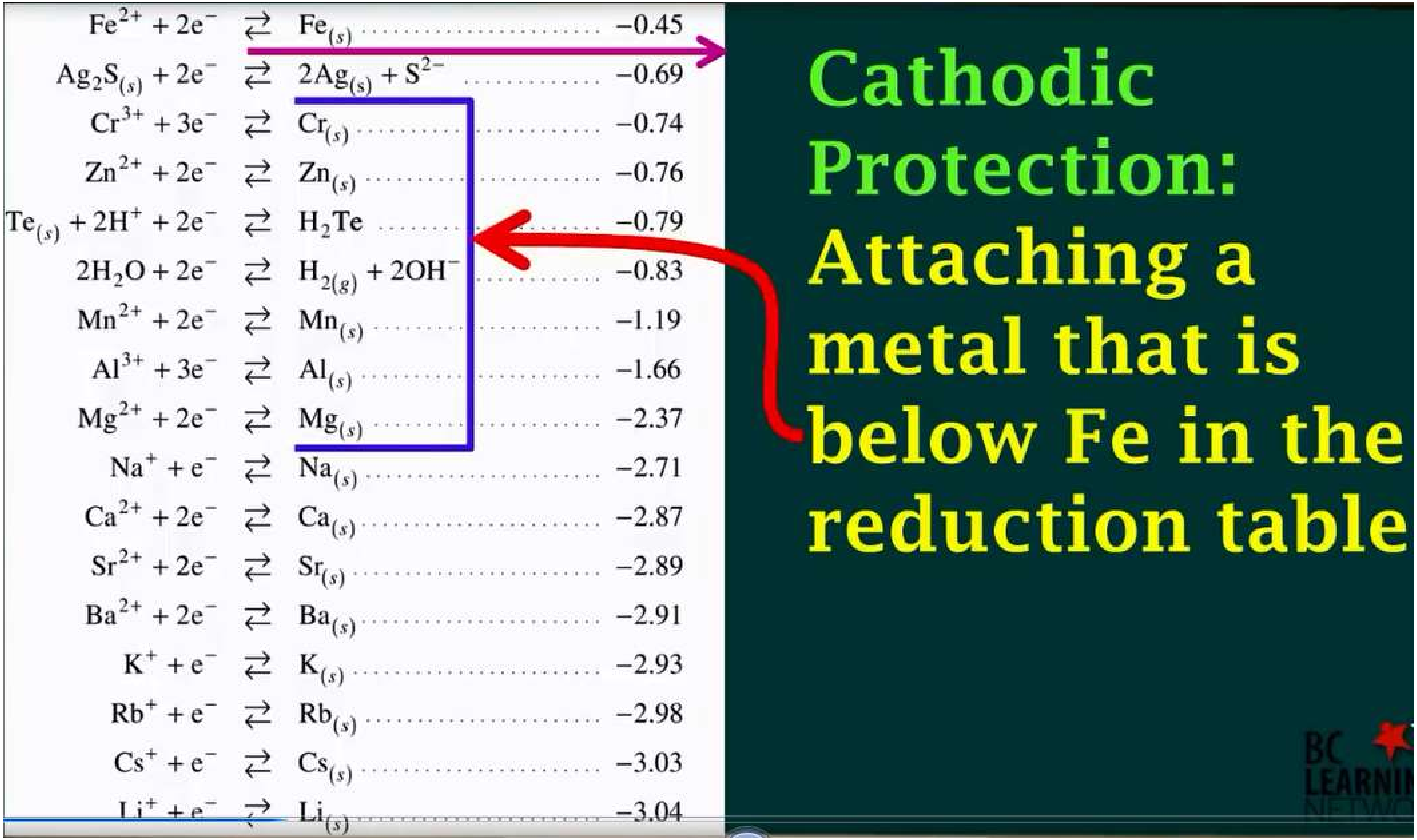
Zn corrodes but not Fe.
This process is known as
cathodic protection.

The use of Sacrificial Anodes to prevent iron Corrosion



Sacrificial anode

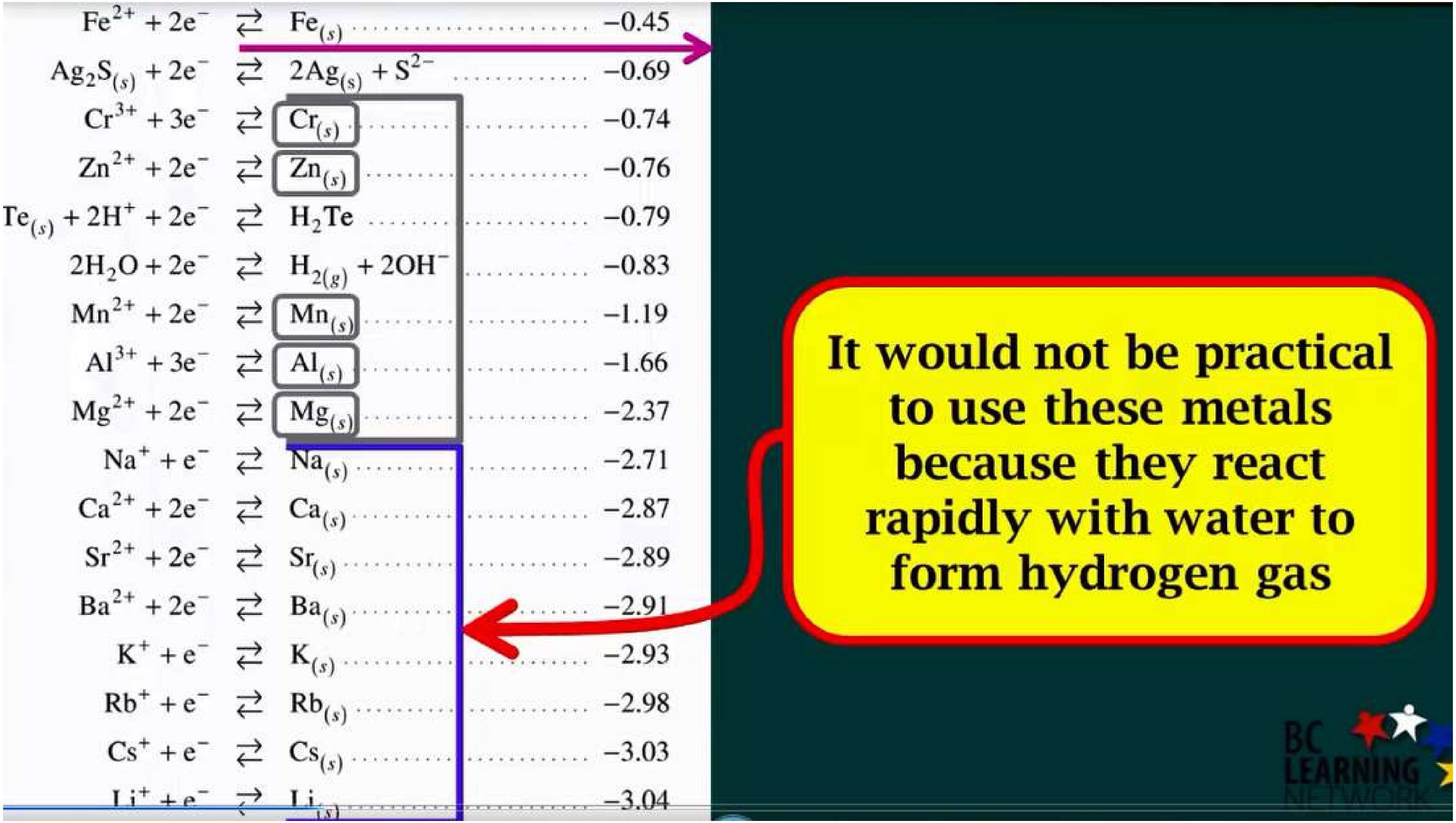
In cathodic protection, an active metal, such as zinc, magnesium, or aluminum, acts as the anode and is sacrificed instead of the iron.



$Fe^{2+} + 2e^-$	$\rightleftarrows$	$Fe_{(s)}$	−0.45
$Ag_2S_{(s)} + 2e^-$	$\rightleftarrows$	$2Ag_{(s)} + S^{2-}$	−0.69
$Cr^{3+} + 3e^-$	$\rightleftarrows$	$Cr_{(s)}$	−0.74
$Zn^{2+} + 2e^-$	$\rightleftarrows$	$Zn_{(s)}$	−0.76
$Te_{(s)} + 2H^+ + 2e^-$	$\rightleftarrows$	H_2Te	−0.79
$2H_2O + 2e^-$	$\rightleftarrows$	$H_{2(g)} + 2OH^-$	−0.83
$Mn^{2+} + 2e^-$	$\rightleftarrows$	$Mn_{(s)}$	−1.19
$Al^{3+} + 3e^-$	$\rightleftarrows$	$Al_{(s)}$	−1.66
$Mg^{2+} + 2e^-$	$\rightleftarrows$	$Mg_{(s)}$	−2.37
$Na^+ + e^-$	$\rightleftarrows$	$Na_{(s)}$	−2.71
$Ca^{2+} + 2e^-$	$\rightleftarrows$	$Ca_{(s)}$	−2.87
$Sr^{2+} + 2e^-$	$\rightleftarrows$	$Sr_{(s)}$	−2.89
$Ba^{2+} + 2e^-$	$\rightleftarrows$	$Ba_{(s)}$	−2.91
$K^+ + e^-$	$\rightleftarrows$	$K_{(s)}$	−2.93
$Rb^+ + e^-$	$\rightleftarrows$	$Rb_{(s)}$	−2.98
$Cs^+ + e^-$	$\rightleftarrows$	$Cs_{(s)}$	−3.03
$Li^+ + e^-$	$\rightleftarrows$	$Li_{(s)}$	−3.04

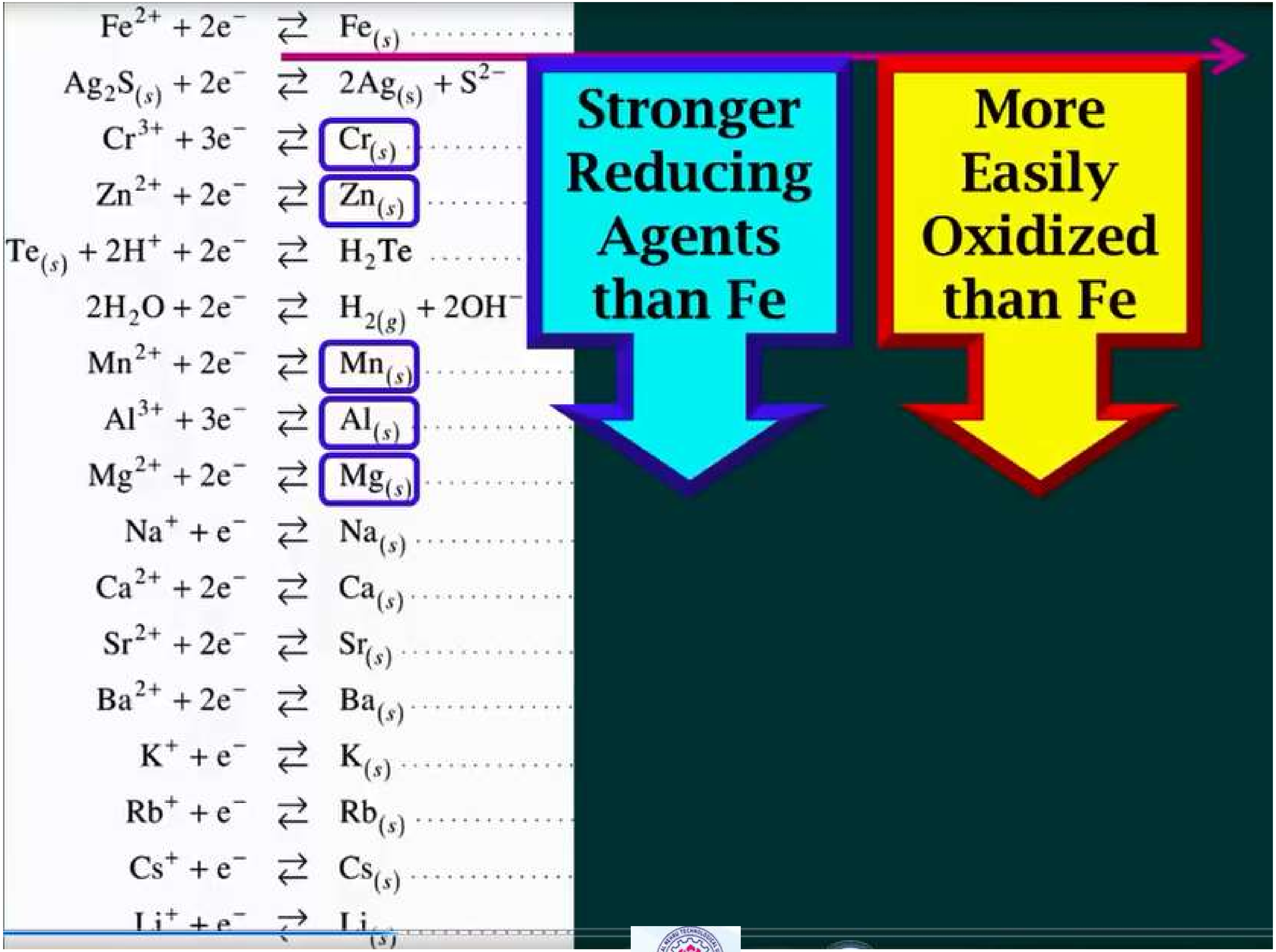
Cathodic Protection:

Attaching a metal that is below Fe in the reduction table



$Fe^{2+} + 2e^-$	⇌	$Fe_{(s)}$	−0.45
$Ag_2S_{(s)} + 2e^-$	⇌	$2Ag_{(s)} + S^{2-}$	−0.69
$Cr^{3+} + 3e^-$	⇌	$\boxed{Cr_{(s)}}$	−0.74
$Zn^{2+} + 2e^-$	⇌	$\boxed{Zn_{(s)}}$	−0.76
$Te_{(s)} + 2H^+ + 2e^-$	⇌	H_2Te	−0.79
$2H_2O + 2e^-$	⇌	$H_{2(g)} + 2OH^-$	−0.83
$Mn^{2+} + 2e^-$	⇌	$\boxed{Mn_{(s)}}$	−1.19
$Al^{3+} + 3e^-$	⇌	$\boxed{Al_{(s)}}$	−1.66
$Mg^{2+} + 2e^-$	⇌	$\boxed{Mg_{(s)}}$	−2.37
$Na^+ + e^-$	⇌	$Na_{(s)}$	−2.71
$Ca^{2+} + 2e^-$	⇌	$Ca_{(s)}$	−2.87
$Sr^{2+} + 2e^-$	⇌	$Sr_{(s)}$	−2.89
$Ba^{2+} + 2e^-$	⇌	$Ba_{(s)}$	−2.91
$K^+ + e^-$	⇌	$K_{(s)}$	−2.93
$Rb^+ + e^-$	⇌	$Rb_{(s)}$	−2.98
$Cs^+ + e^-$	⇌	$Cs_{(s)}$	−3.03
$Li^+ + e^-$	⇌	$Li_{(s)}$	−3.04

It would not be practical to use these metals because they react rapidly with water to form hydrogen gas



$Fe^{2+} + 2e^- \rightleftarrows Fe_{(s)}$

$Ag_2S_{(s)} + 2e^- \rightleftarrows 2Ag_{(s)} + S^{2-}$

$Cr^{3+} + 3e^- \rightleftarrows \boxed{Cr_{(s)}}$

$Zn^{2+} + 2e^- \rightleftarrows \boxed{Zn_{(s)}}$

$Te_{(s)} + 2H^+ + 2e^- \rightleftarrows H_2Te$

$2H_2O + 2e^- \rightleftarrows H_{2(g)} + 2OH^-$

$Mn^{2+} + 2e^- \rightleftarrows \boxed{Mn_{(s)}}$

$Al^{3+} + 3e^- \rightleftarrows \boxed{Al_{(s)}}$

$Mg^{2+} + 2e^- \rightleftarrows \boxed{Mg_{(s)}}$

$Na^+ + e^- \rightleftarrows Na_{(s)}$

$Ca^{2+} + 2e^- \rightleftarrows Ca_{(s)}$

$Sr^{2+} + 2e^- \rightleftarrows Sr_{(s)}$

$Ba^{2+} + 2e^- \rightleftarrows Ba_{(s)}$

$K^+ + e^- \rightleftarrows K_{(s)}$

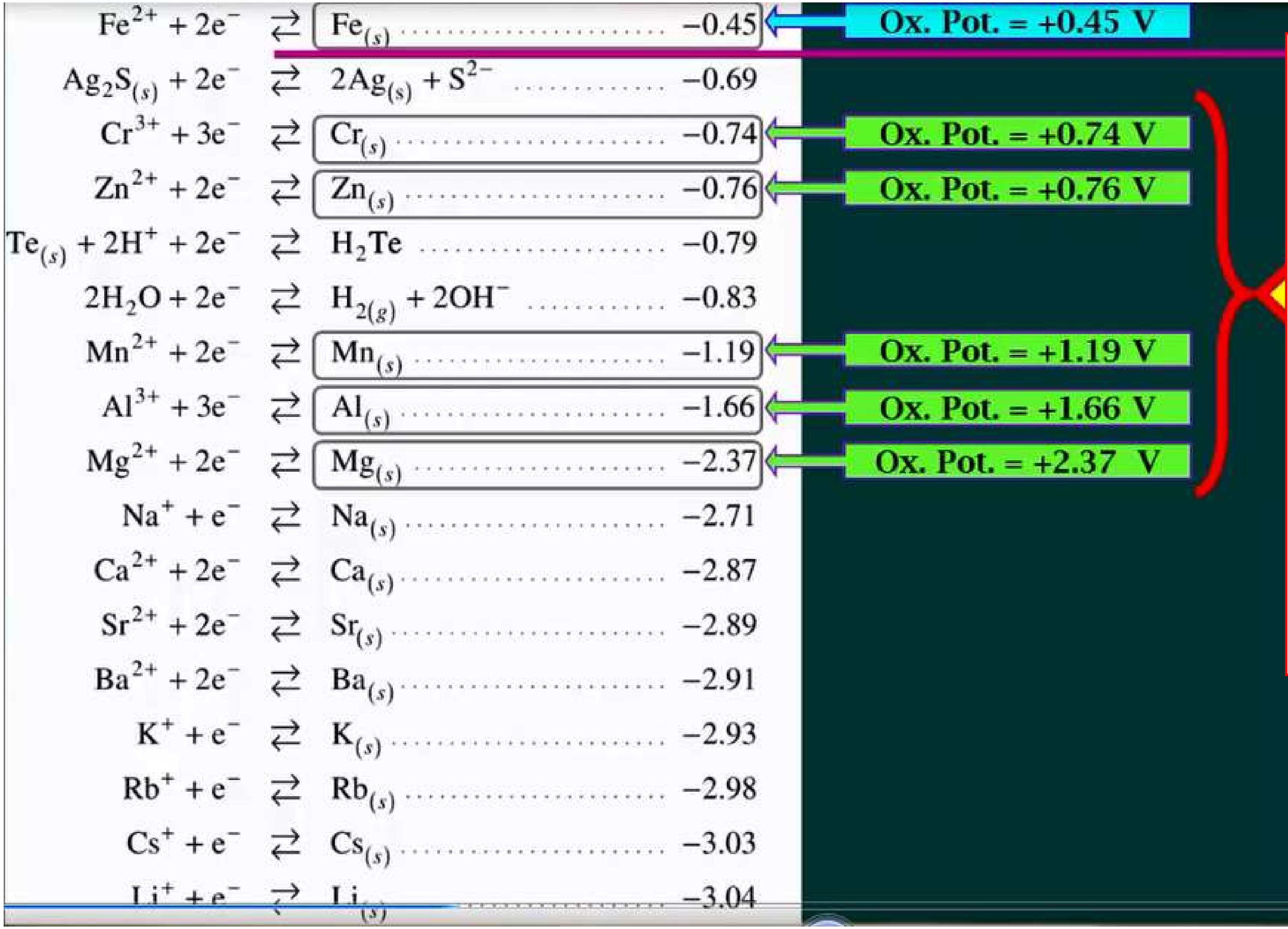
$Rb^+ + e^- \rightleftarrows Rb_{(s)}$

$Cs^+ + e^- \rightleftarrows Cs_{(s)}$

$Li^+ + e^- \rightleftarrows Li_{(s)}$

Stronger Reducing Agents than Fe

More Easily Oxidized than Fe



$Fe^{2+} + 2e^-$	⇄	$Fe_{(s)}$	−0.45	Ox. Pot. = +0.45 V
$Ag_2S_{(s)} + 2e^-$	⇄	$2Ag_{(s)} + S^{2-}$	−0.69	
$Cr^{3+} + 3e^-$	⇄	$Cr_{(s)}$	−0.74	Ox. Pot. = +0.74 V
$Zn^{2+} + 2e^-$	⇄	$Zn_{(s)}$	−0.76	Ox. Pot. = +0.76 V
$Te_{(s)} + 2H^+ + 2e^-$	⇄	H_2Te	−0.79	
$2H_2O + 2e^-$	⇄	$H_{2(g)} + 2OH^-$	−0.83	
$Mn^{2+} + 2e^-$	⇄	$Mn_{(s)}$	−1.19	Ox. Pot. = +1.19 V
$Al^{3+} + 3e^-$	⇄	$Al_{(s)}$	−1.66	Ox. Pot. = +1.66 V
$Mg^{2+} + 2e^-$	⇄	$Mg_{(s)}$	−2.37	Ox. Pot. = +2.37 V
$Na^+ + e^-$	⇄	$Na_{(s)}$	−2.71	
$Ca^{2+} + 2e^-$	⇄	$Ca_{(s)}$	−2.87	
$Sr^{2+} + 2e^-$	⇄	$Sr_{(s)}$	−2.89	
$Ba^{2+} + 2e^-$	⇄	$Ba_{(s)}$	−2.91	
$K^+ + e^-$	⇄	$K_{(s)}$	−2.93	
$Rb^+ + e^-$	⇄	$Rb_{(s)}$	−2.98	
$Cs^+ + e^-$	⇄	$Cs_{(s)}$	−3.03	
$Li^+ + e^-$	⇄	$Li_{(s)}$	−3.04	

If these are present with Fe, and an oxidizing agent appears, they will oxidize instead of the Fe, this saving the Fe from being oxidized

The white blocks are zinc anodes attached to this ship. They are there to cathodically protect the propeller

Powerboat Zincs

6 Zincs

Trim Tab

- Metals and alloys are arranged in a qualitative scale which gives a measure of the tendency to corrode → *The Galvanic Series*

Galvanic series

Galvanic series in marine water									
Noble end	*More reactive*								*Active end*
18-8 SS *Passive*	Ni	Cu	Sn	Brass	18-8 SS *Active*	MS	Al	Zn	Mg

Surface Area Effect

When a piece of metal is freely corroding, the electrons generated at anodic areas flow through the metal to react at cathodic areas similarly exposed to the environment where they restore the electrical balance of the system. The fact that there is no net accumulation of charges on a corroding surface is quite important for understanding most corrosion processes and ways to mitigate them. However, the absolute equality between the anodic and cathodic currents expressed in Eq. (3.23) does not mean that the current densities for these currents are equal.

$$I_{\text{anodic}} = I_{\text{cathodic}} \tag{3.23}$$

When Eq. (3.23) is expressed in terms of current densities in Eq. (3.24) by considering the relative anodic (S_a) and cathodic (S_c) surface areas and their associated current densities I_a and i_c expressed in units of $mAcm^{-2}$, for example, it becomes clear that a difference in the surface areas occupied by each reaction will have to be compensated by inequalities in the current densities as expressed in Eq. (3.25).

$$I_{\text{anodic}} = i_a \times S_a = I_{\text{cathodic}} = i_c \times S_c \tag{3.24}$$

$$\boxed{i_a = i_c \frac{S_c}{S_a}} \tag{3.25}$$

The implications of the surface area ratio Sc/Sa in Eq. (3.25) are particularly important in association with various forms of local cell corrosion such as pitting and stress corrosion cracking for which a large surface area ratio is a serious aggravating factor.

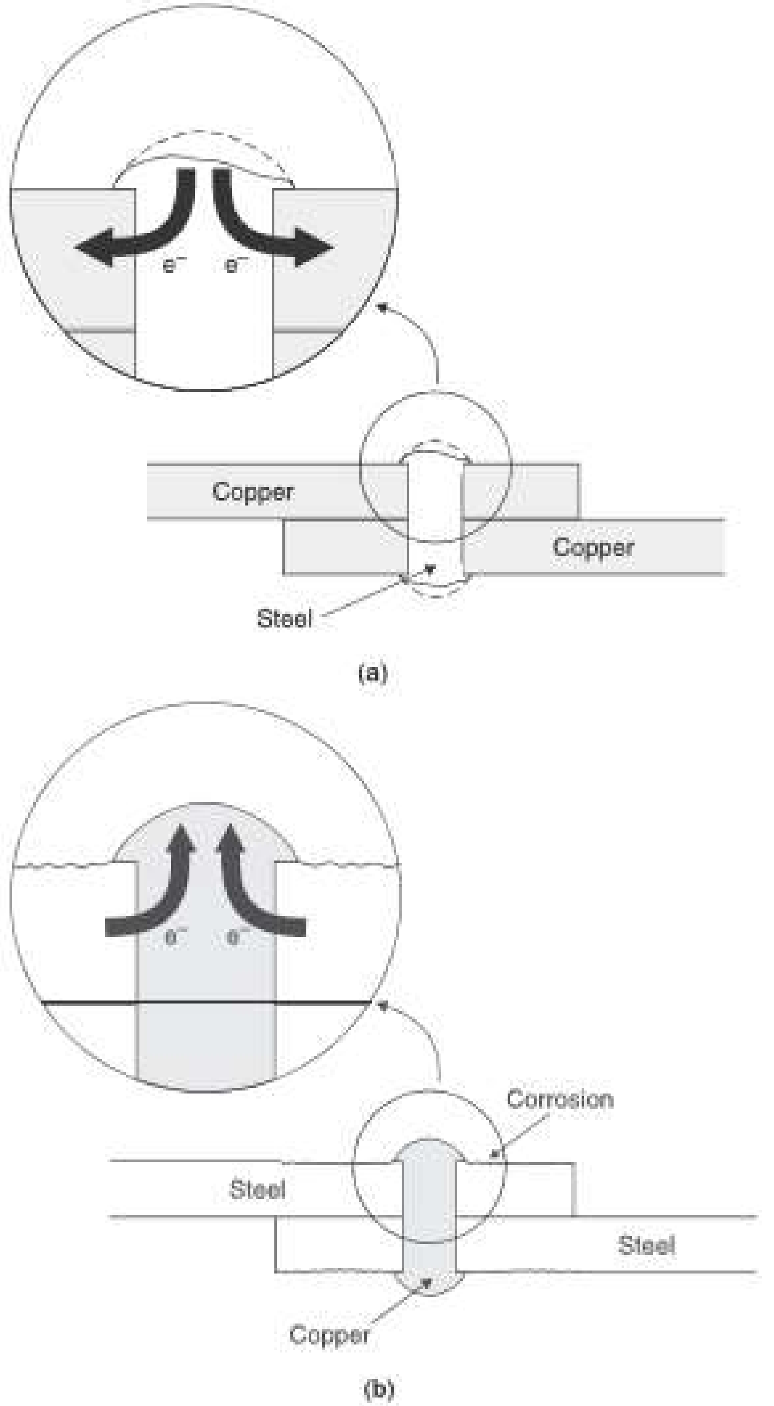
It is easy to understand that the effect of a certain amount of anodic current concentrated on a small area of metal surface will be much greater than when the effect of the same amount of current is dissipated over a much larger area.

This factor is expressed in Eq. (3.25) which states that the ratio of cathodic to anodic surfaces is an important amplifying factor of the anodic current when

$$S_c/S_a \text{ is} >> 1$$

and a stifling factor when it is << 1

When small anodic metals touch a large cathode, corrosion occurs at ***a much higher rate***. You might even say that ***galvanic corrosion matters most*** when it comes to ***smaller metal components***.



IRE 3.8 Galvanic coupling caused by riveting with dissimilar meta
steel rivets on copper plates, (b) copper rivets on steel plates.

This area effect in terms of current density is illustrated by combinations of steel and copper as either plates or the fasteners used to join them and immersed in a corrosive solution. If steel rivets are used to join copper plates, the current density on the relatively large cathodic copper plates will be low, cathodic polarization of the copper will be slight, and the voltage of the galvanic couple will maintain a value close to the open circuit potential. At the same time, the current density on the small anodic steel rivets will be high and the consequent corrosion quite severe, giving rise to a particularly vicious form of corrosion called galvanic corrosion [Fig. 3.8(a)].

With the opposite arrangement of copper rivets joining steel plates, the current density on the copper cathodes will be high, with consequently considerable cathodic polarization of the copper reducing the open circuit potential below its initial value. The diminished anodic current will be spread over the relatively large steel plates and the undesirable galvanic effect will hardly be noticeable [Fig. 3.8(b)]. Open circuit potential measurements are grossly inadequate for predicting the magnitude of galvanic effects since they do not take into account area and polarization effects. They are reliable only for predicting the direction of such effects.

Surface Area Effects in a Galvanic Situation

Another important factor in galvanic corrosion is the area effect or the ratio of cathodic to anodic area. The larger the cathode compared with the anode, the more oxygen reduction, or other cathodic reaction, can occur and, hence, the greater the galvanic current. From the standpoint of practical corrosion resistance, the least favorable ratio is a very large cathode connected to a very small anode. This effect is illustrated in the **following series of pictures**. The galvanic Table indicates that iron is anodic with respect to copper and therefore is more rapidly corroded when placed in contact with it. This effect is greatly accelerated if the area of the iron is small in comparison to the area of the copper, as shown below

Steel rivets on a copper bar submerged in 3% sodium chloride solution at the start of the experiment

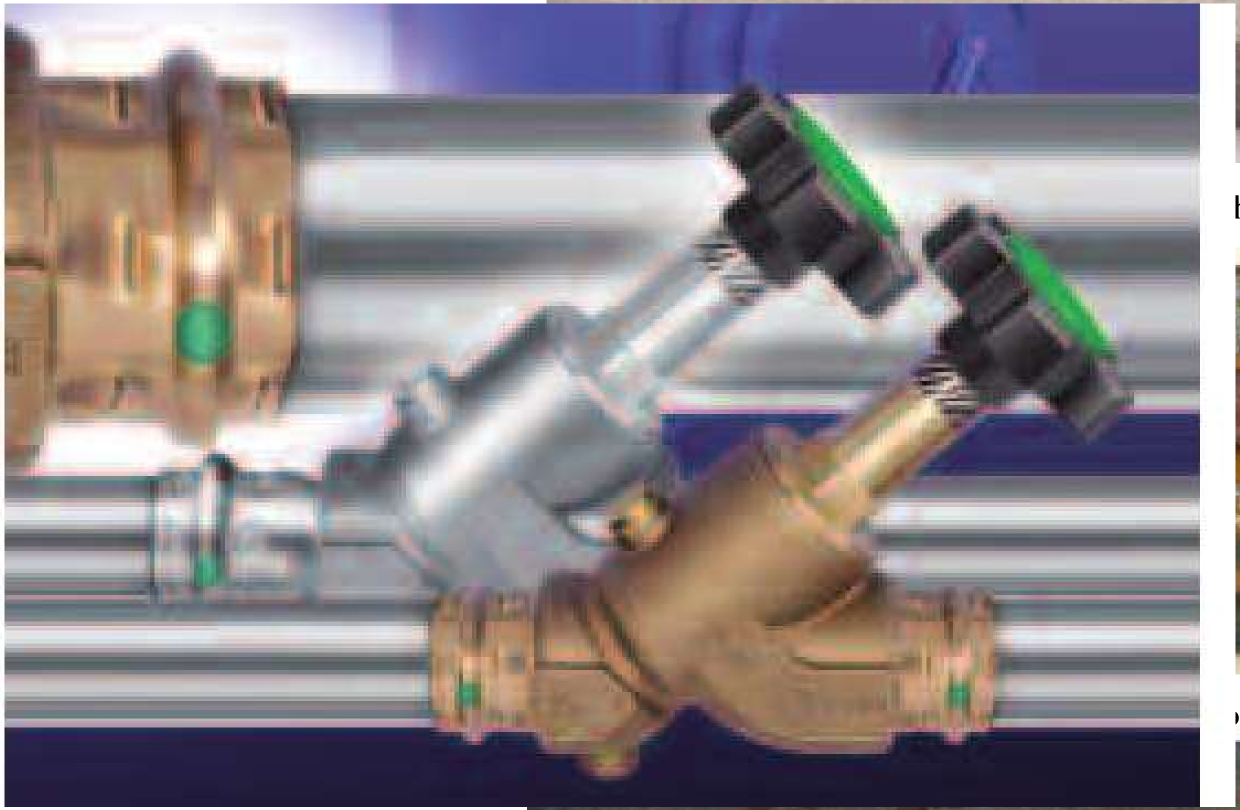
Steel rivets on a copper bar submerged in 3% sodium chloride solution after six months

Steel rivets on a copper bar submerged in 3% sodium chloride solution after ten months

However, under the reverse conditions when the area of the iron is very large compared to the copper, the corrosion of the iron is only slightly accelerated.

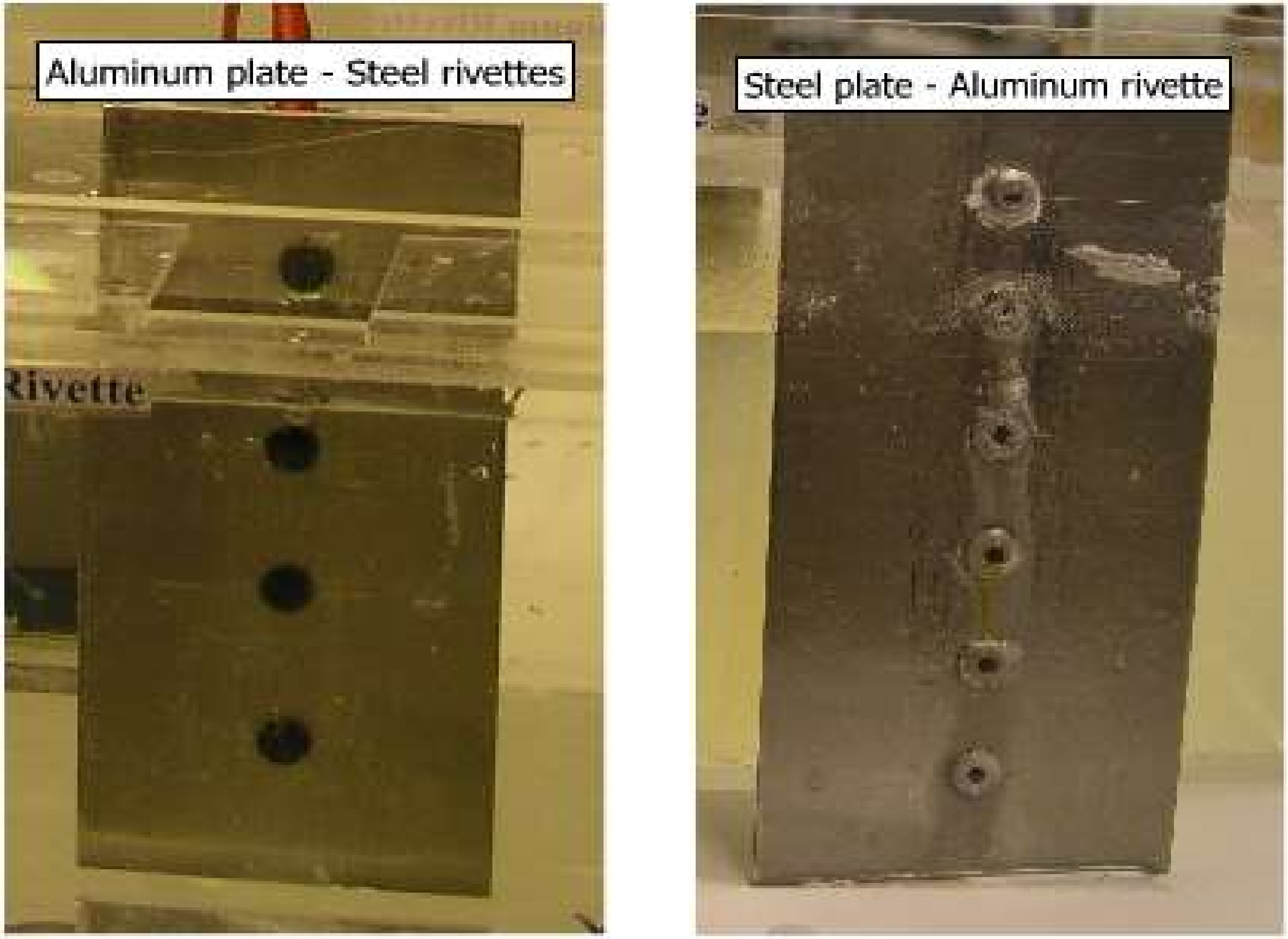
hloride solution at the start of the experiment

sodium chloride solution after six months



In plumbing, combinations of stainless steel with copper and copper alloys such as gun metal are successfully used.

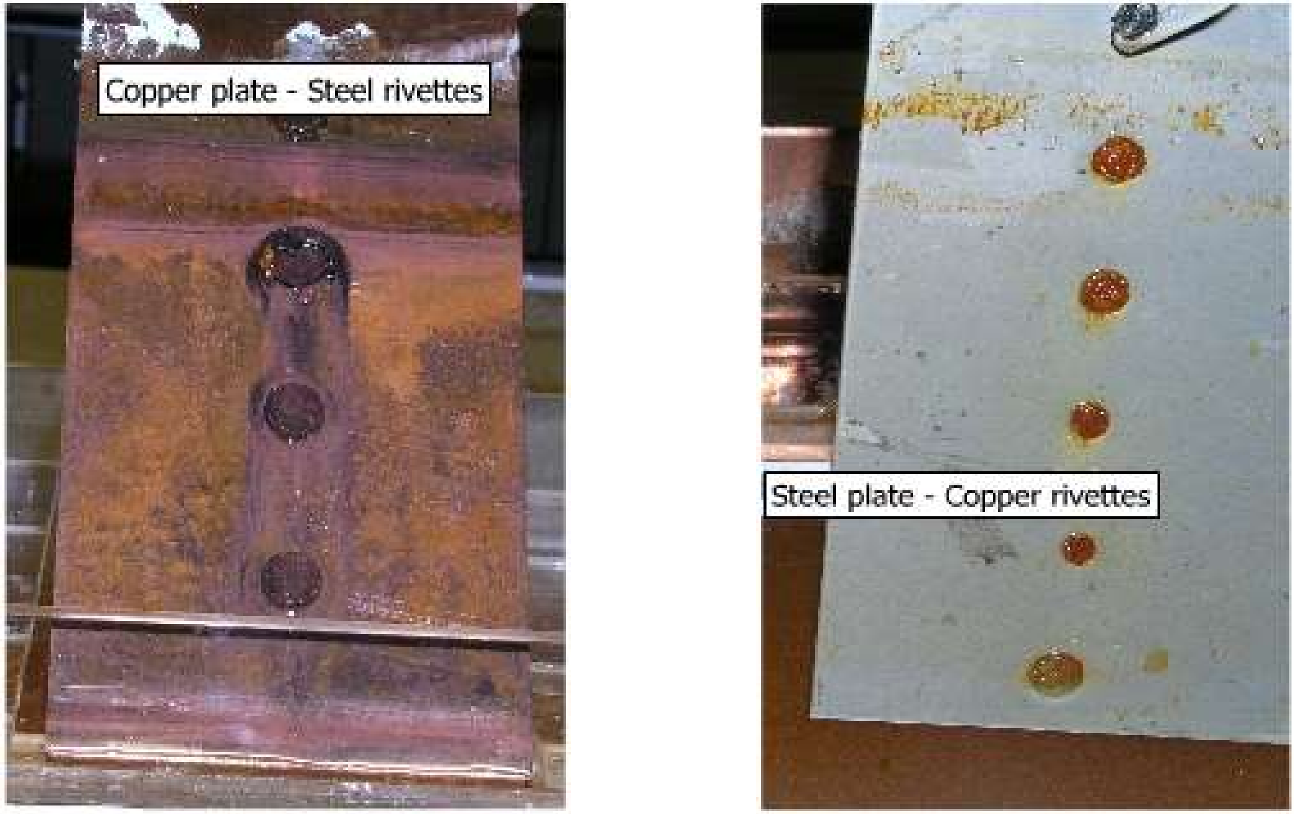
Copper rivets on a steel bar submerged in 3% sodium chloride solution after ten months



(a) Coupling of steel and aluminum

In galvanic series Aluminum is anodic to Steel (-1.03 V vs -0.44 V). Aluminum plate has a larger anodic area and steel rivettes, smaller cathodic area. Because of the larger anodic area, the current density would be very small, and then corrosion is hardly expected. Corrosion on aluminum plate is observed as shown in adjacent figure..

An opposite situation is shown in adjacent figure where steel plate is joined to aluminum rivette. The corrosion is clearly shown on aluminum rivettes because of smaller anodic area



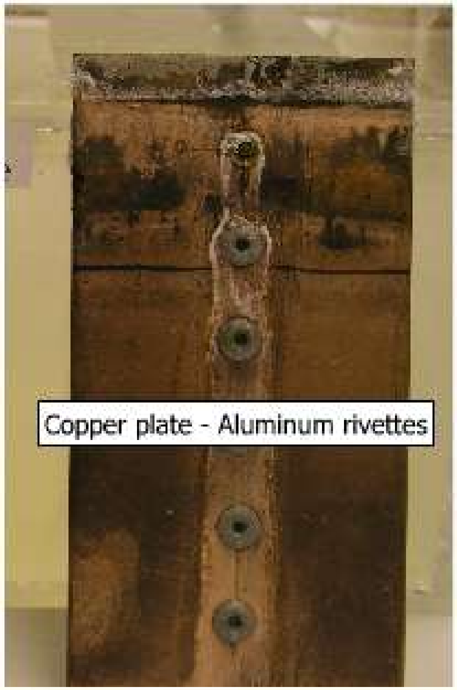
(b) Copper coupled to Steel

In this case, copper plate is cathodic to steel (+0.344 V) and has a larger area, where as steel rivettes are anodic to copper (-0.44 V) and has a smaller area. The steel rivetees are subjected to a higher anodic current density because of a smaller area and hence, subjected to corrosion. Corrosion of steel rivettes can be clearly observed in the picture.

When steel plates are coupled with copper rivettes, the situation here is reversed to what is shown above because of larger surface area of steel plate which are anodic to copper, the steel plates are not corroded. The pair is a good example of minimizing corrosion by keeping a larger anodic area and a smaller cathodic area.

A copper plate with Aluminum rivette is shown in this figure.

It is a case of large cathodic (copper) and small anodic (aluminum) area, resulting in corrosion of aluminum rivette.


Copper plate - Aluminum rivettes

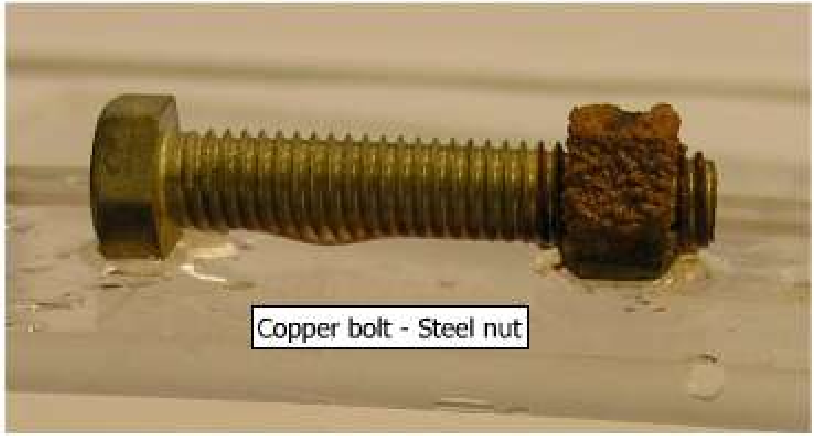
Nut and Bolt Assemblies:

(a) Steel bolt and copper nut assembly

Steel bolt is anodic to copper nut and has a larger surface area. Copper nut is cathodic to steel. Hence there is no appreciable evidence of corrosion in the assembly.

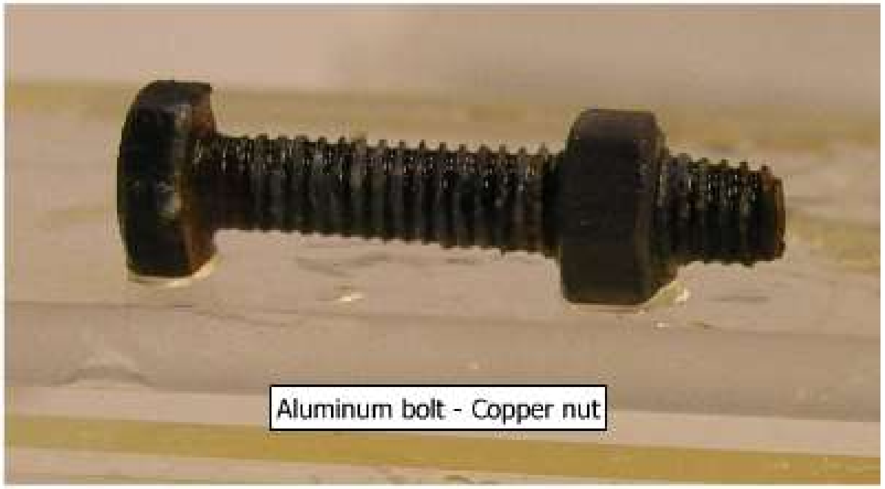

Steel bolt - Copper nut

The reverse situation is shown below. Corrosion is clearly observed on steel nut, because of smaller anodic area.


Copper bolt - Steel nut

(b) Aluminum bolt and copper nut

Because of larger anodic area of aluminum bolt and a smaller cathodic area of copper nut, corrosion is not appreciable in this system



a stainless steel screw in contact with a cadmium plated steel washer.

Avoid small base metals against large noble metals. Screws and other small anchors made from base metals will corrode when mounted to a larger noble metal.

Dielectric couplings prevent galvanic corrosion

Any time a bimetallic assembly contains metal systems that are subject to galvanic corrosion, the ratio of the cathodic area to that of the anode must be carefully considered. The corrosion current that flows between the cathode and anode is independent of area, but the rate of penetration at the anode is dependent on the current per unit area, that is, current density. Therefore, it is undesirable to have a large cathode surface in contact with a small anode surface. The rate of penetration from corrosion increases as the ratio of the cathode to anode surface area increases.

For example, when using a bare steel plate with a zinc rivet, the ratio of the cathode surface area to the anode surface area is large, and the rivet will fail rapidly because of accelerated corrosion. When combining a zinc plate with a stainless steel rivet, the area ratio between the cathode and anode is reversed, and although more surface area is affected, the depth of penetration is small; the fastener should not fail because of corrosion.

For example, if a window frame made of stainless steel and it is attached with carbon steel screws, the screws will probably corrode at an accelerated rate. If the area of the cathode (noble metal – stainless steel) is very small, and the anode (active metal – carbon steel) is very large, the current produced will be very low and the corrosion rate of the anode may not be affected. If the window frame is made of carbon steel and it is attached with stainless steel screws there will be very little, if any, galvanic corrosion.

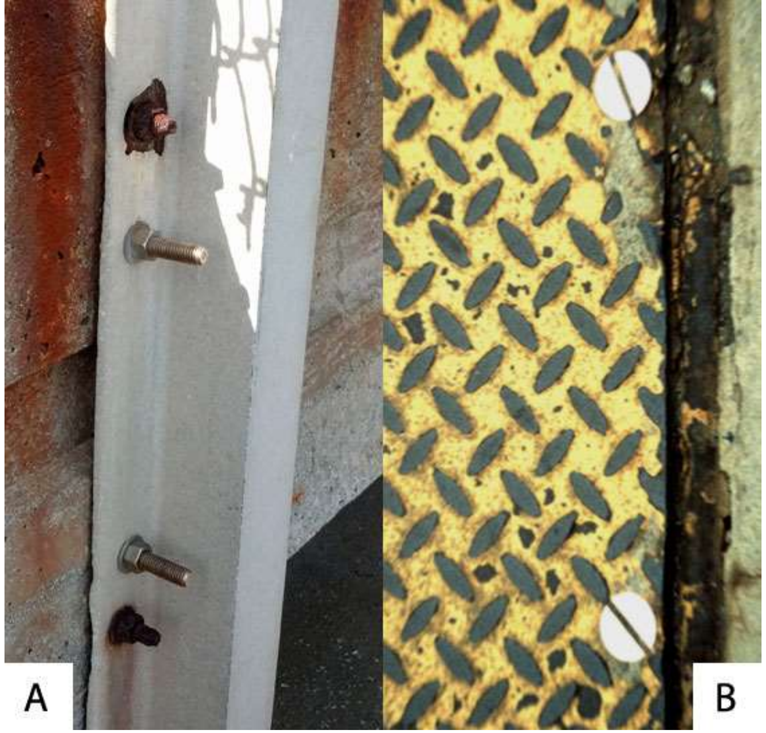


Figure 3A shows the galvanic corrosion of carbon steel bolts (anode) used to secure a stainless steel structural railing (cathode) support on a bridge. The small surface area of the active bolts results in an undesirable galvanic couple and they are exhibiting an accelerated corrosion rate. Image 3B shows stainless steel fasteners used to secure a carbon steel tread plate. The relatively small surface area of the stainless steel fasteners means that they have essentially no galvanic effect on the corrosion rate of the carbon steel plate.

In material combinations, the fasteners should always be made up of more noble material, so that cathodic surface area is small.

Weather also has a large effect on the rate of galvanic corrosion. In "harsher" environments (typically outdoors; highly humid; salty environments) a potential difference of ~0.15V is sufficient enough to cause galvanic corrosion. In what is considered to be a "normal" environment (storage places; warehouses; humidity-controlled areas) there should not be a potential difference of more than ~0.25V, otherwise galvanic corrosion can occur.

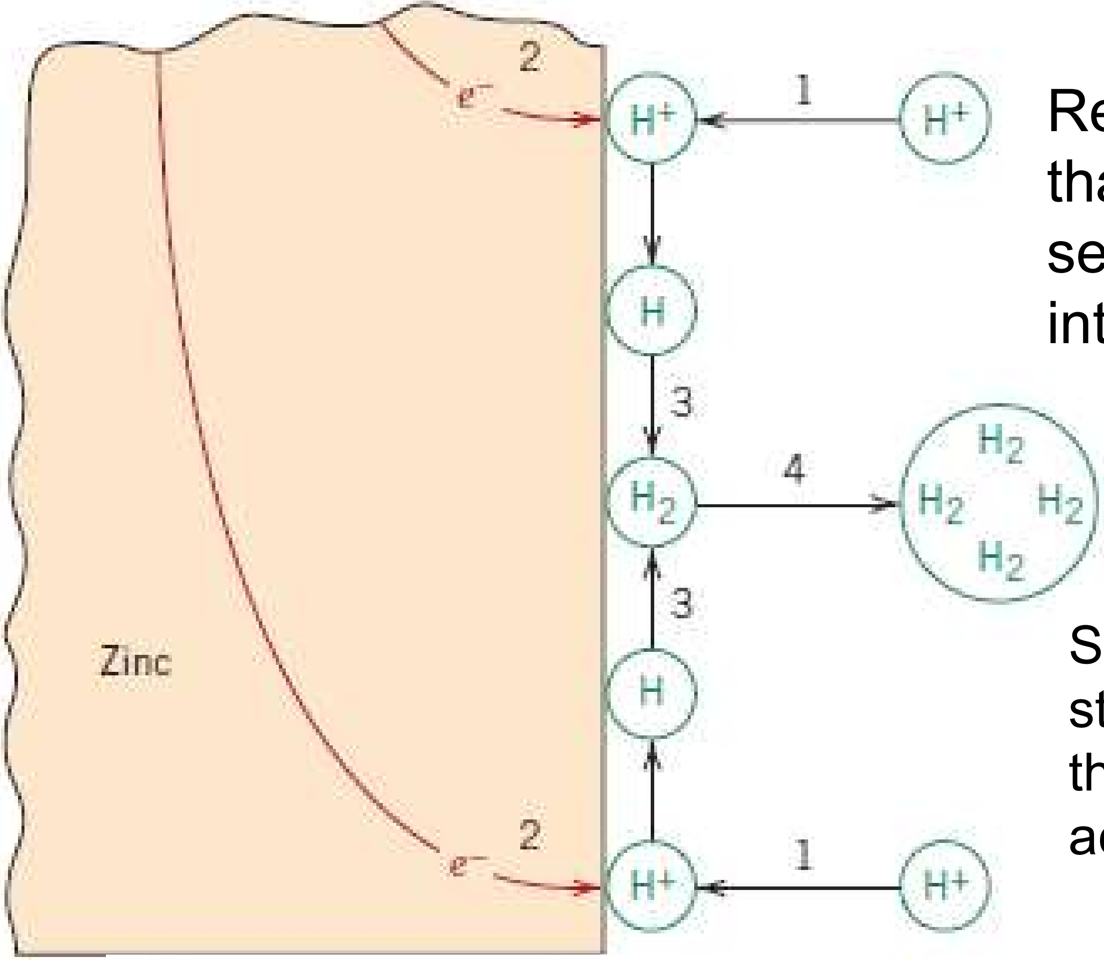
One of the most famous examples of galvanic corrosion is in the *Statue of Liberty*, New York. Built in 1886, the exterior of the statue was made from copper and the interior from cast iron. The large exterior skin was therefore cathodic and the interior a smaller anode, separated only by a thin asbestos skin impregnated with shellac, which eventually failed.

In 1984 the statue was shut down due to safety concerns as it was observed that some galvanic corrosion had occurred.
Upon removal of the paint surface on the copper skin, significant corrosion was found and it turned out that the torch famously held high in the air in the statue’s right hand had been leaking rain water into the structure.
The entire cast iron interior was removed and replaced with a low-carbon, corrosion resistant stainless steel.

Polarization

- ❑ Understanding Corrosion behavior and corrosion reactions, Polarization is important.
- ❑The rate of an electrochemical reaction is limited by various physical and chemical factors.
- ❑ Hence, an electrochemical reaction is said to be polarized or retarded by these environmental factors
- ❑Anodic and Cathodic reactions lead to concentration differences near the electrodes
- ❑ This leads to variation in cathode and anode potentials *(towards each other)* → *Polarization*

Activation Polarization



Refers to an electrochemical process that is controlled by the reaction sequence at the metal-electrolyte interface.

Schematic representation of possible steps in the hydrogen reduction reaction, the rate of which is controlled by activation polarization.

1. Adsorption of H^+ ions from the solution onto the zinc surface
2. Electron transfer from the zinc to form a hydrogen atom,

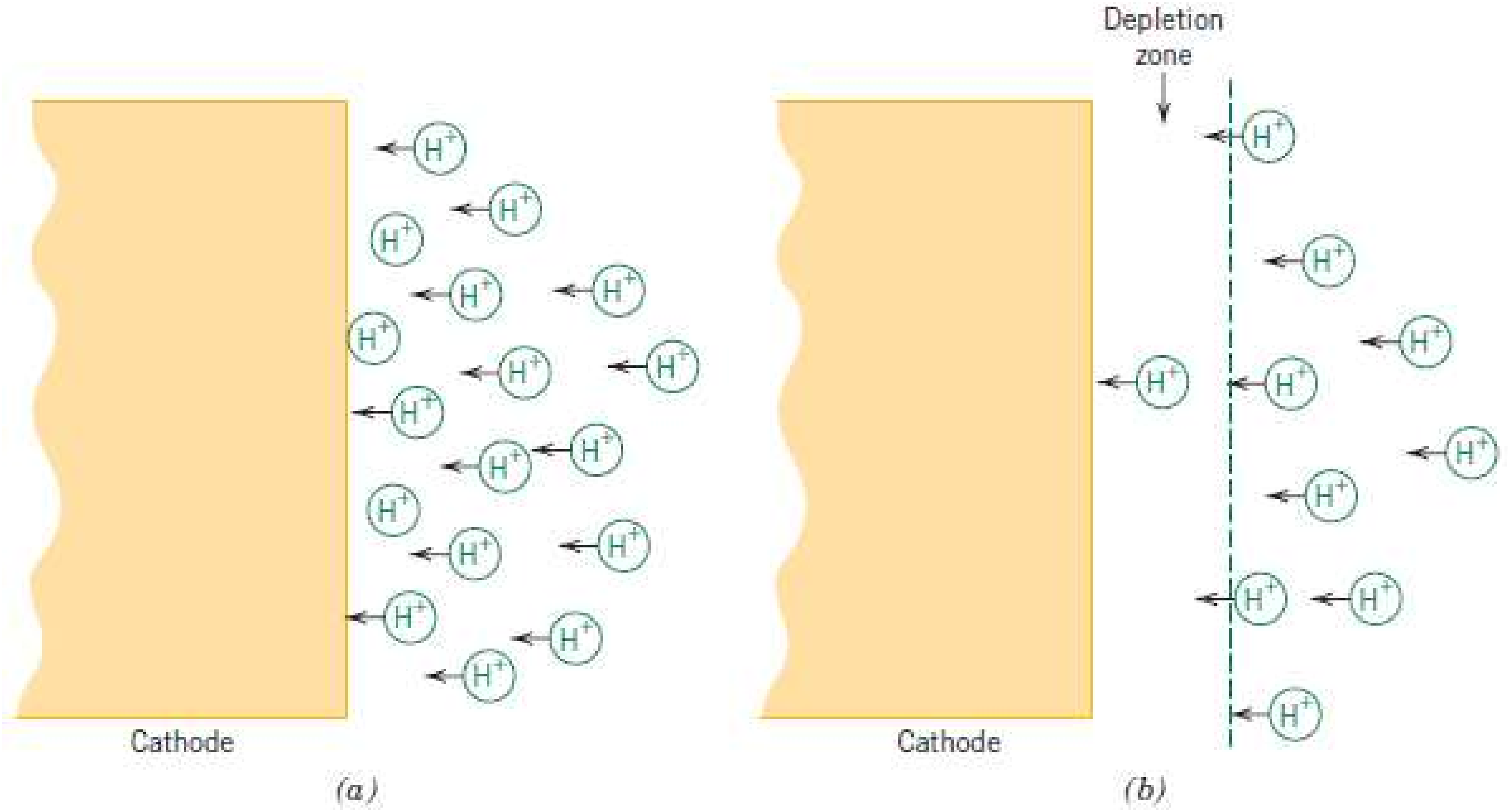
$$H^+ + e^- \longrightarrow H$$

3. Combining of two hydrogen atoms to form a molecule of hydrogen,

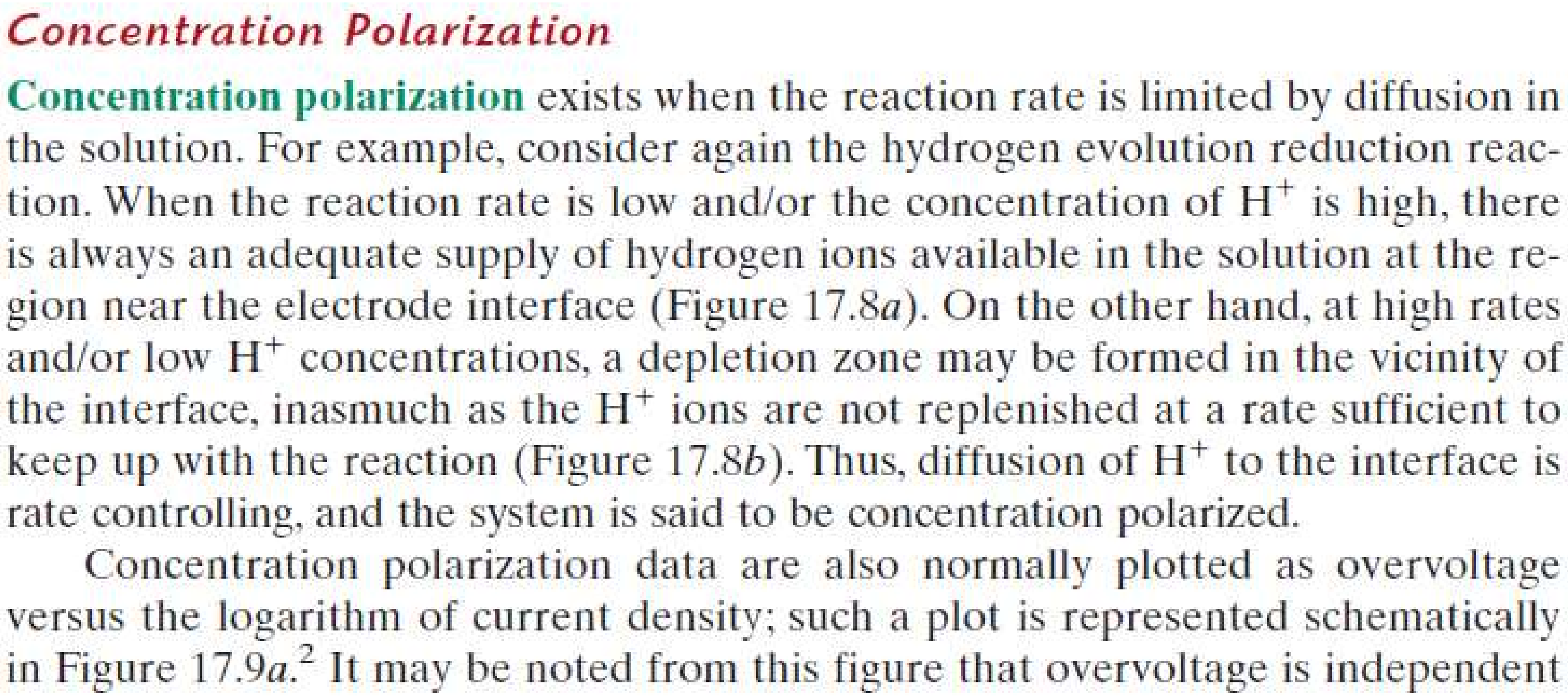
$$2H \longrightarrow H_2$$

4. The coalescence of many hydrogen molecules to form a bubble

Concentration Polarization



For hydrogen reduction, schematic representations of the distribution in the vicinity of the cathode for (*a) low reaction rates and/or high concentrations, and (b) high* reaction rates and/or low concentrations wherein a depletion zone is formed that gives rise to concentration polarization.



Concentration Polarization

Concentration polarization exists when the reaction rate is limited by diffusion in the solution. For example, consider again the hydrogen evolution reduction reaction. When the reaction rate is low and/or the concentration of H^+ is high, there is always an adequate supply of hydrogen ions available in the solution at the region near the electrode interface (Figure 17.8*a*). On the other hand, at high rates and/or low H^+ concentrations, a depletion zone may be formed in the vicinity of the interface, inasmuch as the H^+ ions are not replenished at a rate sufficient to keep up with the reaction (Figure 17.8*b*). Thus, diffusion of H^+ to the interface is rate controlling, and the system is said to be concentration polarized.

Concentration polarization data are also normally plotted as overvoltage versus the logarithm of current density; such a plot is represented schematically in Figure 17.9*a*.[2] It may be noted from this figure that overvoltage is independent

Activation polarization usually is the controlling factor during corrosion in media containing a high concentration of active species (e.g concentrated acids).
Concentration polarization generally predominates when the concentration of the reducible species is small (e.g. dilute acids, aerated salt solutions).

In most instances Concentration polarization during metal dissolution is usually small and can be neglected; it is only important during reduction reactions.

Classification of Corrosion

- ❑ Based on Temperature
  - ✓ Low Temperature Corrosion
  - ✓ High Temperature Corrosion

- ❑ Preferred Classification
  - ✓ Wet Corrosion
  - ✓ Dry Corrosion

- ❖ Wet corrosion occurs when a liquid is present. This usually involves aqueous solutions or electrolytes and accounts for the greatest amount of corrosion by far.
  - ○ A common example is corrosion of steel by water.
- ❖ Dry Corrosion occurs in the absence of liquid phase or above the dew point of the environment. Vapors and gases are usually the corrodents. Dry corrosion is most often associated with the high temperatures.
  - ○ An example is attack on steel by furnace gases.

Presence of even small amounts of moisture could change the corrosion picture completely. For ex, dry chlorine is practically non corrosive to ordinary steel, but moist chlorine, or chlorine Dissolved in water is extremely corrosive and attacks most of the common metals and alloys. The reverse is True for titanium- dry chlorine gas is more corrosive than wet chlorine

Oxidizing Agents

In wet corrosion, two principal oxidizing agents are encountered in practice:

- solvated protons;
- dissolved oxygen.

However, other oxidizing agents can also cause corrosion in wet environments, such as:

- oxidizing metal cations: Cu^{2+}, Fe^{3+}, Sn^{4+};
- oxidizing anions: NO_2^- , NO_3^-, CrO_4^{2-}, MnO_4^-, OCl^-;
- dissolved oxidizing gases: O_3, Cl_2, SO_3.

At high temperatures, certain chemical substances, normally inoffensive, become corrosive. Among the oxidizing agents responsible for dry corrosion, one finds:

- gaseous oxygen;
- water vapor;
- carbon dioxide, CO_2;
- sulfur-containing compounds: S_2, SO_2, SO_4^{2-}.

1.2.3 Corrosion rate

The rate of corrosion can be expressed in many different ways depending on the application and personal preferences:

- as a mass loss per unit of surface and per unit of time;
- as the number of moles transformed per unit of surface and per unit of time;
- as corroded depth per unit of time;
- as a current density.

Corrosion rate expressions

❑ Percent weight loss. Milligrams per square centimeter per day and grams per Square inch per hour.

But rate of penetration or thinning of structural piece is missing which can be used to predict the life of a given component

$$\frac{mm}{year} = \frac{87.6\,W}{DAT}$$

Where W=weight loss, mg
D=density of specimen, g/cm^3
A=Area of specimen, cm^2
T=exposure time, hr

❑ The expression **mils per year** (milli inch per year) s the most desirable way of expression the corrosion rates

$$\text{mpy} = \frac{534W}{DAT}$$

Where W=weight loss, mg
D=density of specimen, g/cm^3
A=Area of specimen, sq.in
T=exposure time, hr

A mil is one thousandth of an inch.

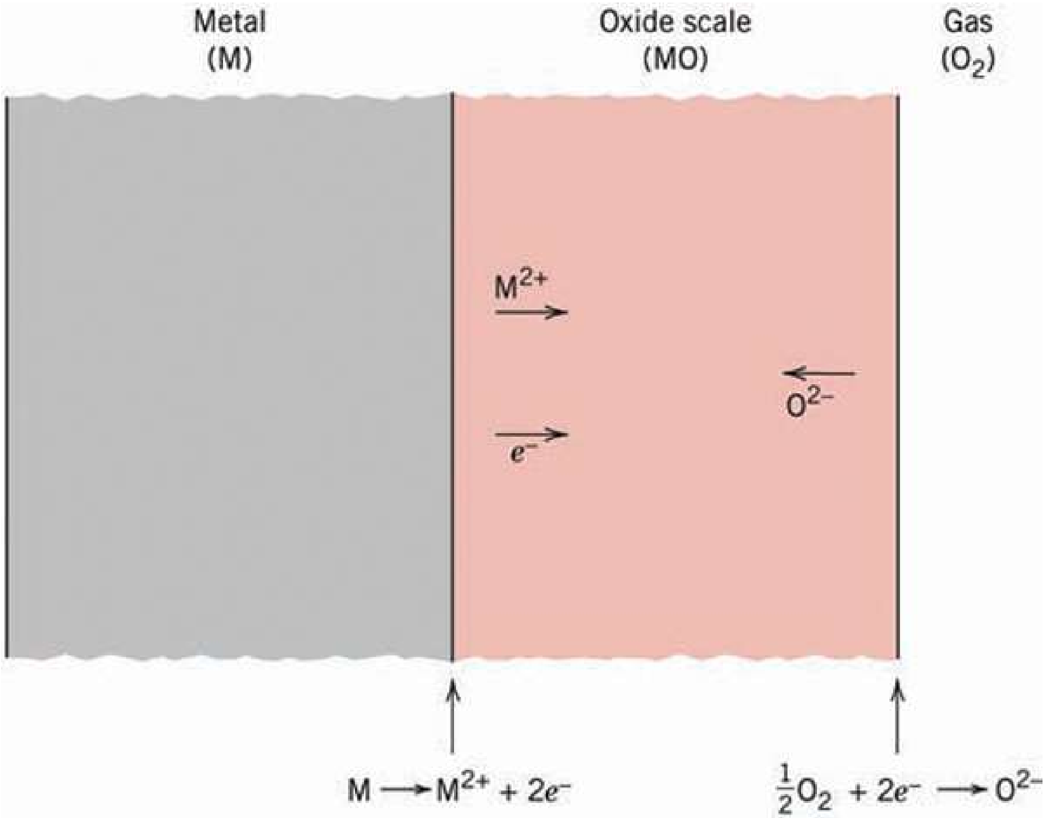
Table 1.4 Frequently used units for measuring corrosion rate. To obtain the units indicated in the first row, one multiplies the unit in the first column by the corresponding conversion factor.

	$\frac{\text{mole}}{\text{m}^2\text{s}}$	$\frac{\text{mole}}{\text{cm}^2\text{s}}$	$\frac{\text{A}}{\text{m}^2}$	$\frac{\mu\text{A}}{\text{cm}^2}$	$\frac{\text{mg}}{\text{dm}^2\text{day}}$	$\frac{\text{mm}}{\text{year}}$
$\frac{\text{mole}}{\text{m}^2\text{s}}$	1	10^{-4}	$9.65\times10^4\,n$	$9.65\times10^6\,n$	$8.64\times10^5\,M$	$3.15\times10^4\,\frac{M}{\rho}$
$\frac{\text{mole}}{\text{cm}^2\text{s}}$	10^4	1	$9.65\times10^8\,n$	$9.65\times10^{10}\,n$	$8.64\times10^9\,M$	$3.15\times10^8\,\frac{M}{\rho}$
$\frac{\text{A}}{\text{m}^2}$	$\frac{1.04\times10^{-5}}{n}$	$\frac{1.04\times10^{-9}}{n}$	1	100	$8.96\,\frac{M}{n}$	$0.327\,\frac{M}{n\rho}$
$\frac{\mu\text{A}}{\text{cm}^2}$	$\frac{1.04\times10^{-7}}{n}$	$\frac{1.04\times10^{-11}}{n}$	0.01	1	$8.96\times10^{-2}\,\frac{M}{n}$	$3.27\times10^{-3}\,\frac{M}{n\rho}$
$\frac{\text{mg}}{\text{dm}^2\text{day}}$	$\frac{1.16\times10^{-6}}{M}$	$\frac{1.16\times10^{-10}}{M}$	$0.112\,\frac{n}{M}$	$11.2\,\frac{n}{M}$	1	$\frac{3.65\times10^{-2}}{\rho}$
$\frac{\text{mm}}{\text{year}}$	$3.17\times10^{-5}\,\frac{\rho}{M}$	$3.17\times10^{-9}\,\frac{\rho}{M}$	$3.06\,\frac{n\rho}{M}$	$306\,\frac{n\rho}{M}$	$27.4\,\rho$	1

M = atomic mass in g/mol, ρ = volumetric mass en g/cm^3, n = charge number (dimensionless).

Passivity

- ❑ Loss of chemical reactivity experienced by certain metals and alloys under particular environmental conditions
- ❑ That is certain metals and alloys become essentially inert and act as if they were noble metals such as platinum and gold
- ❑ Passivity means the lack of activity under conditions where a metal would be expected to react readily. There are certain metals which are passive to certain corroding agents. For example; iron is passive to conc. HNO_3. Aluminium has no action with conc. HNO_3 in absence of chlorides etc.



Silicon

Aluminium

Stainless Steel

Nickle

Oxide Scale/film acts as both electrolyte and electronconductor

Mesawit [y-Fe-OOH]

Fe-98%
P-1%
Pb-0.66%
Bell Metal-0.17%
Calx-Brass-0.17%

Vajra Sanghata

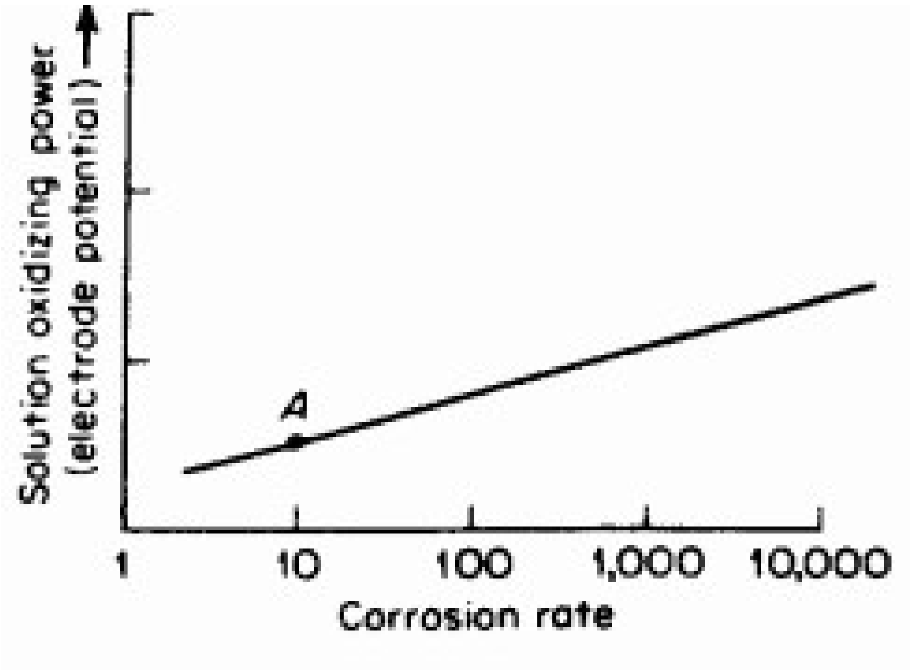
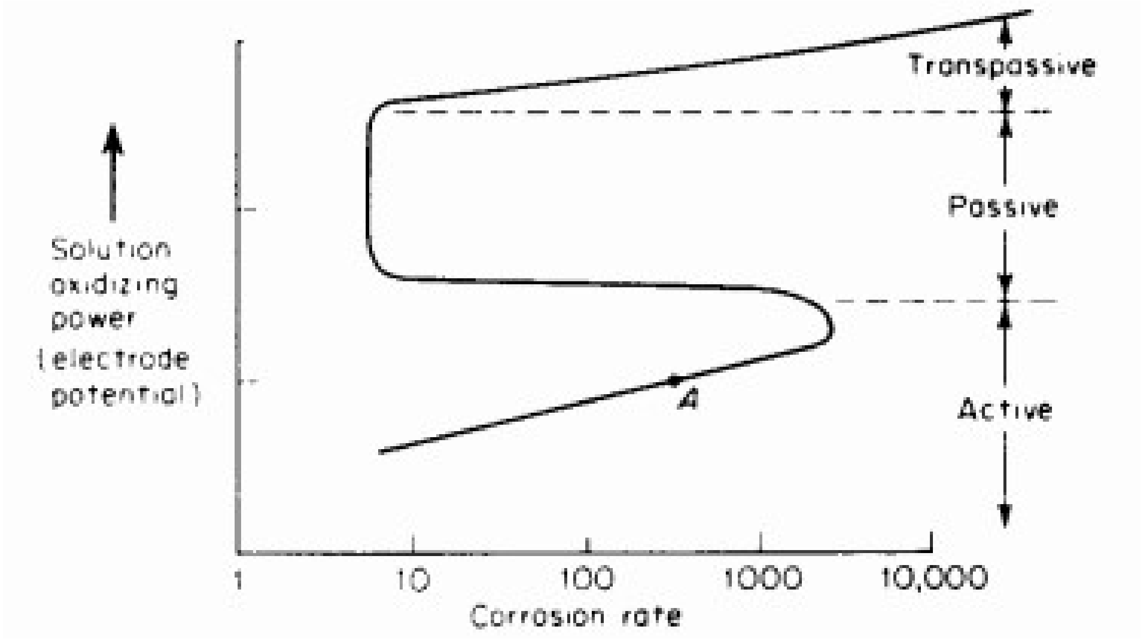


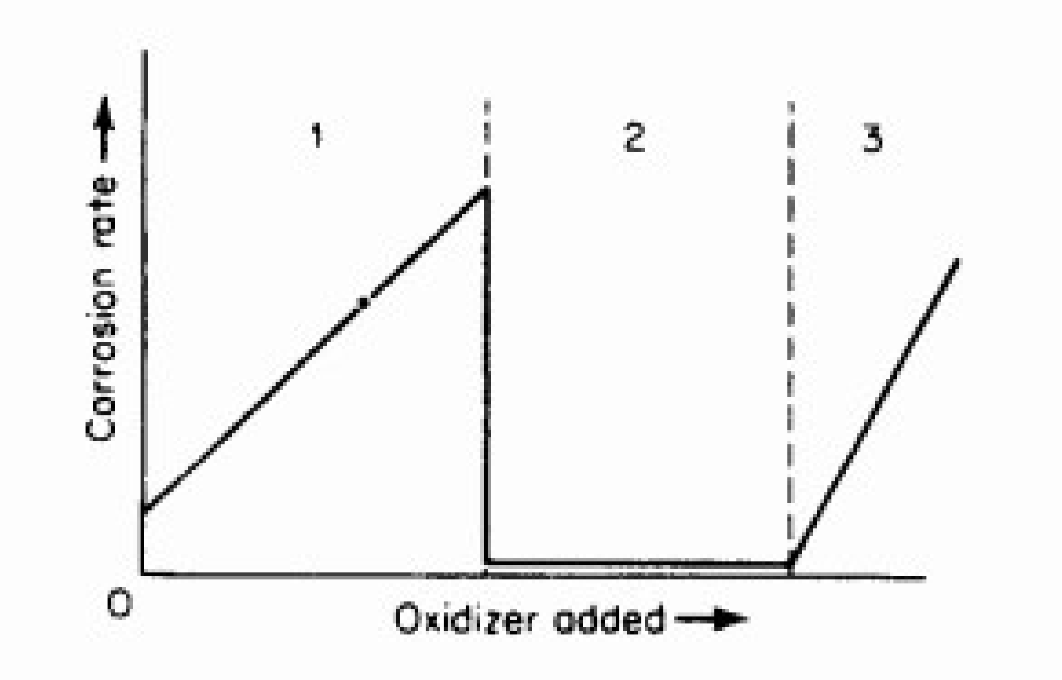
Figure 2-7 Corrosion rate of a metal as a function of solution oxidizing power (electrode potential).

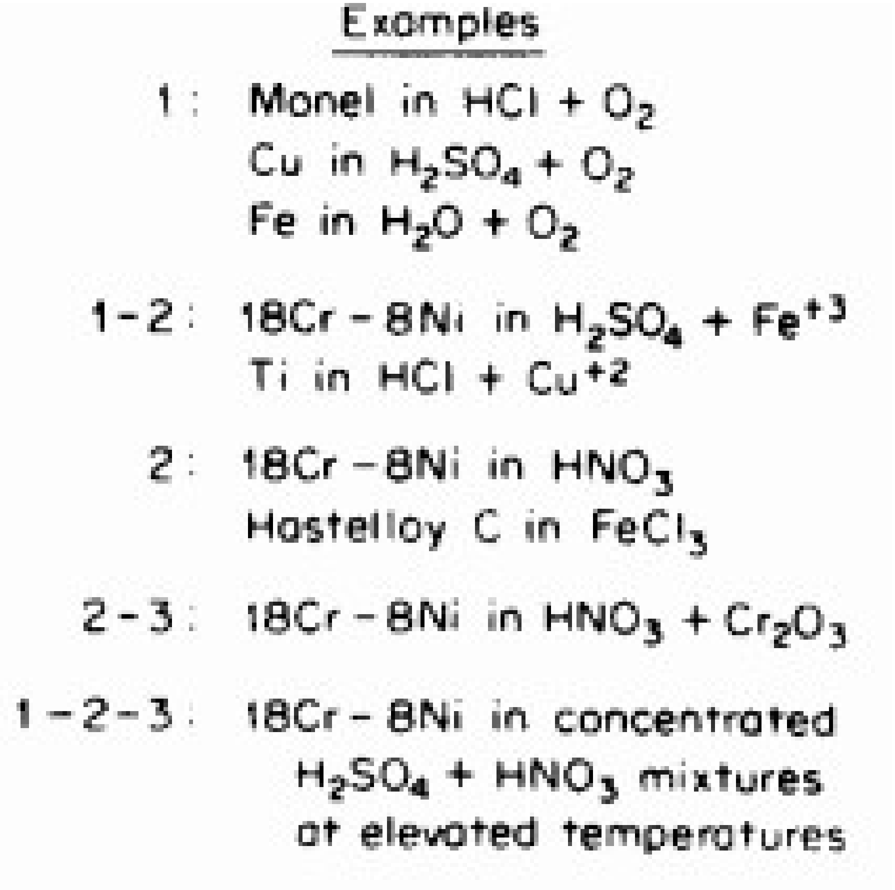


Corrosion characteristics of an active-passive metal as a function of solution oxidizing power

Environmental Effects

Effect of Oxygen and Oxidizers





Examples

1: Monel in $HCl + O_2$
Cu in $H_2SO_4 + O_2$
Fe in $H_2O + O_2$

1-2: 18Cr-8Ni in $H_2SO_4 + Fe^{+3}$
Ti in $HCl + Cu^{+2}$

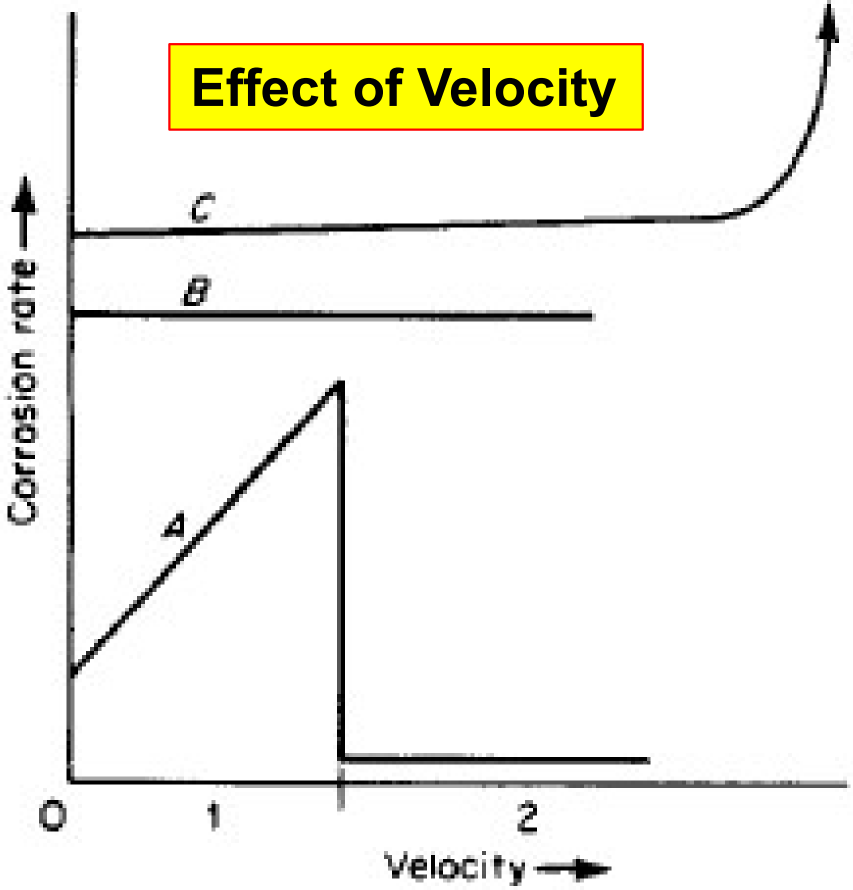
2: 18Cr-8Ni in HNO_3
Hastelloy C in $FeCl_3$

2-3: 18Cr-8Ni in $HNO_3 + Cr_2O_3$

1-2-3: 18Cr-8Ni in concentrated
$H_2SO_4 + HNO_3$ mixtures
at elevated temperatures

Corrosion Engineering by Mars G Fontana

Effect of Velocity



Examples

Curve A :
1 : Fe in $H_2O + O_2$
Cu in $H_2O + O_2$
1–2 : 18Cr–8Ni in $H_2SO_4 + Fe^{+3}$
Ti in $HCl + Cu^{+2}$

Curve B : Fe in dilute HCl
18Cr–8Ni in H_2SO_4

Curve C : Pb in dilute H_2SO_4
Fe in concentrated H_2SO_4

Figure 2-10 Effect of velocity on corrosion rate.

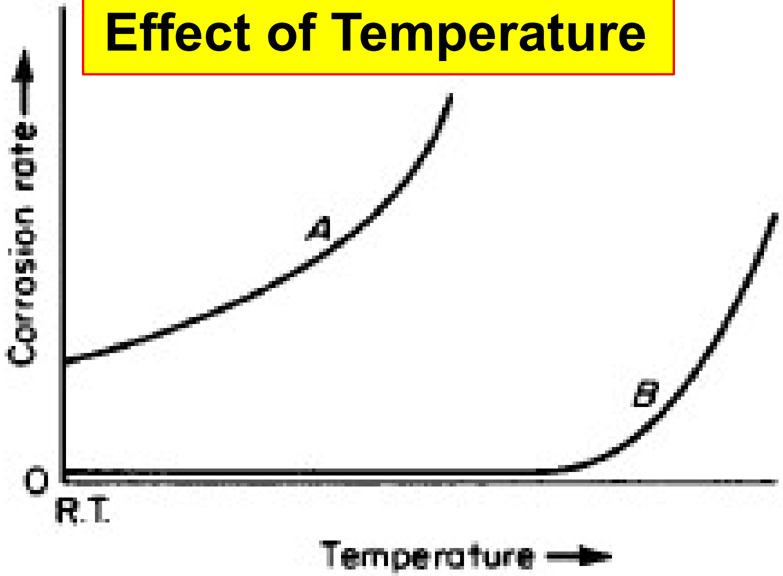
For corrosion processes that are controlled by activation polarization, agitation and Velocity have no effect on the corrosion rate as shown in Curve B.

If the corrosion processes is under cathodic diffusion control, then agitation increases the corrosion rate as shown in Curve A, section 1. this effect is generally occurs when an Oxidizer is present in very small amounts, as is the case for dissolved oxygen in acids or water

If the corrosion processes is under diffusion control and the metal is readily passivated, then the behavior corresponding as shown in Curve A, section 1 and 2. That is with Increasing agitation, the metal will undergo an active –to-passive transition. Easily passivated Materials such as stainless steel and Titanium frequently are more corrosion resistant when The velocity of the corrosion medium is high

Some metals owe their corrosion resistance in certain mediums to the formation of massive bulk protective films on their surfaces. These films differ from the usual passivating films in that they are readily visible and much less tenacious. It is believed that both lead and steel are protected from attack in sulfuric acid by insoluble sulfate films. When materials such as these are exposed to extremely high corrosive velocities, mechanical damage or removal of these films can occur, resulting in accelerated attack as shown in curve *C*. This is called erosion corrosion and is discussed in Chap. 3. In the case of curve *C*, note that until mechanical damage actually occurs, the effect of agitation or velocity is virtually negligible.

Effect of Temperature



Examples

Curve A : 18Cr – 8Ni in H_2SO_4
Ni in HCl
Fe in HF

Curve B : 18Cr – 8Ni in HNO_3
Monel in HF
Ni in NaOH

Figure 2-11 Effect of temperature on corrosion rate.

Temperature increases the rate of almost all chemical reactions. Figure 2-11 illustrates two common observations on the effect of temperature on the corrosion rates of metals. Curve *A* represents the behavior noted above, a very rapid or exponential rise in corrosion rate with increasing temperature. Behavior such as noted in curve *B* is also quite frequently observed. That is, an almost negligible temperature effect is followed by a very rapid rise in corrosion rate at higher temperatures. In the case of 18-8 stainless steel in nitric acid, this effect is readily explained. Increasing the temperature of nitric acid greatly increases its oxidizing power. At low or moderate temperatures, stainless steels exposed to nitric acid are in the passive state very close to the transpassive region. Hence, an increase in oxidizing power causes a very rapid increase in the corrosion rate of these materials. A similar sort of mechanism may explain the behavior of Monel and nickel, as noted in Fig. 2-11. However, it is possible that curves such as *B* in many instances erroneously represent actual behavior. If the corrosion rate at low temperature is very low, and increases exponentially, linear plots will appear as curve *B*. That is, corrosion rate increases rapidly with temperature; this is not evident in the usual plots of corrosion rate versus temperature because of the choice of scales.

Effect of Corrosive Concentration

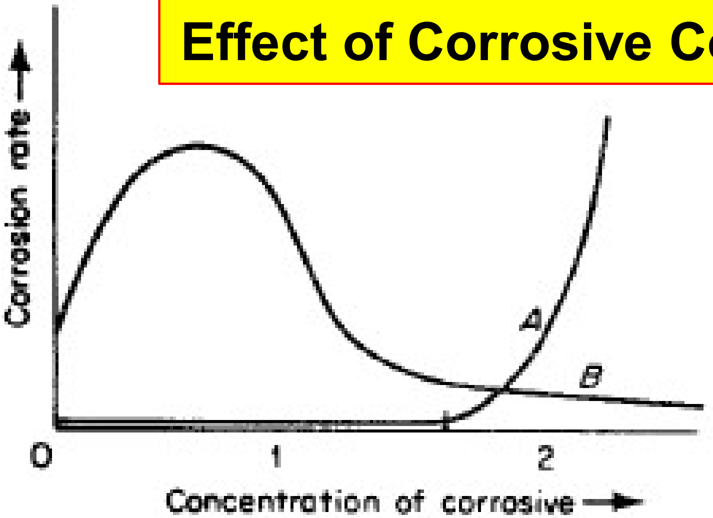


Fig 2.12 Effect of corrosive concentration on corrosion rate

Examples

Curve A:

1: Ni in NaOH
18Cr−8Ni in HNO_3
Hastelloy B in HCl
Ta in HCl

1−2: Monel in HCl
Pb in H_2SO_4

Curve B:

Al in acetic acid and HNO_3
18Cr−8Ni in H_2SO_4
Fe in H_2SO_4

Fig 2.12 shows schematically the effects of corrosive concentration on corrosion rate. Note that curve A has two sections, 1 and 2. Many materials that exhibit passivity effects are only negligibly affected by wide changes in corrosive concentration, as shown in curve A, section 1. Other materials show similar behavior except at very high corrosive concentrations, when the corrosion rate increases rapidly as shown curve A, sections1 and 2. Lead is a material that shows this effect and it is believed to be due to the fact that lead sulfate, which forms a protective film in low concentrations of sulphuric acid, is soluble in concentrated sulfuric acid. The behavior of acids that are soluble in all concentrations of water often yield curves similar to curve B in Fig 2.12. Initially as the concentration of corrosive is increased, the corrosion rate is likewise increased. This is primarily due to the fact that the amount of hydrogen ions, which are the active species, are increased as acid concentration is increased. However, as acid concentration is increased further, corrosion rate reaches a maximum and then decreases. This is undoubtedly due to the fact that at very high concentrations of acids ionization is reduced. Because of this, many of the common acids such as H2So4, HF, CH3COOH and other, are virtually inert when in the pure state or 100% concentration and at moderate temperatures.

According to Faraday’s Law, when n_i *moles of a given substance react, a* proportional electric charge Q *passes across the electrode-electrolyte interface:*

$$Q = n \cdot F \cdot n_{\mathrm{i}}$$

Where, F *is called Faraday constant:* $F = 96{,}485$ *C/mol,*
n*, is the stoichiometric coefficient of the* electrons in the equation for the electrode reaction.

Gibbs Free Energy is defined as the thermodynamic potential that signifies the maximum or reversible work performed by a thermodynamic system at constant temperature and pressure.

$$H_2(g, 10\ \text{atm}) \rightarrow H_2(g, 1\ \text{atm})$$

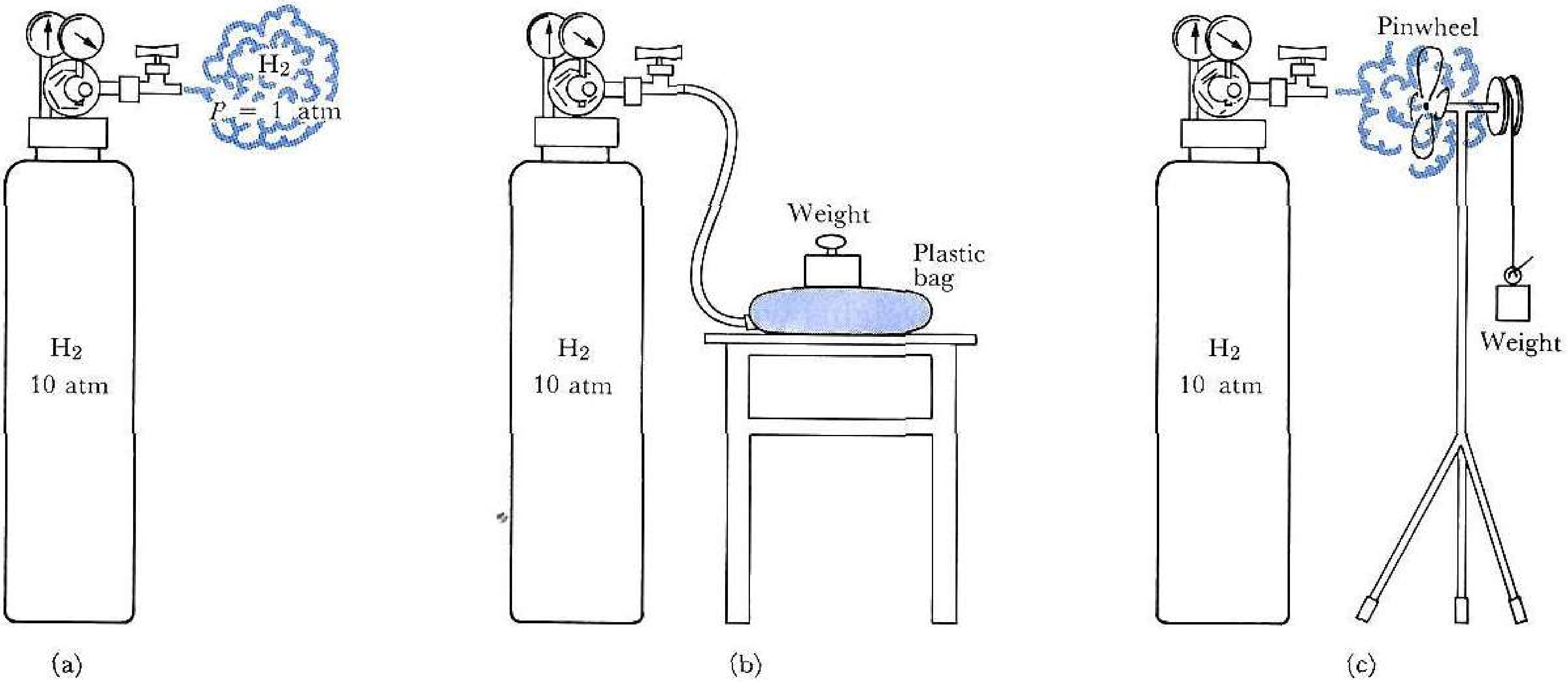


Figure 19-1 Nonproductive and productive use of the free energy stored in hydrogen gas at 10 atm pressure. (a) Expansion to 1 atm with dissipation of energy. (b) Use of part of the available free energy to lift a weight by inflating a plastic bag. (c) Use of part of the free energy to lift a weight by turning a pinwheel or windmill.

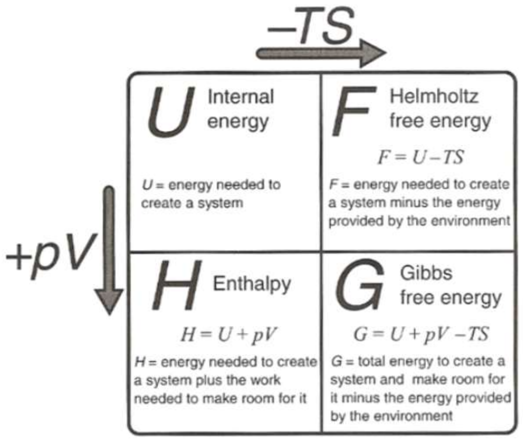
$$\Delta G = \Delta G^0 + RT \ln (p_2/p_1)$$

$$\Delta G = 0 + RT \ln (1/10) = -RT \ln (10) = -5.706\ \text{kJ mole}^{-1}$$

- The chemical potential or electrochemical potential (if we are dealing with a charged particle) is the measure of how all the thermodynamic properties vary when we change the amount of the material present in the system. Formally we can write:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} \qquad \mu = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

$$\mu = \left(\frac{\partial H}{\partial n}\right)_{S,P} \qquad \mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}$$



U Internal energy

U = energy needed to create a system

F Helmholtz free energy

$F = U - TS$

F = energy needed to create a system minus the energy provided by the environment

H Enthalpy

$H = U + pV$

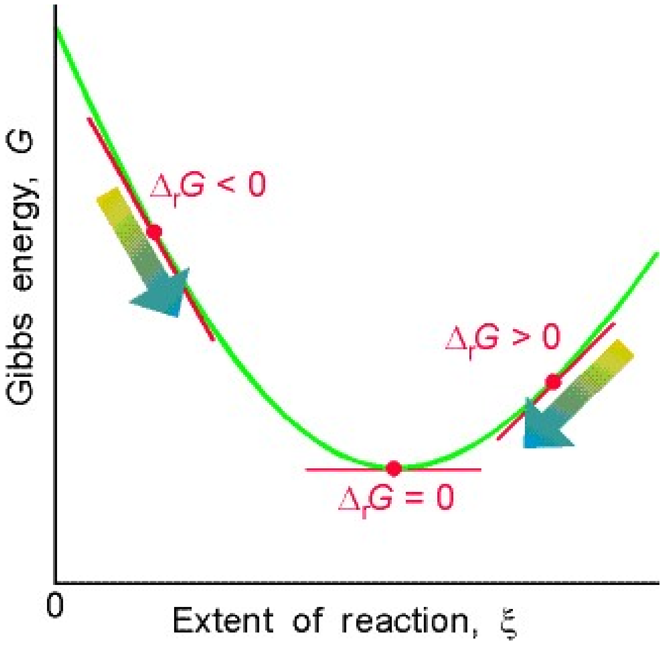
H = energy needed to create a system plus the work needed to make room for it

G Gibbs free energy

$G = U + pV - TS$

G = total energy to create a system and make room for it minus the energy provided by the environment

F
=A



Start with the First Law of Thermodynamics and some standard thermodynamic relations and we find:

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

$$\mathrm{d}q = T\,\mathrm{d}S$$

$$\mathrm{d}w = -P\,\mathrm{d}V + \mathrm{d}w_{electrical}$$

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \mathrm{d}w_{electrical}$$

$$\mathrm{d}H_P = \mathrm{d}U_P + P\,\mathrm{d}V$$

$$\begin{aligned}\mathrm{d}G_T &= \mathrm{d}H_T - T\,\mathrm{d}S \\ &= \mathrm{d}U_{T,P} + P\,\mathrm{d}V - T\,\mathrm{d}S \\ &= \cancel{T\,\mathrm{d}S} - \cancel{P\,\mathrm{d}V} + \mathrm{d}w_{electrical} + \cancel{P\,\mathrm{d}V} - \cancel{T\,\mathrm{d}S}\end{aligned}$$

$$\boxed{\mathrm{d}G_{T,P} = \mathrm{d}w_{electrical}}$$

- And therefore, the Gibbs function is at the heart of electrochemistry, for it identifies the amount of work we can extract electrically from a system.

Relation between Equilibrium constant, Gibbs free energy and EMF of a cell

The free energy function is the key to assessing the way in which a chemical system will spontaneously evolve. In the Gibbs-Duhem formalism of the Gibbs free energy we can write:

$$\mathrm{d}G = \cancel{-S\,\mathrm{d}T} + \cancel{V\,\mathrm{d}P} + \sum \mu_i\,\mathrm{d}n_i + \cancel{\gamma\,\mathrm{d}A} + \cancel{f\,\mathrm{d}l}$$

constant T

constant P

don’t change shape

don’t stretch it

$$\mathrm{d}G = \sum \mu_i\,\mathrm{d}n_i$$

- Every substance has a unique propensity to contribute to a system's energy. We call this property **Chemical Potential**:

$$\mu$$

- When the substance is a charged particle (such as an electron or an ion) we must include the response of the particle to an electrical field in addition to its Chemical Potential. We call the **Electrochemical Potential** (F is the Faraday constant, z the charge on the particle and ϕ the potential):

$$\overline{\mu} = \mu + z F \phi$$

Relation between Equilibrium constant, Gibbs free energy and EMF of a cell

- Now we can easily see how this Gibbs function relates to a potential. The electrical work (electrical energy) is equal to the product of the EMF of the cell and electrical charge that flows through the external circuit

$$w_{electrical} = V Q$$

$$\text{since} \quad Q = n F$$

$$= n F E$$

According to thermodynamics the free energy change (ΔG) is equal to the maximum work. In the cell work is done on the surroundings by which electrical energy flows through the external circuit,

$$\boxed{\Delta G_{T,P} = -w_{electrical} = -n F E}$$

By convention, we identify work which is negative with work which is being done by the system on the surroundings. And negative free energy change is identified as defining a spontaneous process.

The bottom line is we now have a relationship between the ΔG_{rxn} and the electric potential, E. Under standard conditions,

$$\boxed{\mathbf{\Delta G^0 = -nFE^0}}$$

- The propensity for a given material to contribute to a reaction is measured by its **activity, a**.
- How "active" is this substance in this reaction compared to how it would behave if it were present in its standard state?
- Activity scales with concentration or partial pressure.

$$a \propto C/C^\circ \text{ (solution) and } a \propto P/P^\circ \text{ (gas)}$$

BUT…

- intermolecular interactions
- deviation from a direct correspondence with pressure or concentration

- Definition of activity is then: $a = \gamma \dfrac{C}{C^{o}}$ $a = \gamma \dfrac{P}{P^{o}}$

- Activity coefficients close to 1 for dilute solutions and low partial pressures.
- Activity changes with concentration, temperature, other species, etc. Can be very complex.
- Generally, we ignore activity coefficients for educational simplicity, but careful work always requires its consideration.

If the concentrations of all the reacting species are below about 0.01 mol/l , the activity coefficients are generally close to unity, and the activities can be replaced by concentrations with little error

- How does chemical potential change with activity?
- Integration of the expressions for the dependence of amount of material on the Gibbs function, leads to the following relationship :

$$\mu = \mu^{o} + RT \ln a$$

$$dG = -SdT + VdP + \sum \mu_i dn_i + \gamma dA + f dl$$

The total temperature and pressure P remain constant, but the partial pressure P_i of each specie changes. Therefore, if we don't change the geometry of our cell, we have

$$\boxed{\left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_j} = \mu_i} \rightarrow G = \mu_i n_i, \boxed{\left(\frac{\delta G}{\delta P}\right)_{T,n_i} = V} \rightarrow \frac{\delta G}{\delta P} = \frac{\delta \mu_i}{\delta P} n_i = V$$

Ideal gas law$PV = n_i RT \rightarrow \frac{V}{n_i} = \frac{RT}{P}$. So:

$$\frac{RT}{P} = \frac{\delta \mu}{\delta P} \rightarrow \int_{\mu^0}^{\mu} d\mu = RT \int_{P^0}^{P} \frac{1}{P} dP \rightarrow \boxed{\mu = \mu^0 + RT \ln \frac{P}{P^0}}$$

$$a = \gamma \frac{P}{P^0} \rightarrow \boxed{\mu = \mu^0 + RT \ln a}$$

Must introduce gamma for the non-ideal gas law!

- How does Gibbs free energy change with concentration/activity? Same dependence as for the chemical potential:

$$G = G^{o} + RT \ln a$$

- When we apply this to a reaction, the reaction quotient comes into to play, giving us:
- Say we have the reaction :

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

$$\mathrm{w}A + \mathrm{x}B \rightarrow \mathrm{y}C + \mathrm{z}D$$

- The above reaction is a generic reaction and in order to analyze this chemical process mathematically, we formulate the reaction quotient Q:

$$Q = \frac{a_C^y \, a_D^z}{a_A^w \, a_B^x}$$

- It always has products in the numerator and reactants in the denominator
- It explicitly requires the activity of each reaction participant.
- Each term is raised to the power of its stoichiometric coefficient.

Relation between Equilibrium constant, Gibbs free energy and EMF of a cell- Nernst Equation

- Take the expression for the Gibbs dependence on activity and rewrite this in terms of cell potential:

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

- The relation between cell potential E and free energy gives:

$$-nFE = -nFE^{o} + RT\ln Q$$

- Rearrange and obtain the Nernst Equation:

$$\boxed{E = E^{o} - \frac{RT}{nF}\ln Q}$$

- The equation is often streamlined by restricting discussion to T = 25 °C and inserting the values for the constants, R and F.

$$\boxed{\begin{aligned} E &= E^{o} - \frac{0.0257}{n}\ln Q \\ E &= E^{o} - \frac{0.0592}{n}\log Q \end{aligned}}$$

This is the Nernst equation that relates the cell potential to the standard potential and to the activities of the electro-active species. Notice that the cell potential will be the same as E°only if Q is unity. The Nernst equation is more commonly written in base-10 log form and for 25 °C:

Significance of the Nernst Equation

The Nernst equation tells us that a half-cell potential will change by 59 milli volts 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 milli volts per decade concentration change.

The Nernst equation is a thermodynamic equation which relates the change in the free energy and the potential with concentration, M^{n+} . The decrease in free energy represents the maximum amount of work that can be obtained from a chemical reaction. Nernst derived a quantitative relationship between electrode potential and concentration of the electrolyte species involved. Let the electrode reaction be

$$M^{n+} + ne \rightleftharpoons M$$

The change in free energy, ΔG, accompanying the process is given by the well known thermodynamic equation,

$$\Delta G = \Delta G^0 + RT \ln Q$$

where G^0 is the standard free energy change, accompanying the same process when the reactants and products of the reaction are in their standard states of unit activity, Q is the reaction quotient. Substituting the value of Q, we have

$$\Delta G = \Delta G^0 + RT \ln a_M / a_{M^{n+}}$$

As an approximation, substituting molar concentration for activities,

$$\Delta G = \Delta G0 + RT \ln [M]/[M]$$

If E is the electrode potential of the electrode in volts, and the electrode reaction involves transfer of n electrons, *i.e., nF coulombs, the electrical work* available from the electrode is nFE volt coulomb or joules. Hence free energy decrease of the system (– ΔG) is given by the expression,

$$-\Delta G = nFE$$

$$-nFE = -nFE^0 + RT \ln \frac{[M]}{[M^{n+}]}$$

Dividing by – nF

$$E = E^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$= E^0 + \frac{RT}{nF} \ln [M^{n+}]$$

(Since [M] = 1).

$$E = E^0 + \frac{2.303\,RT}{nF} \log [M^{n+}].$$

where E^0 is the standard electrode potential, *i.e.,* when [M*n*+] is equal to 1M. The equation can be used to calculate the electrode potential of an electrode if the concentration is known. At 298 K, when the values of R, T and F are substituted, the equation reduces to,

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}] \quad \text{at 298 K}$$

This equation is known as the Nernst equation for single electrode potential. In general for any electrode, Nernst equation can be written as:

$$\boxed{E = E^0 + \frac{2.303\,RT}{nF} \log \frac{[\text{Oxidised Species}]}{[\text{Reduced Species}]}}$$

Standard hydrogen electrode

For the study of electrochemistry and corrosion one must be able to compare the equilibrium potentials of different electrode reactions. To these ends, *by convention,* a scale of standard electrode potentials is defined by arbitrarily assigning the value of zero to the equilibrium potential of the electrode (2.42), under standard conditions (P_{H2} = 1 bar =1.013 atm , T = 298 K, $a_{H+} = 1$):

$$2\ H^{+} + 2\ e = H_2 \tag{2.42}$$

$$2\ H^{+}(a_{H+} = 1) + 2\ e = H_2 \qquad (P_{H2} = 1\,\text{bar}) \qquad E^{\circ} = 0 \tag{2.45}$$

Because thermodynamic data for ionic species are not directly available, one arbitrarily sets the values for the solvated proton to zero,

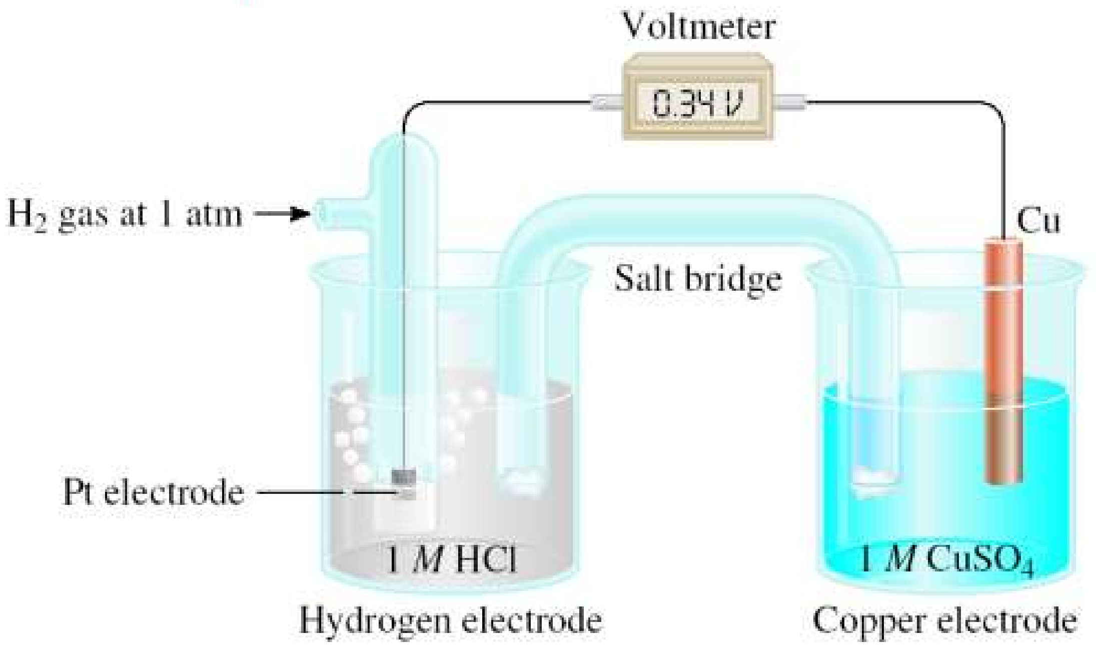
$$\Delta G^{\circ}_{H+} = \Delta H^{\circ}_{H+} = S^{\circ}_{H+} = 0 \tag{2.55}$$

Table 2.9 Thermodynamic properties of ionic and neutral species at 25 °C (adapted from ref. [6]).

Species	ΔH° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
$H^+_{(aq)}$	0	0	0
$H_{2(g)}$	0	0	130.7
$O_{2(g)}$	0	0	205.0
$O_{2(aq)}$	–11.7	16.3	110.9
$H_2O_{(l)}$	–285.8	–237.2	69.9
$OH^-_{(aq)}$	–230.0	–157.3	–10.75
$Cu_{(s)}$	0	0	33.2
$Cu^+_{(aq)}$	72.1	50.3	41
$Cu^{2+}_{(aq)}$	65.8	65.7	–97.2
$Ag_{(s)}$	0	0	42.6
$Ag^+_{(aq)}$	105.6	77.2	72.7
$AgCl_{(s)}$	–127.1	–109.8	96.3
Cl^-	–166.9	–131.1	56.7

Standard Reduction Potentials

$E^\circ_{cell} = 0.34\ V$



$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{H^+/H_2}$

$0.34 = E^\circ_{Cu^{2+}/Cu} - 0$

$E^\circ_{Cu^{2+}/Cu} = 0.34\ V$

$Pt\ (s)\ |\ H_2\ (1\ atm)\ |\ H^+\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu\ (s)$

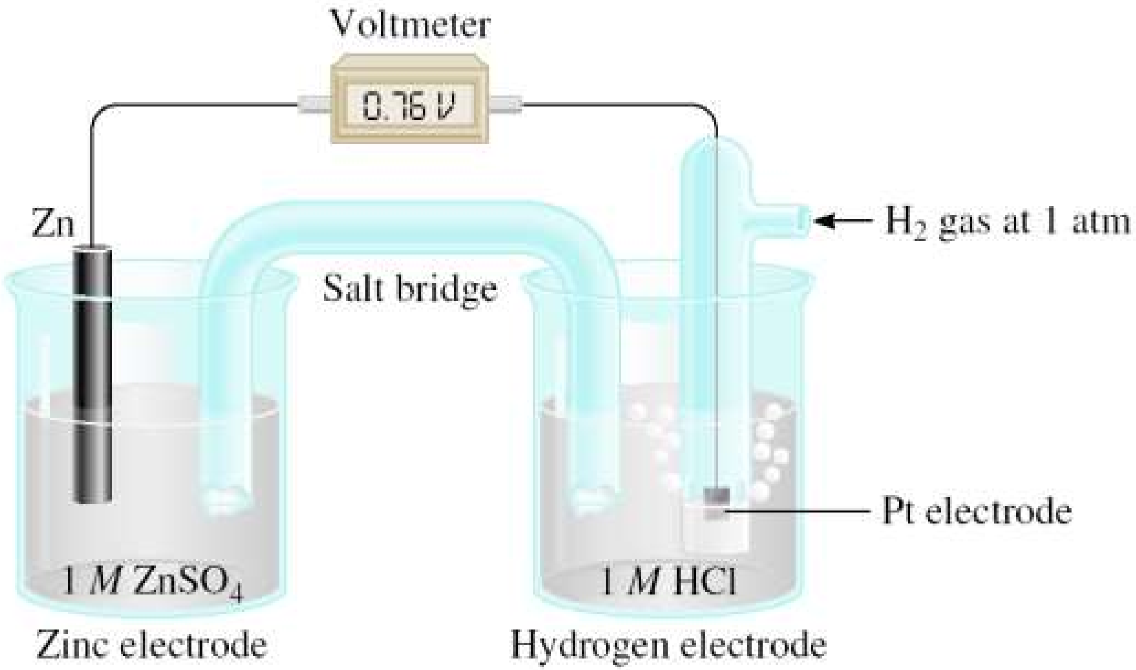
Anode (oxidation): $H_2\ (1\ atm) \longrightarrow 2H^+\ (1\ M) + 2e^-$

Cathode (reduction): $2e^- + Cu^{2+}\ (1\ M) \longrightarrow Cu\ (s)$

$$H_2\ (1\ atm) + Cu^{2+}\ (1\ M) \longrightarrow Cu\ (s) + 2H^+\ (1\ M)$$

Standard Reduction Potentials

$E^0_{cell} = 0.76\ \text{V}$



Standard emf (E°_{cell})

$$\boxed{E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}}$$

$\text{Zn}\ (s)\ |\ \text{Zn}^{2+}\ (1\ M)\ ||\ \text{H}^+\ (1\ M)\ |\ \text{H}_2\ (1\ \text{atm})\ |\ \text{Pt}\ (s)$

$$E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{Zn^{2+}/Zn}$$

$$0.76\ \text{V} = 0 - E^\circ_{Zn^{2+}/Zn}$$

$$E^\circ_{Zn^{2+}/Zn} = -0.76\ \text{V}$$

$$\text{Zn}^{2+}\ (1\ M) + 2e^- \longrightarrow \text{Zn} \qquad E^\circ = -0.76\ \text{V}$$

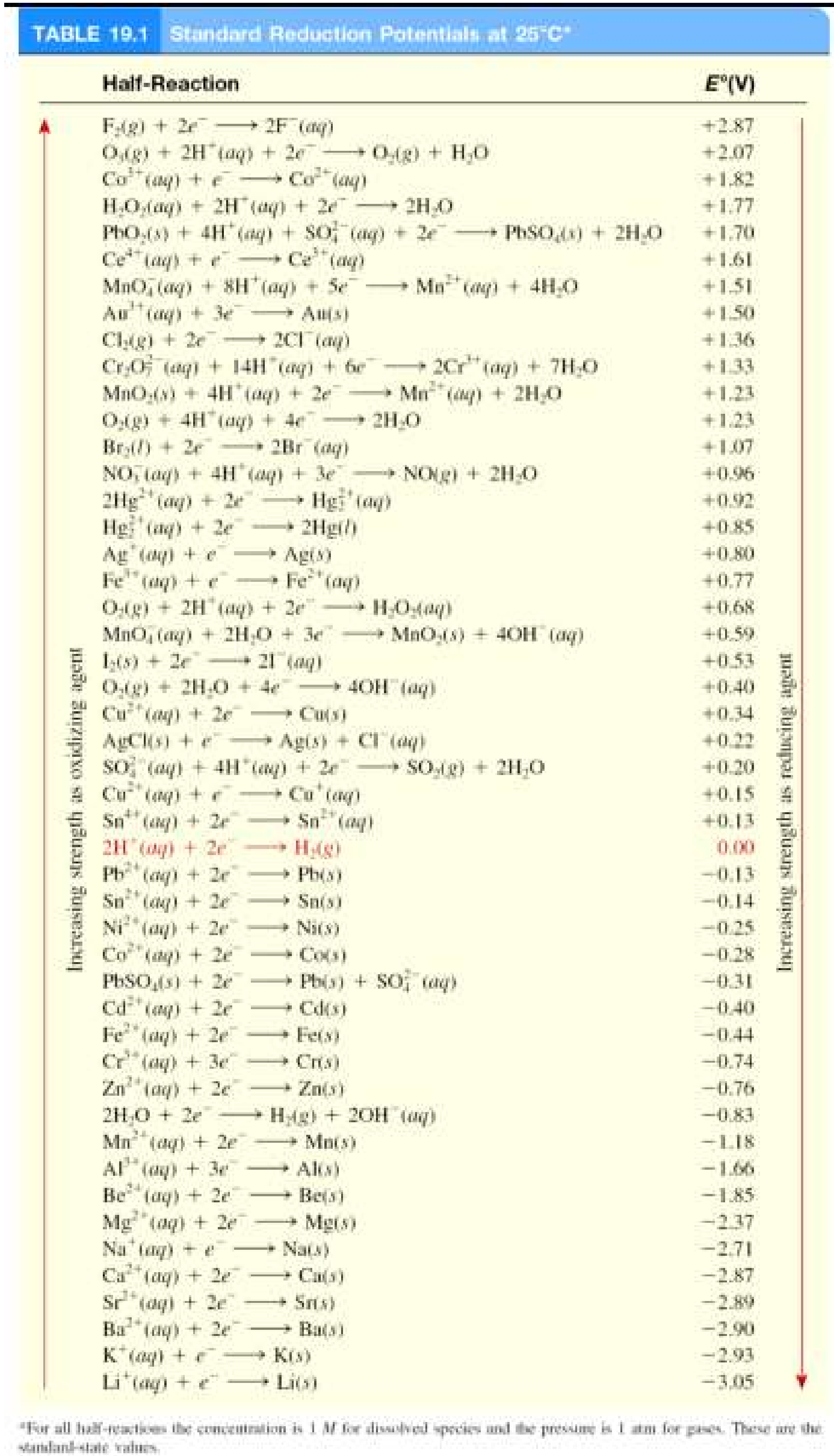


TABLE 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	E°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

*For all half-reactions the concentration is 1 *M* for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

- E° is for the reaction as written
- The more positive E° the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of E° changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of E°

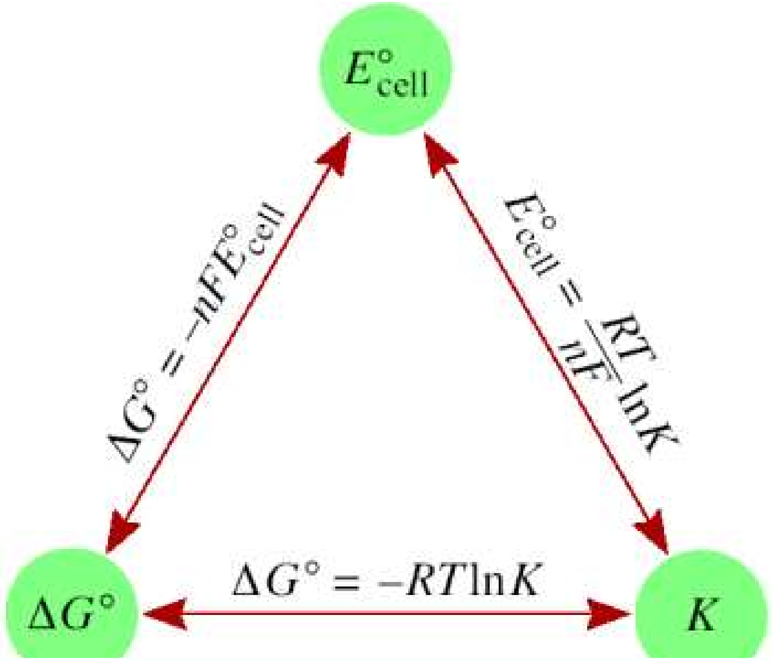


TABLE 19.2 Relationships Among ΔG°, K, and E°_{cell}

ΔG°	K	E°_{cell}	Reaction Under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	$=1$	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

ΔG° — Negative is called Excergonic

ΔG° — Positive is called Endergonic

$$\Delta G^\circ = -RT\ln K = -nFE^\circ_{\text{cell}}$$

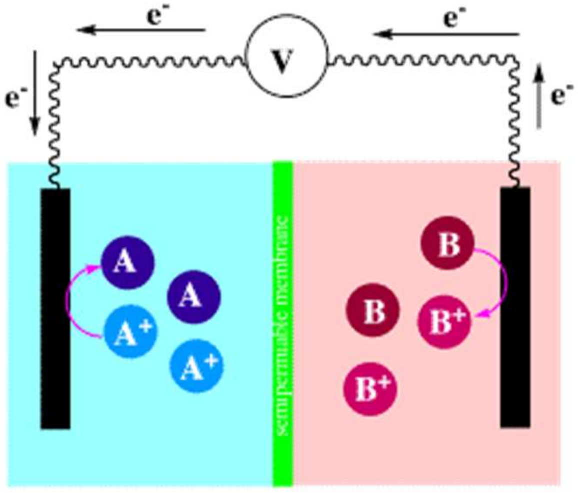
Galvanic & Electrolytic Cells

An electrochemical cell that releases energy is called a galvanic cell. The electrochemical reaction has a negative value of the Gibbs free energy and a positive cell potential difference. Ex: Daniel Cell.

Spontaneous reactions occur in galvanic (voltaic) cells and non spontaneous reactions occur in electrolytic cells.

An electrolytic cell has an endothermic chemical reaction. The reaction is not spontaneous so a power source is required. Energy is stored in an electrochemical cell. Ex: Electroplating cell.

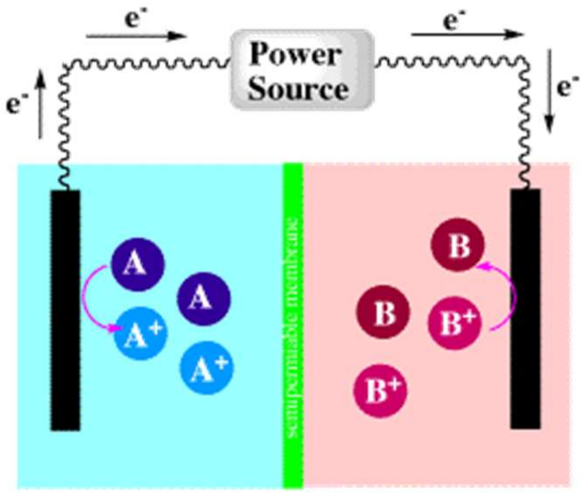
Both types of cells contain electrodes where the oxidation and reduction reactions occur. Oxidation occurs at the electrode called the anode and reduction occurs at the electrode called the cathode.



Galvanic Cell

$A^+ + B \longrightarrow A + B^+$

$E^0 = 0.10$ V



Electrolytic Cell

$A + B^+ \longrightarrow A^+ + B$

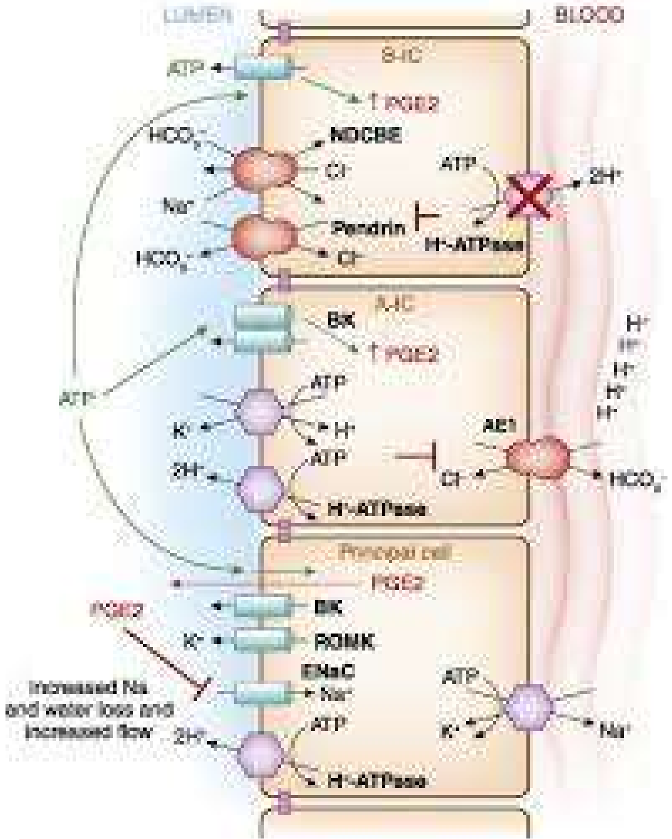
$E^0 = -0.10$ V

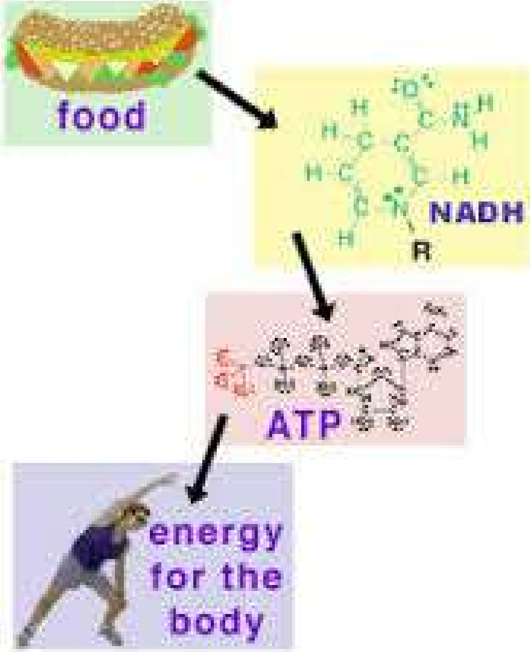
A rechargeable battery, as in the case of a AA NiMH cell or a single cell of a lead-acid battery, acts as a galvanic cell when discharging (converting chemical energy to electrical energy), and an electrolytic cell when being charged (converting electrical energy to chemical energy).

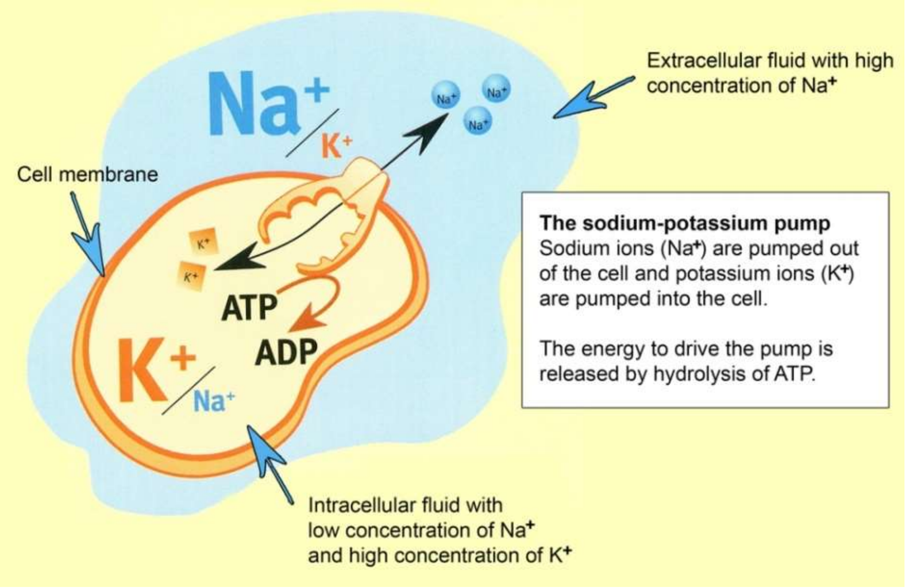
Electrochemical cell (Galvanic Cell)	Electrolytic cell
A Galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.	Both the electrodes are placed in a same container in the solution of molten electrolyte.
Here the anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.	Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.	The external battery supplies the electrons. They enter through the cathode and come out through the anode.

The anode of an electrolytic cell is positive, and the cathode is negative, because the anode attracts anions from the solution. However, the anode of a galvanic cell is negatively charged, since the spontaneous oxidation at the anode is the source of the cell’s electrons or negative charge. The cathode of a galvanic cell is its positive terminal.

The difference between the two cells is that in a galvanic cell this process occurs spontaneously. So electrons produced in the anode will want to flow to the cathode. The positive (+) for a cathode in galvanic cells indicates this spontaneous attraction (a positive charge will attract negatively charged electrons). For an electrolytic cell, the process is non spontaneous and the electrons must be driven to the cathode, indicated by the negative (-) sign.

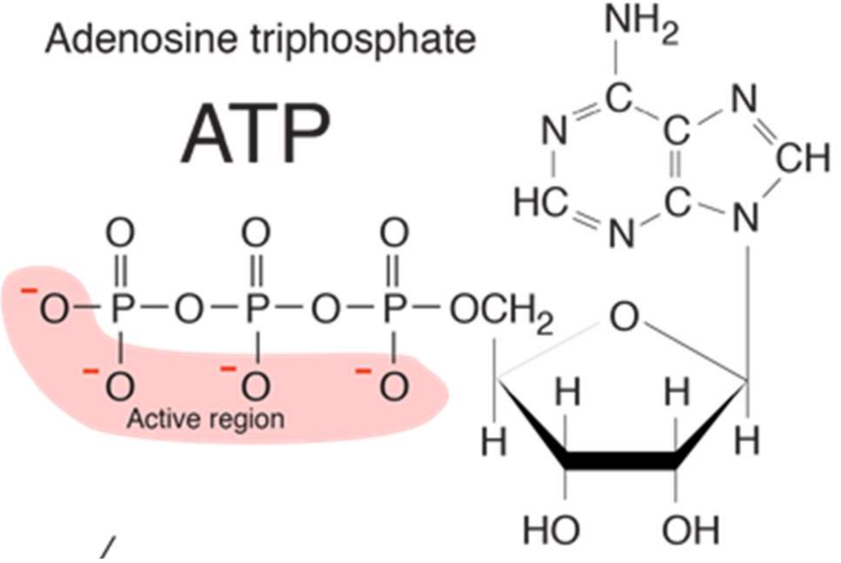






The sodium-potassium pump
Sodium ions (Na+) are pumped out of the cell and potassium ions (K+) are pumped into the cell.

The energy to drive the pump is released by hydrolysis of ATP.



The reaction ATP + H_2O <—-> ADP + P_i transforms adenosine triphosphate (ATP) into adenosine diphosphate (ADP) and inorganic phosphate (P_i). The free energy change associated with this reaction drives a large fraction of cellular reactions with the membrane potential and reducing power being the other two dominant energy sources.

Karp quotes an estimate that more than 2 x 10^{26} molecules or >160kg of ATP is formed in the human body daily! ATP is remarkable for its ability to enter into many coupled reactions, both those to food to extract energy and with the reactions in other physiological processes to provide energy to them. This conversion from ATP to ADP is an extremely crucial reaction for the supplying of energy for life processes. Just the cutting of one bond with the accompanying rearrangement is sufficient to liberate about 7.3 kilocalories per mole = 30.6 kJ/mol.

GRAIN BOUNDARIES

- They are the imperfections which separate crystals or grains of different orientation in a poly crystalline solid during nucleation or crystallization.
- It is a two dimensional imperfection. During crystallization, new crystals form in different parts and they are randomly oriented with respect to one another.
- They grow and impinge on each other.
- The atoms held in between are attracted by crystals on either side and depending on the forces, the atoms occupy equilibrium positions.

- These positions at the boundary region between two crystals are distorted.As a result, a region of transition exists in which the atomic packing is imperfect.
- The thickness of this region is 2 to 10 or more atomic diameters.
- The boundary region is called a ***crystal boundary*** or ***a grain boundary*** .
- The boundary between two crystals which have different crystalline arrangements or different compositions, is called as interphase boundary or commonly an interface.

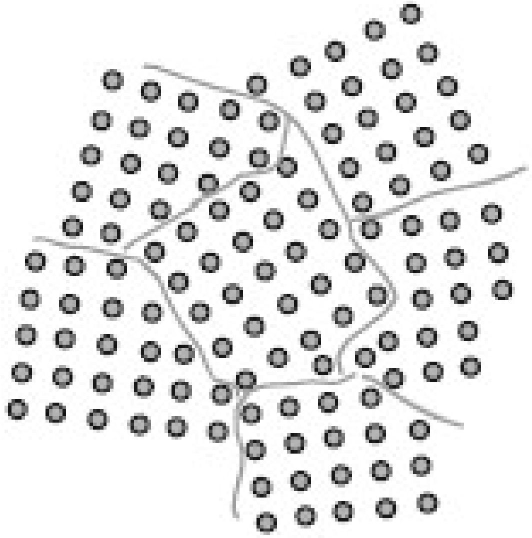
3. Surface imperfections or surface defects (2D)

Surface imperfections are 2D and refer to regions of distortions that lie about a surface having a thickness of a few atomic diameters. The external surface of a crystal is an imperfection in itself as the atomic bonds do not extend beyond the surface

In addition to the external surface, crystals may have surface imperfections inside.

A piece of Cu or Fe us usually not a single crystal. It consists of a number of crystals and is said to be Polycrystalline. During solidification or during a process in the solid state called recrystallization, new crystals form in different parts of the material.

Among the surface defects, grain boundaries, twins, stacking faults and free surfaces are the most common.



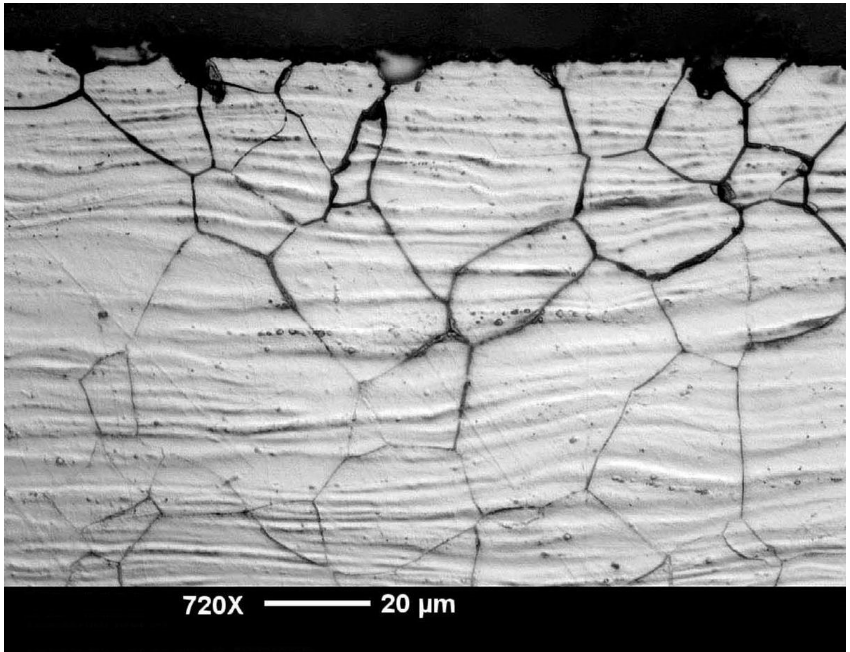
Grain boundary

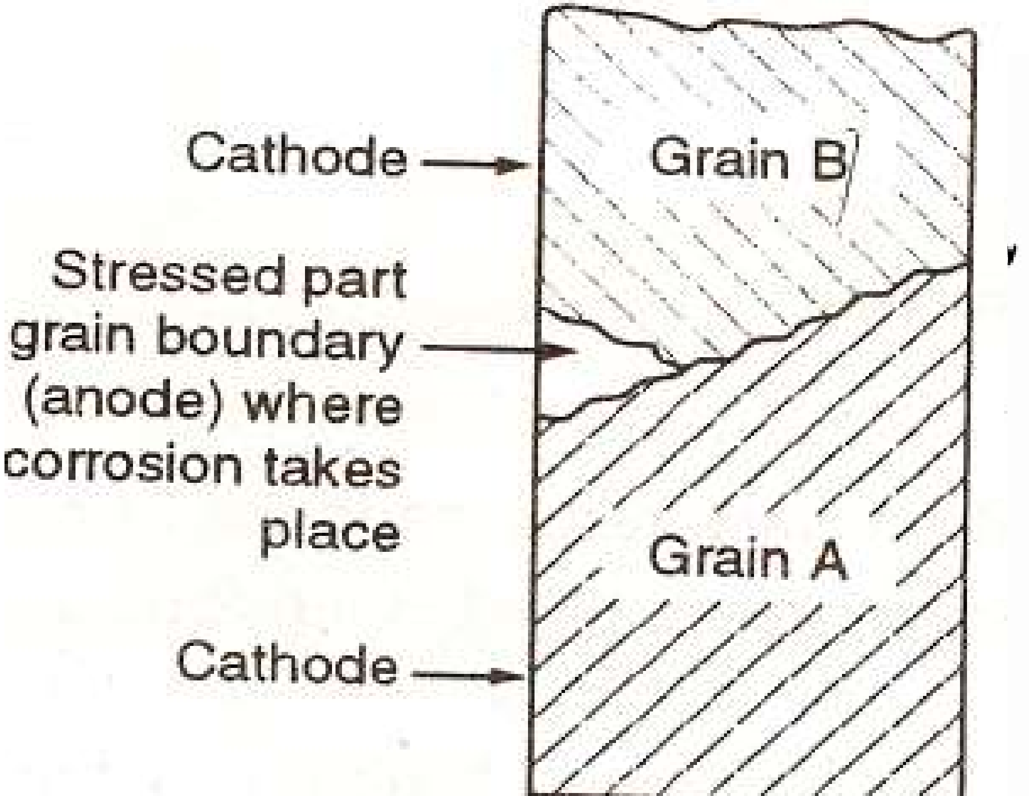
Metallurgical and Other Aspects

Iron and Steel are BCC. Metallic properties differ from crystalline arrangements

When a metal solidifies during casting, the atoms which are randomly distributed in the liquid state, arrange themselves in a crystalline array. However, this ordering begins at many points in the liquid, and as these blocks of crystals or grains meet, there is a mismatch at their boundary. When the metal has solidified and cooled, there will be numerous regions of mismatch between each grain. These grains are called grain boundaries.

Grain boundaries are high energy regions and more active chemically. Hence, grain boundaries are usually attacked slightly more rapidly than grain faces when exposed to a corrosive.





Alloys are quite similar to aqueous solutions. Some substances can be dissolved, whereas others are insoluble. Solubility usually increases rapidly with increasing temperature. For example, iron carbide is completely soluble in iron at high temperatures; hence steel becomes a solid solution when heated to a high temperature. Precipitation of a phase can occur from supersaturated solid solutions as it does in the case of liquid solutions. As noted above, grain boundaries are high-energy areas, so precipitation frequently begins at the grain interfaces.

Other differences in the metal can be chemical, metallurgical, or mechanical in nature. Examples are impurities such as oxides and other inclusions, mill scale, orientation of grains, dislocation arrays, differences in composition of the microstructure, precipitated phases, localized stresses, scratches, and nicks. Highly polished surfaces are used in only special cases. Very pure metals are more corrosion resistant than commercial materials. For example, very pure and smooth zinc will not corrode in very pure hydrochloric acid, yet their commercial counterparts react rapidly. However, pure metals are expensive, and they are usually weak—one would not build a bridge of pure iron.

% aluminum	Relative corrosion rate
99.998	1
99.97	1,000
99.2	30,000

Gold: a particularly good example

In an aqueous environment devoid of complexing agents, gold is present in monovalent (Au^+) and trivalent (Au^{3+}) states. The standard equilibrium potentials favor the Au^{3+} ion.

$$Au^{3+} + 3e = Au \qquad E^\circ = 1.52 \text{ V} \tag{2.90}$$

$$Au^{+} + e = Au \qquad E^\circ = 1.83 \text{ V} \tag{2.91}$$

These high values of E° confirm the fact that gold is a noble metal that does not easily corrode.

The presence of cyanide ions greatly alters this behavior because they form a very stable complex with monovalent gold. The electrode reaction between metallic and monovalent gold now reads:

$$Au(CN)_2^- + e = Au + 2\, CN^- \qquad E^\circ = -0.595 \text{ V} \tag{2.92}$$

The low value of this standard potential indicates that in the presence of cyanide ions, gold no longer behaves as a noble metal. An oxidizing agent, such as dissolved oxygen, is capable of corroding it relatively easily.

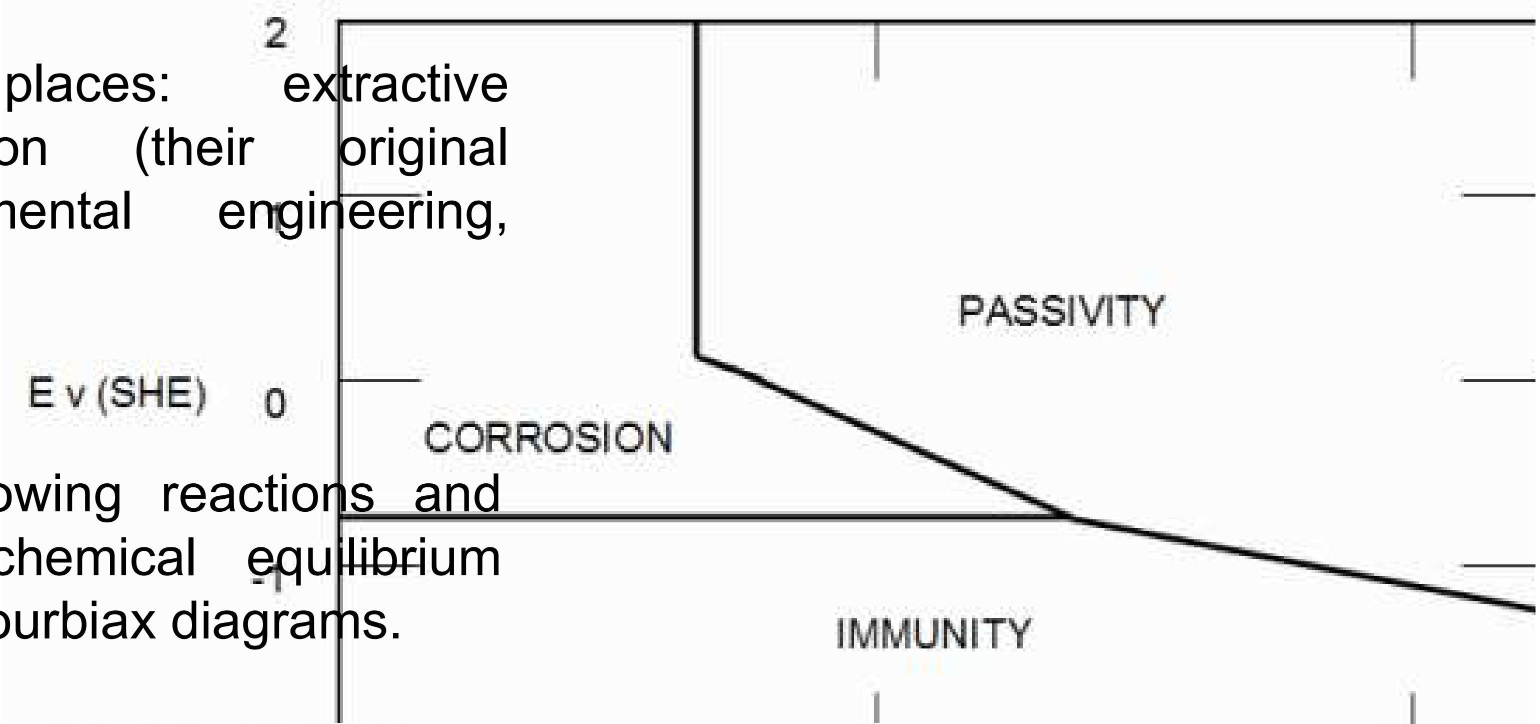
These phenomena are exploited in the mining of gold. Gold is present in mineral deposits in metallic form, but at very dilute concentration. In order to extract it, the rock is ground and the resulting gold–containing slurry is treated with a cyanide solution in the presence of oxygen. The gold dissolves as the complex $Au(CN)_2^-$. Once a gold enriched solution is thus obtained, the complex is reduced to recover the gold metal. (Zn is used to recover)

Eh-pH Diagrams (Pour-biax)

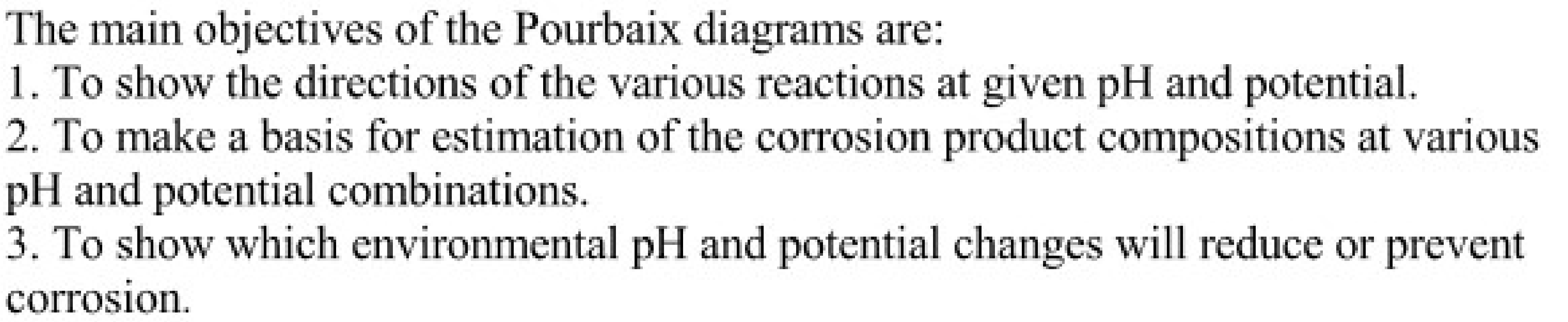
Eh–pH diagram: Pourbaix diagram, potential-pH diagram, electro-chemical phase diagram

Invented in 1930’s by Marcel Pourbaix (Belgian)

Used in lots of places: extractive metallurgy, corrosion (their original purpose), environmental engineering, geochemistry

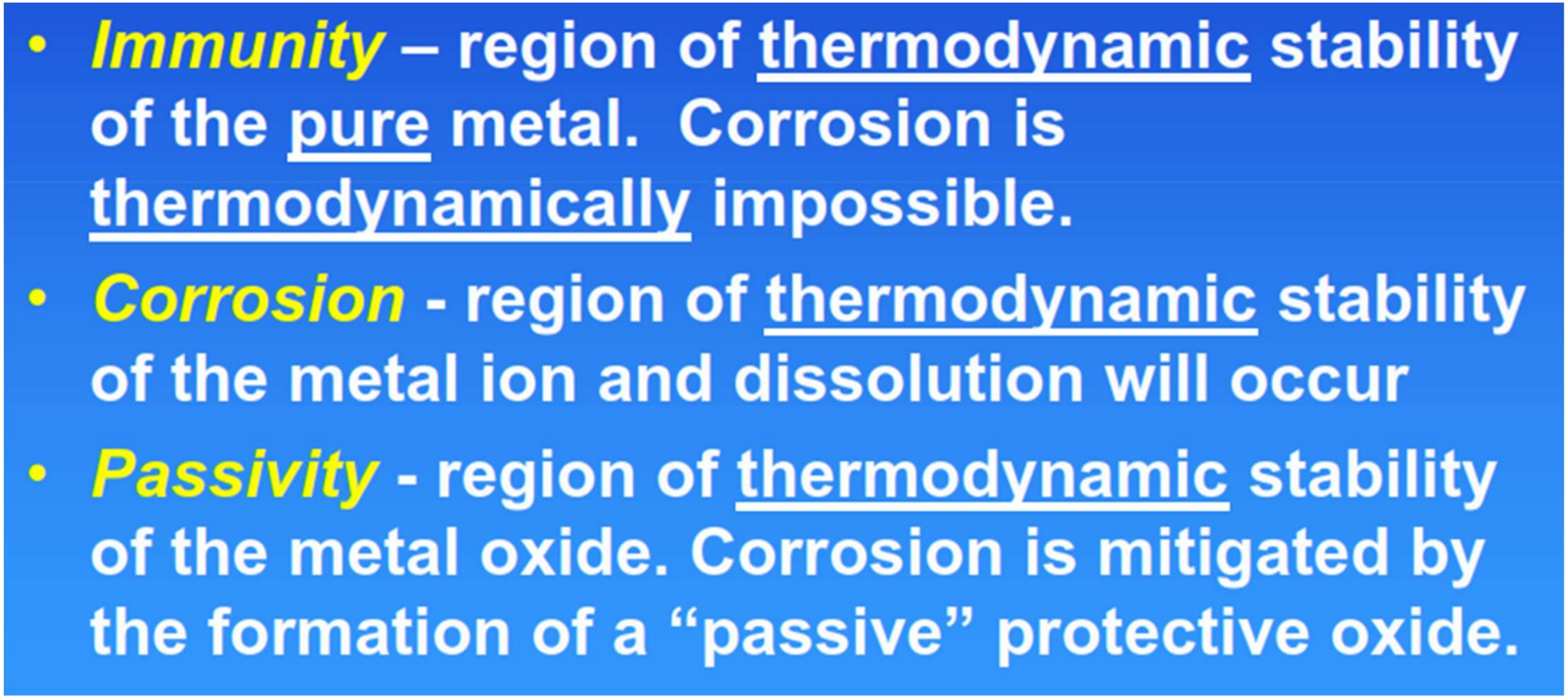


Eh-pH diagrams showing reactions and products at electrochemical equilibrium often referred to as Pourbiax diagrams.



The main objectives of the Pourbaix diagrams are:

1. To show the directions of the various reactions at given pH and potential.
2. To make a basis for estimation of the corrosion product compositions at various pH and potential combinations.
3. To show which environmental pH and potential changes will reduce or prevent corrosion.



- *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.

- These diagrams represent the stability of a metal as a function of potential and pH.

- At a particular combination of pH and potential, a stable phase can be determined from the Pourbiax diagram. These diagrams are constructed from calculations based on Nernst equations and solubility data for metal and its species such as Fe, Fe_2O_3, etc. in equilibrium.

- We can identify stability region (immunity, corrosion, and passivity)

- The information in the diagrams can be beneficially used to control corrosion of pure metals in the aqueous environments. By altering the pH and potential to the regions of immunity and passivation, corrosion can be controlled.

- Pourbiax diagrams introduce the concept of the following three states of metals, depending on the potential in the given aggressive medium and the determination of its corrosion behavior: Corrosion (active state), passivity (forming passive layers inhibiting the corrosion process on the surface of the metal, including thermodynamically active metals) and immunity (thermodynamic stability) of the metals.

The basic diagram for aqueous environments involves upper and lower, stability limits for water, represented by the Oxygen (universal oxidizing agent) and Hydrogen (universal reducing agent) reactions

4 regions in the diagram

Oxidizing (acidic),

Oxidizing (alkaline),

Reducing (acidic),

Reducing (alkaline),

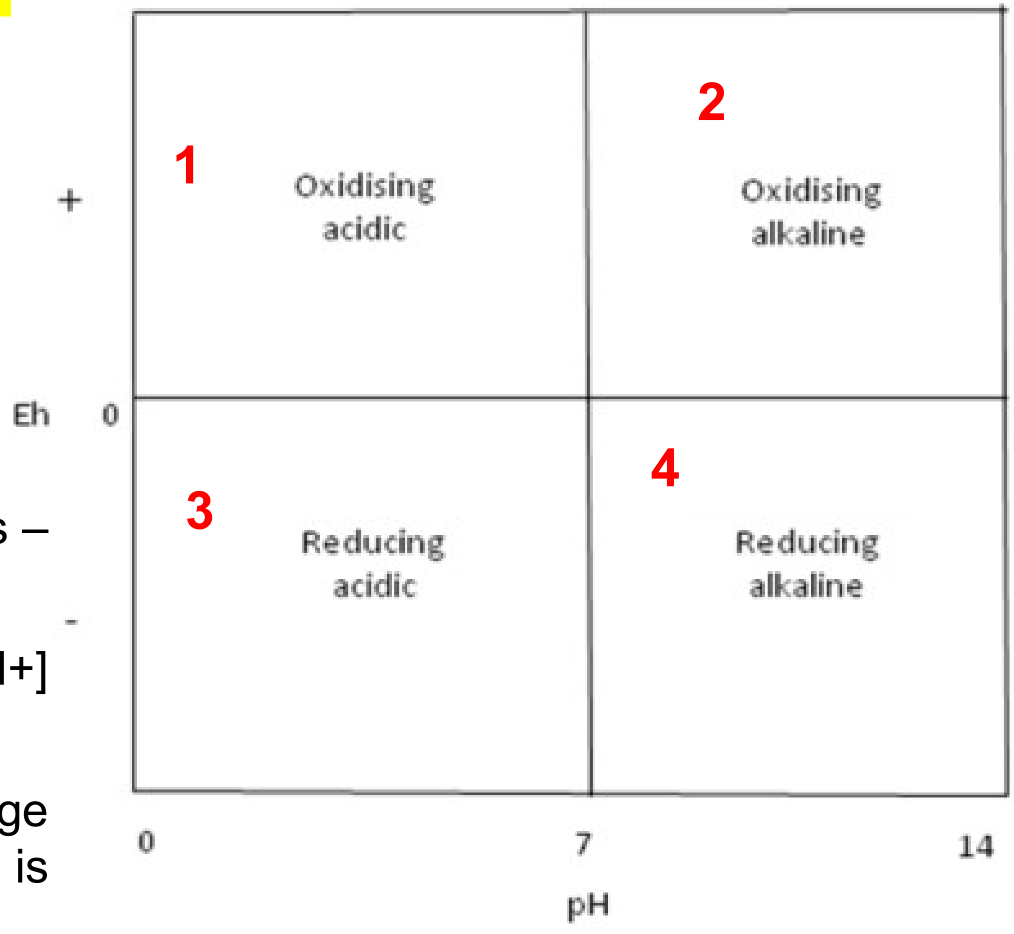


Fig. 5.1 Basic regions in a Eh – pH diagram

x-axis is pH; usually 0–14, but sometimes as low as –3, and sometimes up to 16

pH = –log [H+]; change of 1.0 pH unit changes [H+] by factor of 10

y-axis is electrode potential relative to SHE (range varies); positive is oxidizing condition, negative is reducing

Assumes constant temperature, $a_{H2O} = 1$

- ☐ Those depending only on Eh, but independent of pH (horizontal to X-axis)
- ☐ Those dependent only on pH, but independent of Eh (vertical to X-axis)
- ☐ Those dependent on Eh, pH (Slanted with definite slopes)

Four types of reactions:

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

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

- pH dependent and E independent:

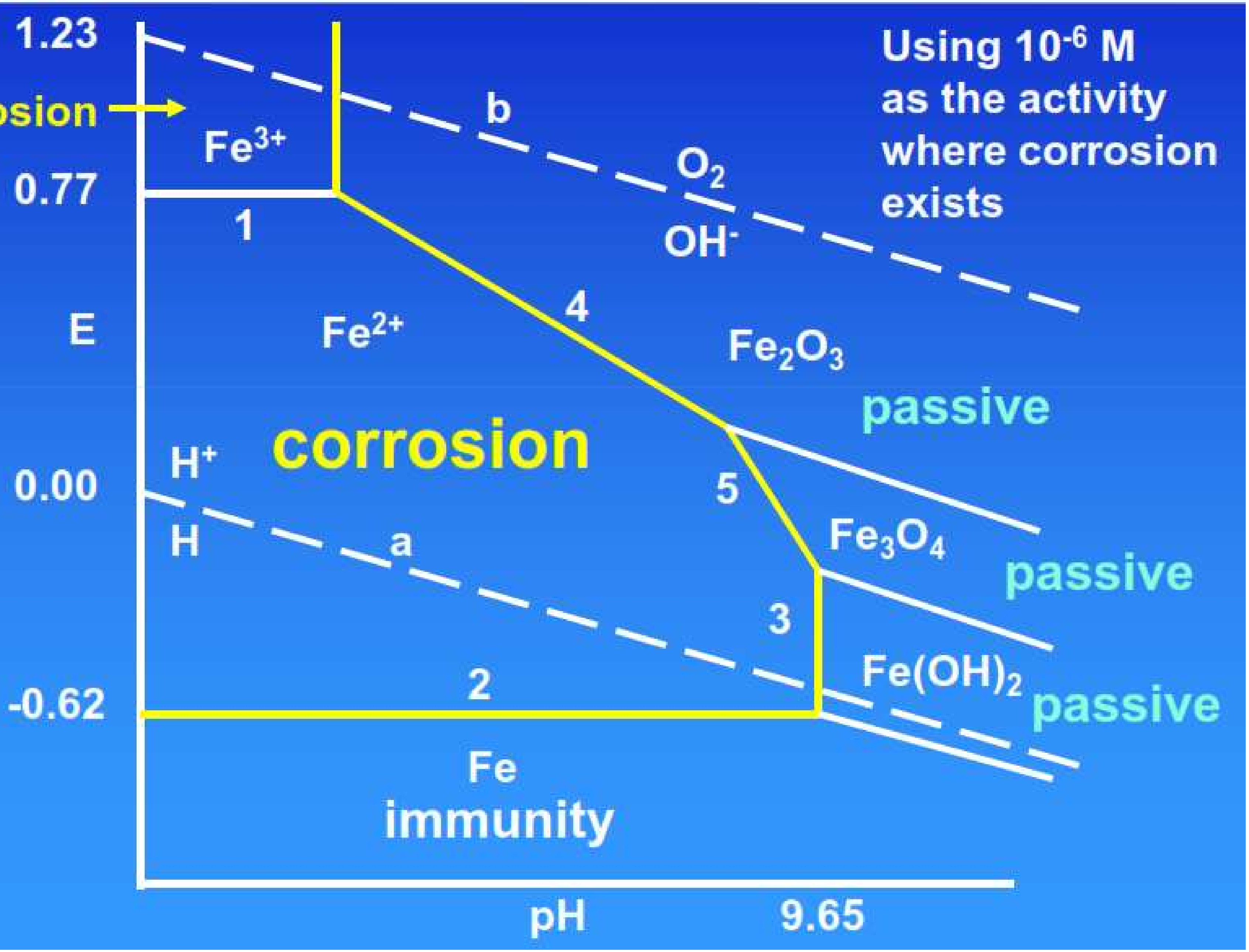
$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$$

- E dependent and pH independent:

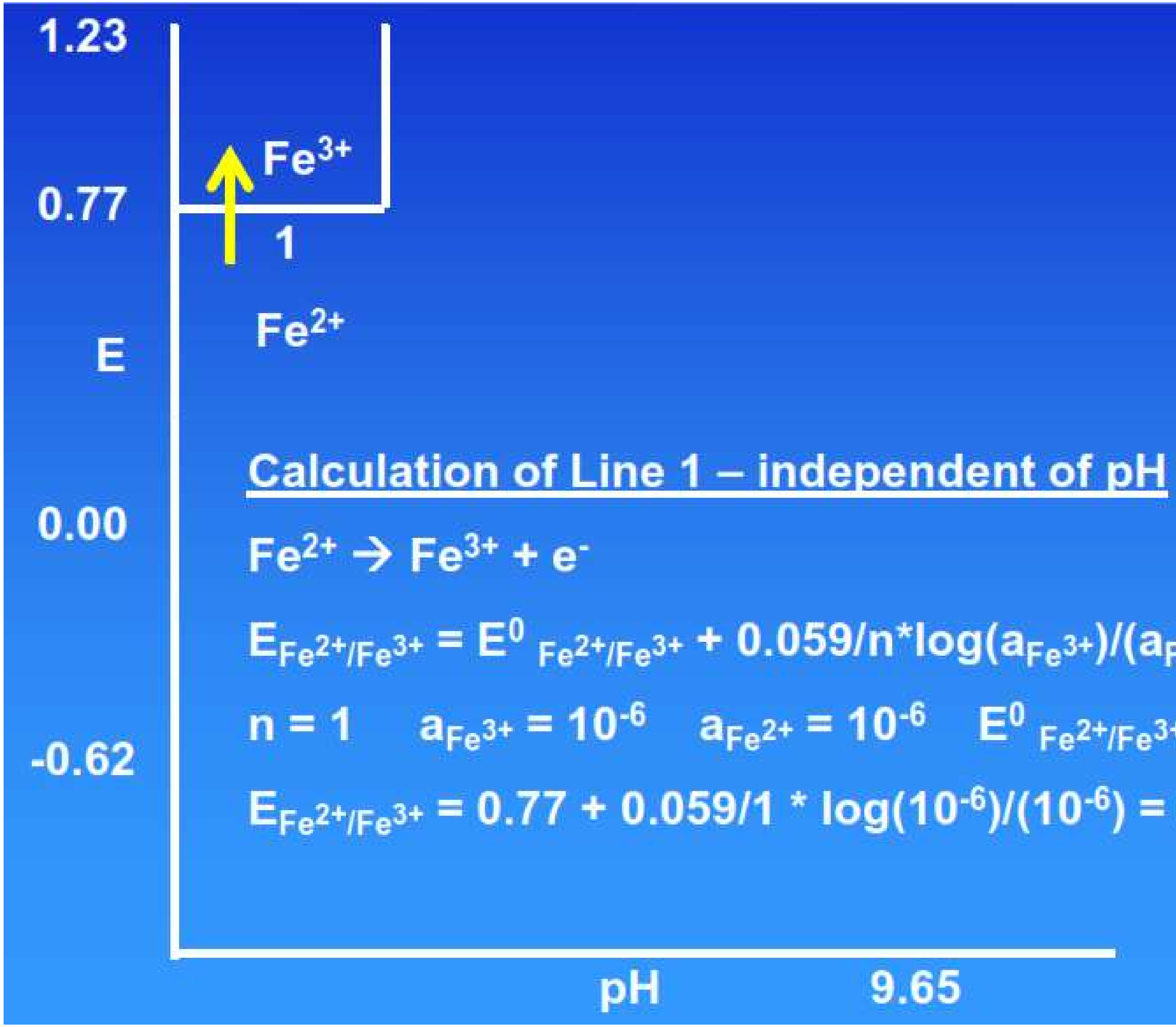
$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

- E and pH dependent

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



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



Calculation of Line 1 – independent of pH

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

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

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

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

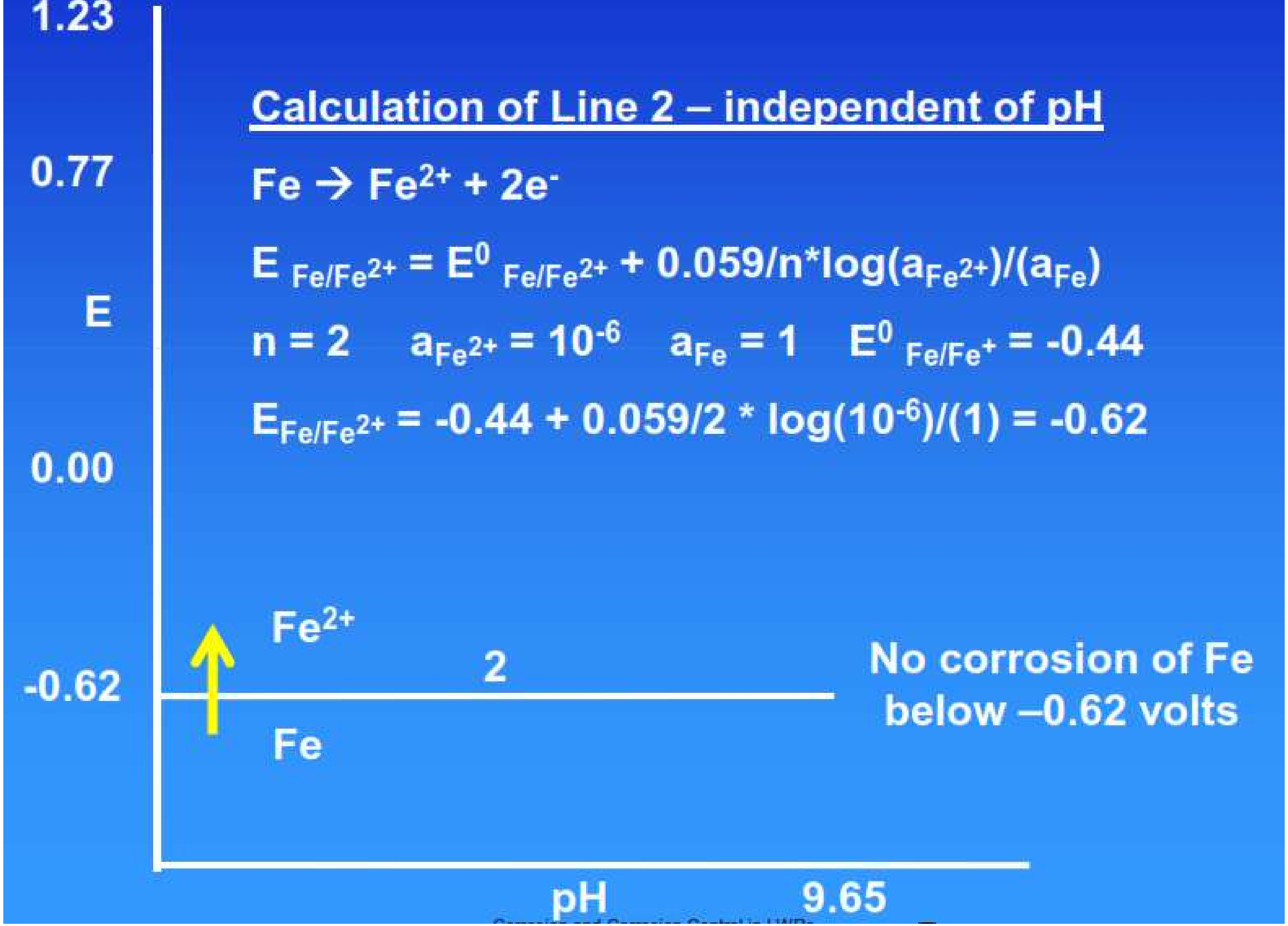
Calculation of Line 2 – independent of pH

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

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

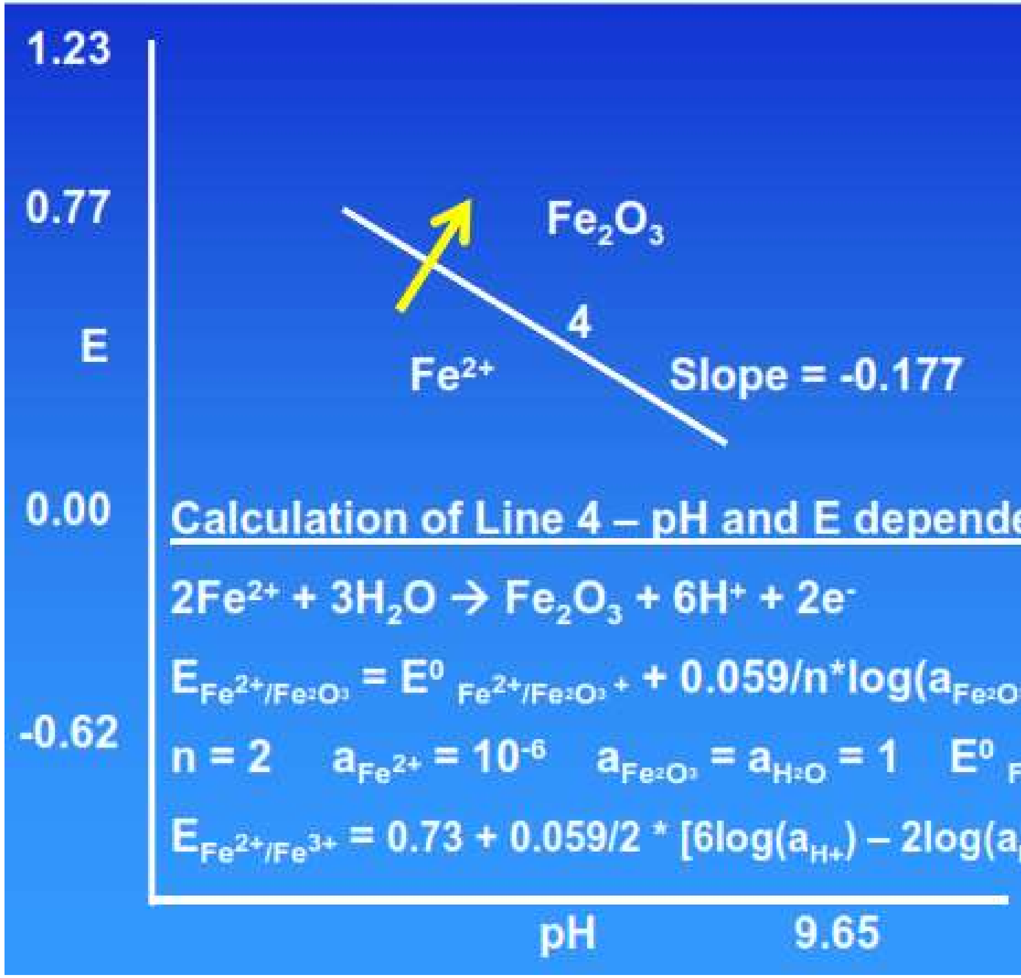
$n = 2 \quad a_{Fe^{2+}} = 10^{-6} \quad a_{Fe} = 1 \quad E^0_{Fe/Fe^{+}} = -0.44$

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



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

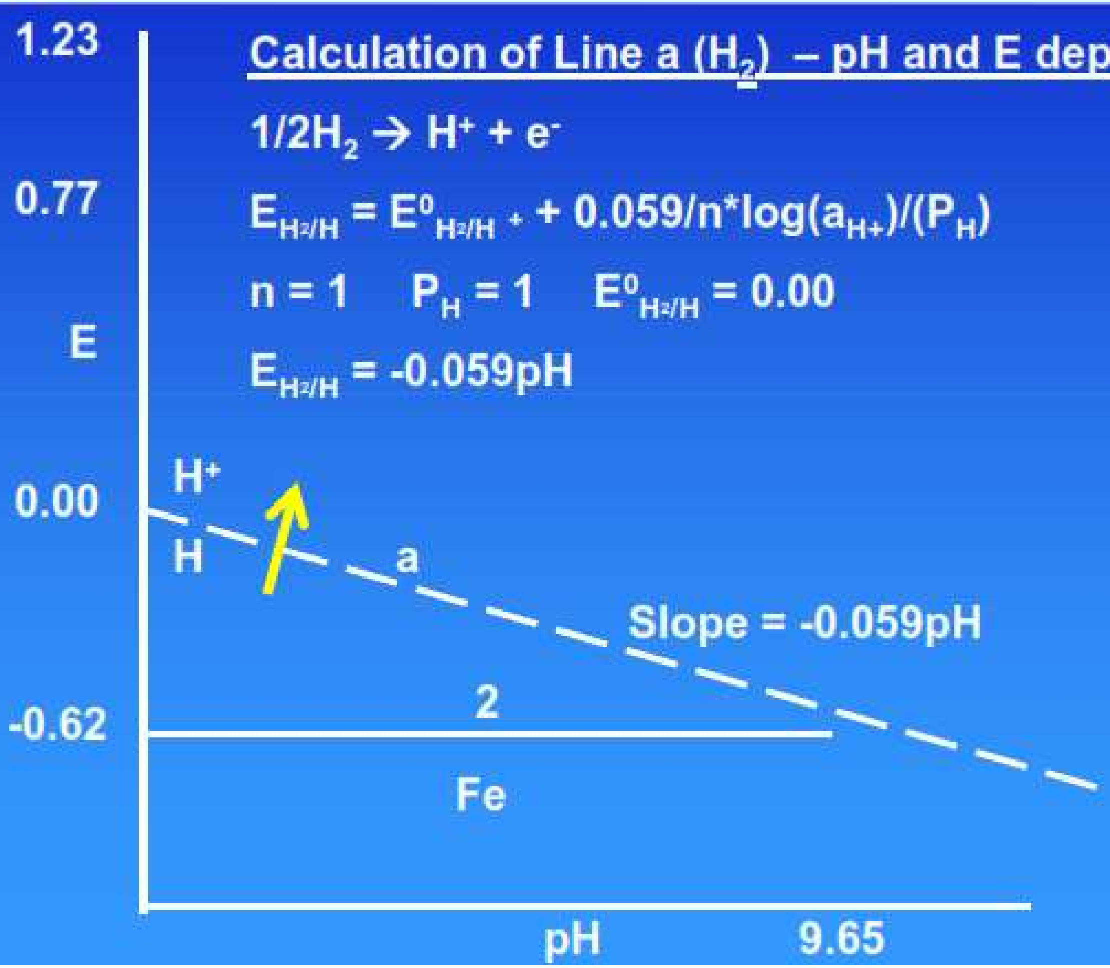
Calculation of Line a (H_2) – pH and E dependent

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

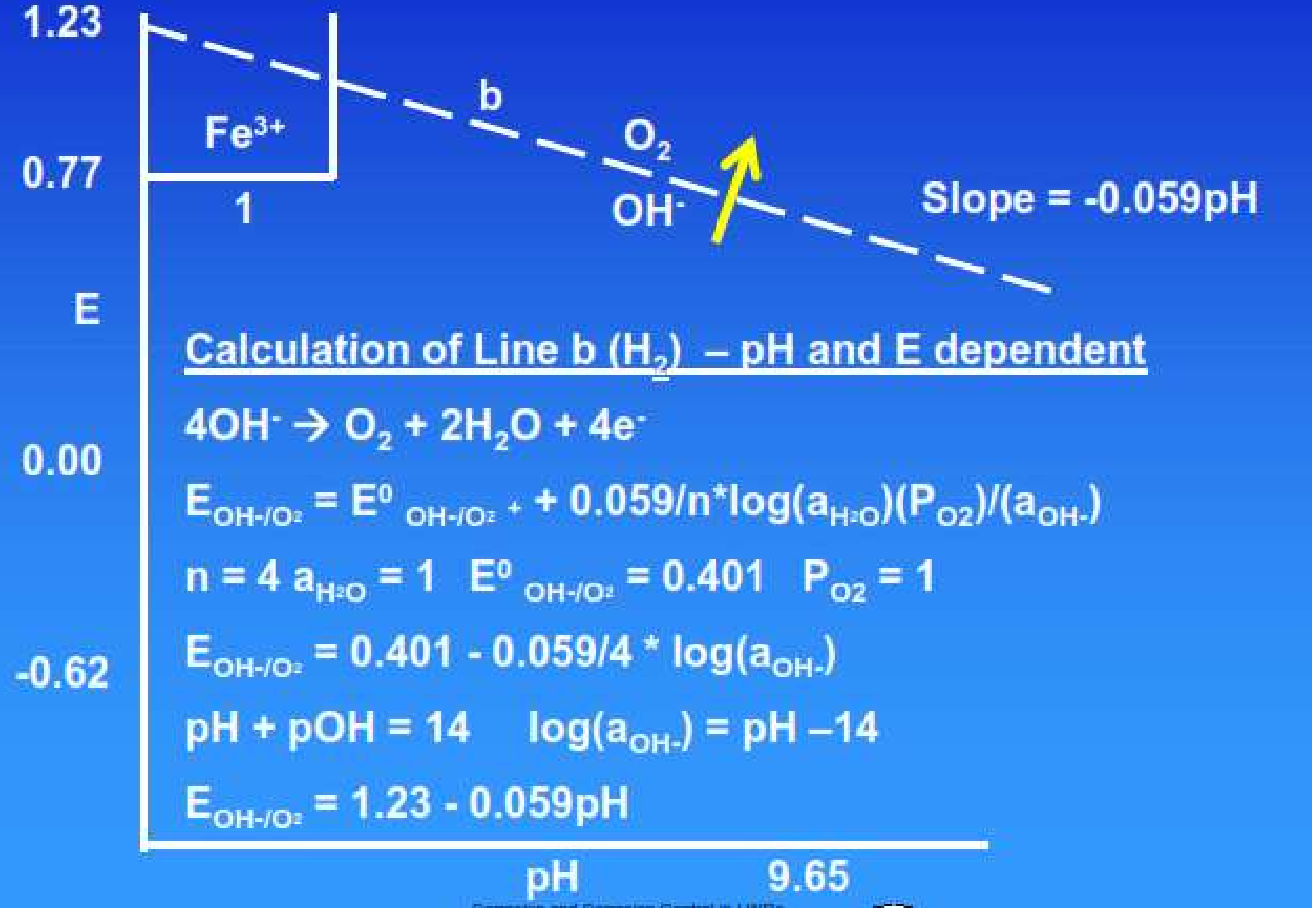
$E_{H_2/H} = E^0_{H_2/H^+} + 0.059/n * \log(a_{H+})/(P_H)$

$n = 1 \quad P_H = 1 \quad E^0_{H_2/H} = 0.00$

$E_{H_2/H} = -0.059pH$



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



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

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

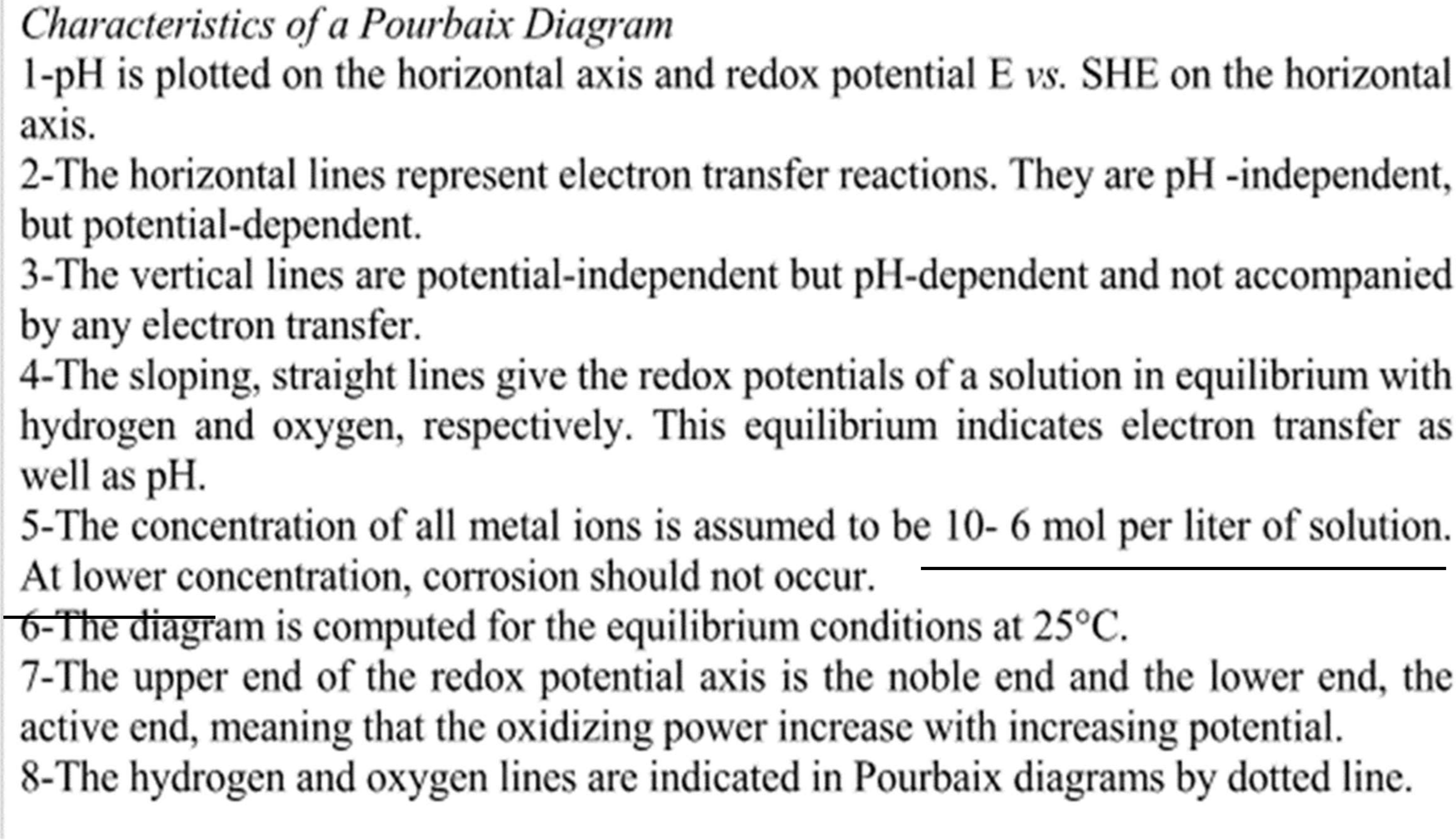
$E_{OH^-/O_2} = E^0_{OH^-/O_2}$ + + 0.059/n*log(a_{H_2O})(P_{O2})/(a_{OH-})

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



Characteristics of a Pourbaix Diagram

1-pH is plotted on the horizontal axis and redox potential E *vs.* SHE on the horizontal axis.

2-The horizontal lines represent electron transfer reactions. They are pH -independent, but potential-dependent.

3-The vertical lines are potential-independent but pH-dependent and not accompanied by any electron transfer.

4-The sloping, straight lines give the redox potentials of a solution in equilibrium with hydrogen and oxygen, respectively. This equilibrium indicates electron transfer as well as pH.

5-The concentration of all metal ions is assumed to be 10- 6 mol per liter of solution. At lower concentration, corrosion should not occur.

6-The diagram is computed for the equilibrium conditions at 25°C.

7-The upper end of the redox potential axis is the noble end and the lower end, the active end, meaning that the oxidizing power increase with increasing potential.

8-The hydrogen and oxygen lines are indicated in Pourbaix diagrams by dotted line.

Pourbaix for water

Each line of a Pourbaix diagram represents conditions of thermodynamic equilibrium for some reaction. The Pourbaix diagram for water is presented in below figure, above line b, oxygen is evolved in accord with the reaction

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

By use the Nernst equation we can write relationship between potential and pH as below

$$E = E^\circ - 2.303\frac{RT}{zF}\log\frac{1}{\left[H^+\right]^2}$$

With E°=1.299 volt, T=298 °K, R=8.134 J/ °K. mol and F=96500 C/ mol we have

$$\boxed{E = 1.299 - 0.0592\,pH}$$

Above line b, defined by this equation, oxygen is evolved at the surface of an immersed electrode. Below this line, water is stable. Below line a, hydrogen is evolved in accord with the reaction : $2H^+ + 2e^- \rightarrow H_2$

Using the Nernst equation for this equilibrium, the relationship between potential and pH is

$$E = E^\circ - 2.303\frac{RT}{zF}\log\frac{1}{\left[H^+\right]^2} = -0.059\,pH$$

$$\boxed{E = 0 - 0.05915\text{ pH}}$$

Below line a, represented by this equation, hydrogen gas is evolved from the surface of an immersed electrode. Between lines a, and b, water is stable.

For solids, activity = 1; for gases, set a partial pressure; for solutions, set an activity =1

Stability limits of water

a) $O_2 + 4H^+ + 4e = 2H_2O$ $\qquad E^0 = +1.23V$

$Eh = 1.23 - 0.059\ pH$ (at $po_2 = 1$)

b) $2H^+ + 2e = H_2$ $\qquad E^0 = 0.00V$

$Eh = 0 - 0.059\ pH$ (at $p_{H2} = 1$)

These equilibria are plotted in Fig. 5.2. Above the oxygen line, oxygen liberation occurs. Below the hydrogen line, hydrogen liberation occurs. Water is stable between the two lines.

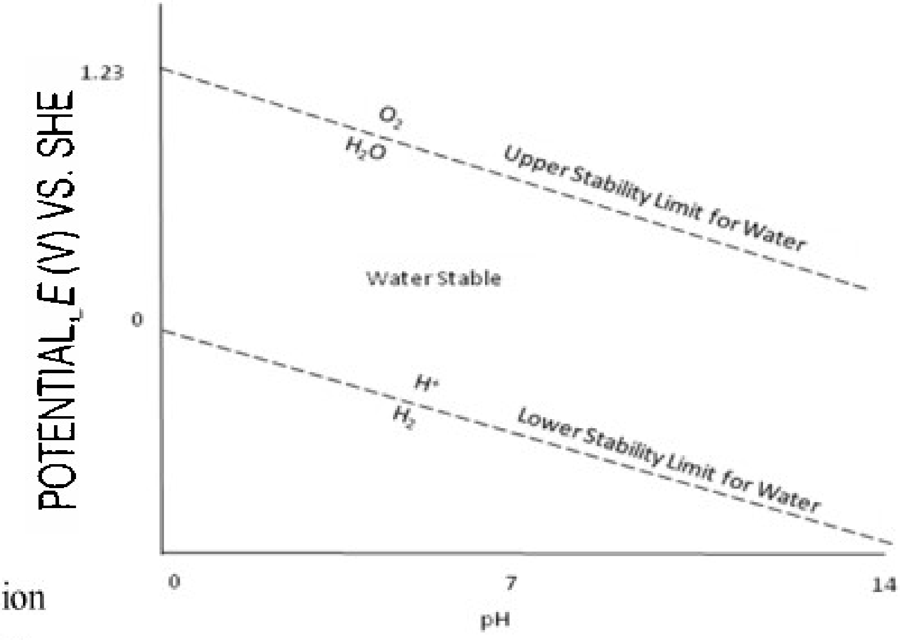


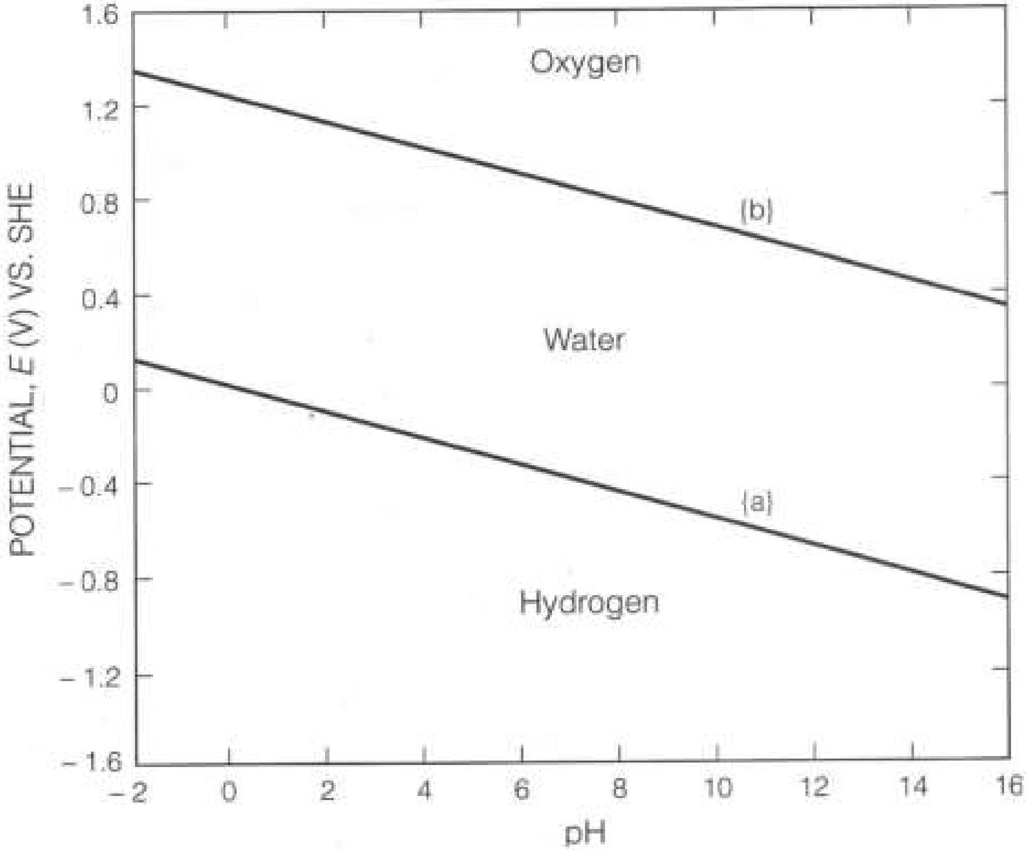
Fig 5.2. Stability limits of water

In neutral or alkaline solutions, the following reactions hold good.

$2H_2O + 2e = H_2 + 2OH^-$

$O_2 + 2H_2O + 4e = 4OH^-$

Electrochemical evolution of hydrogen represents water decomposition. At more positive potentials, oxygen reduction or water oxidation takes place. Slope of both lines correspond to 59 mV/pH.



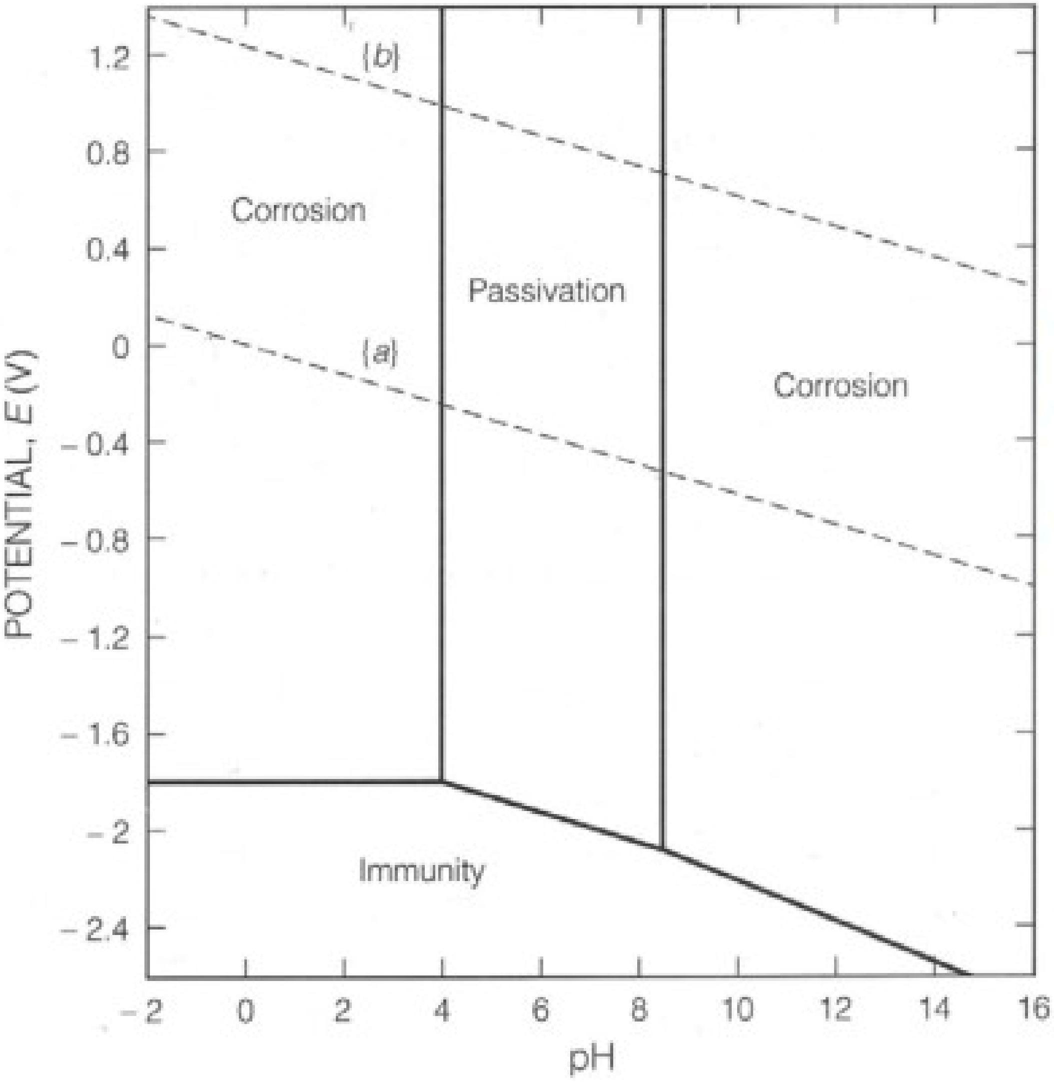
- below line {a} – water is unstable and must decompose to H_2
- above line {a} – water is stable and any H_2 present is oxidised to H^+ or H_2O
- above line {b} – water is unstable and must oxidize to give O_2
- below line {b} – water is stable and any dissolved O_2 is reduced to H_2O

3 regions:

upper: - H_2O electrolysed anodically to O_2
lower: - H_2O electrolysed cathodically to H_2
middle: - H_2O stable and won't decompose

POURBAIX DIAGRAM FOR ALUMINIUM

In aqueous environments:



if pH < 4 - Al^{+++} stable
if pH > 8.3 - $Al_2O_2^-$ stable
if 4 < pH < 8.3 - Al_2O_3 stable and thus protects the metal

If the potential is sufficiently low – aluminium itself is immune to corrosion

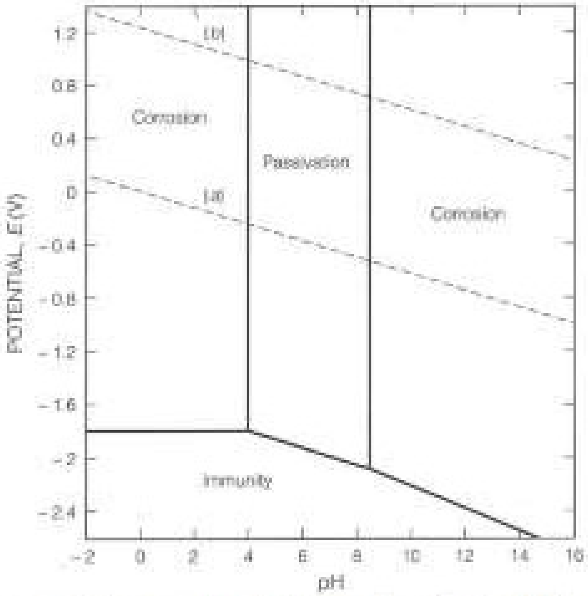
Boundaries define transition from one stable phase to another

3 regions: corrosion, passivation, immunity

In regions where:

Al^{+++} is stable	– corrosion is possible
aluminium oxide is stable	– resistance or passivity is possible
Al is stable	– thermodynamically immune to corrosion

HOW TO READ A POURBAIX DIAGRAM



Vertical lines – separate species that are in acid/alkali equilibrium

Non-vertical lines – separate species at redox equilibrium where:

horizontal lines separate redox equilibrium species not involving hydrogen or hydroxide ions

diagonal lines separate redox equilibrium species involving hydrogen or hydroxide ions

Dashed lines enclose the practical region of stability of the aqueous solvent to oxidation or reduction i.e. the region of interest in aqueous systems

Outside this region, it is the water that breaks down, not the metal

Redox equilibria:

where oxidation and reduction could equally occur and are completely reversible

Any point of the diagram – the most thermodynamically stable (hence, abundant) form of the metal can be found for any given potential or pH

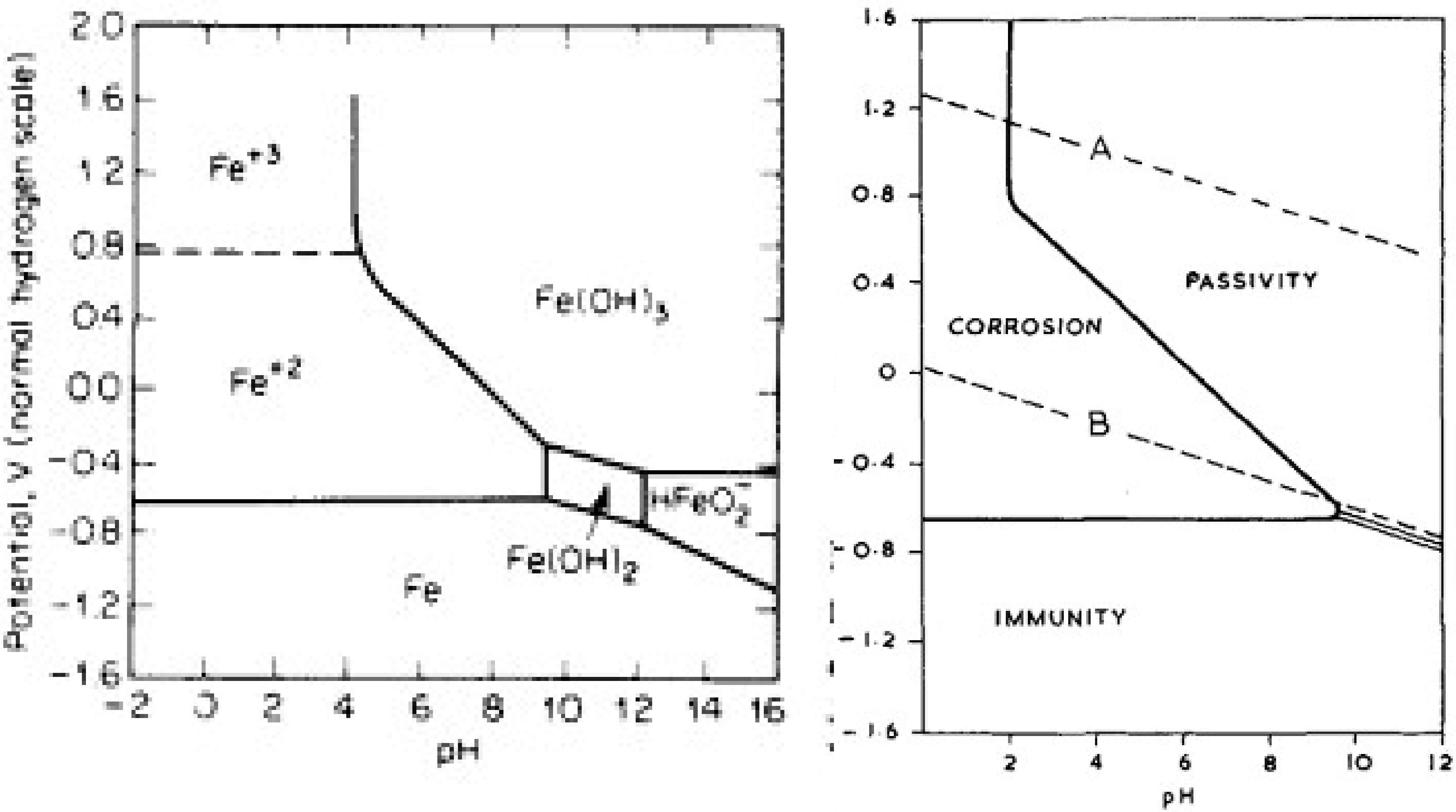
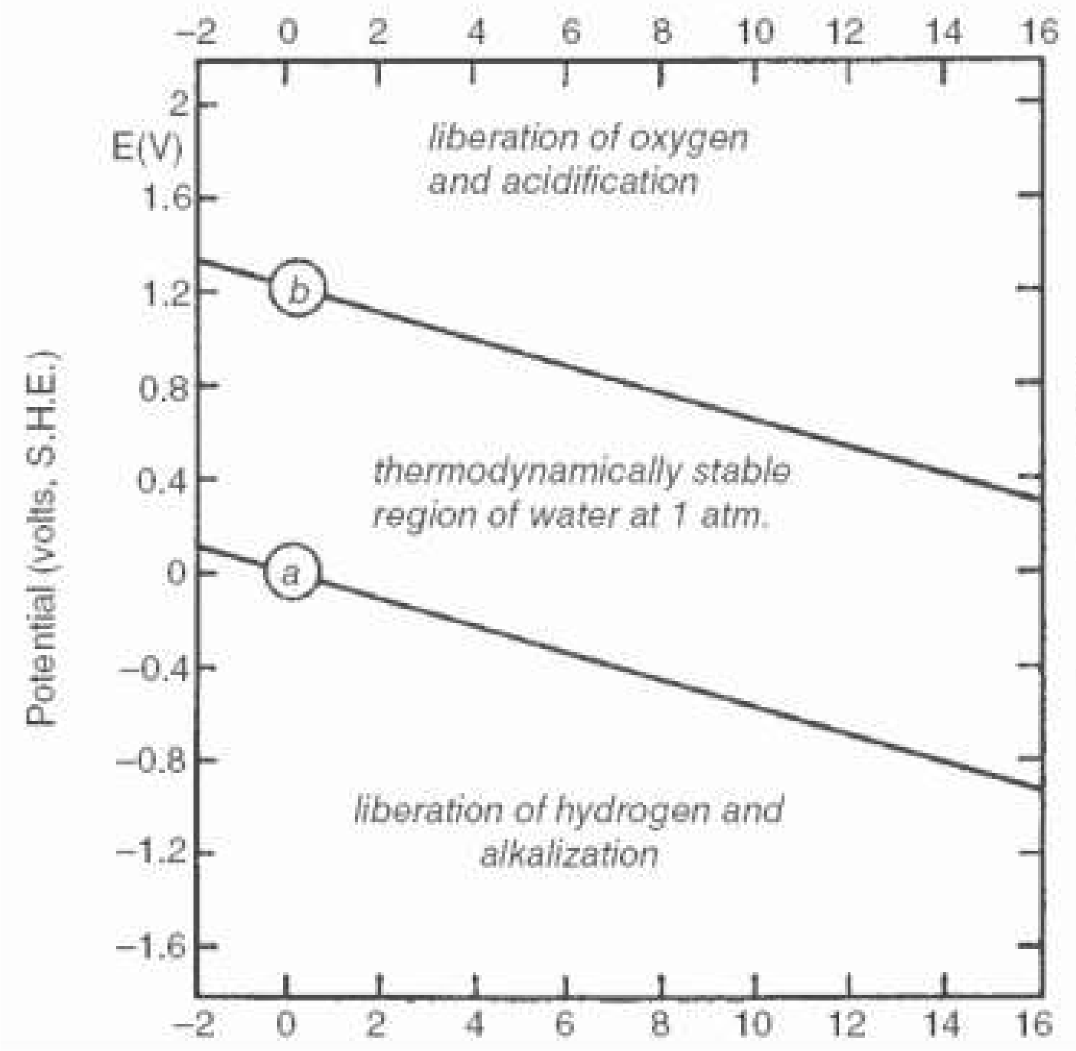
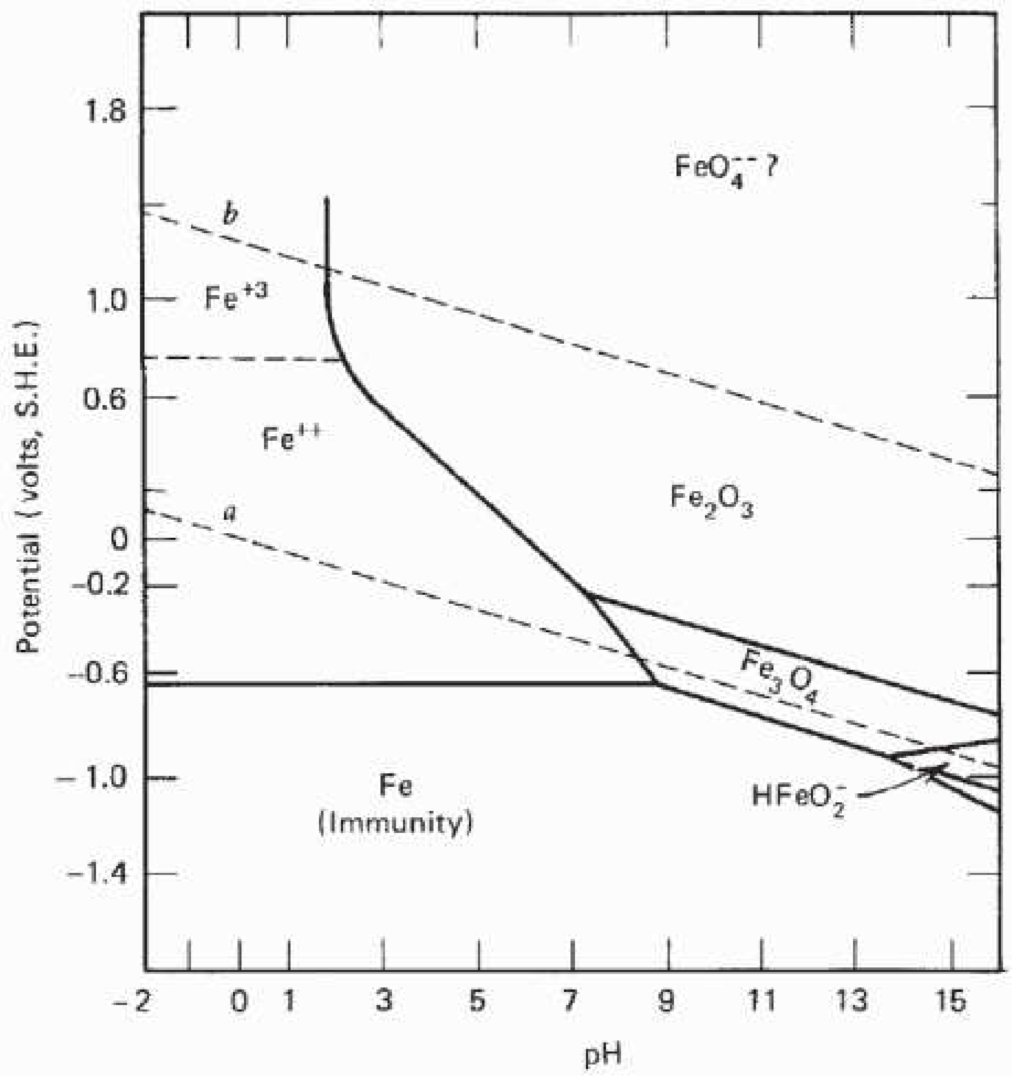


Fig. 1 Pourbaix diagram for iron in aqueous solutions



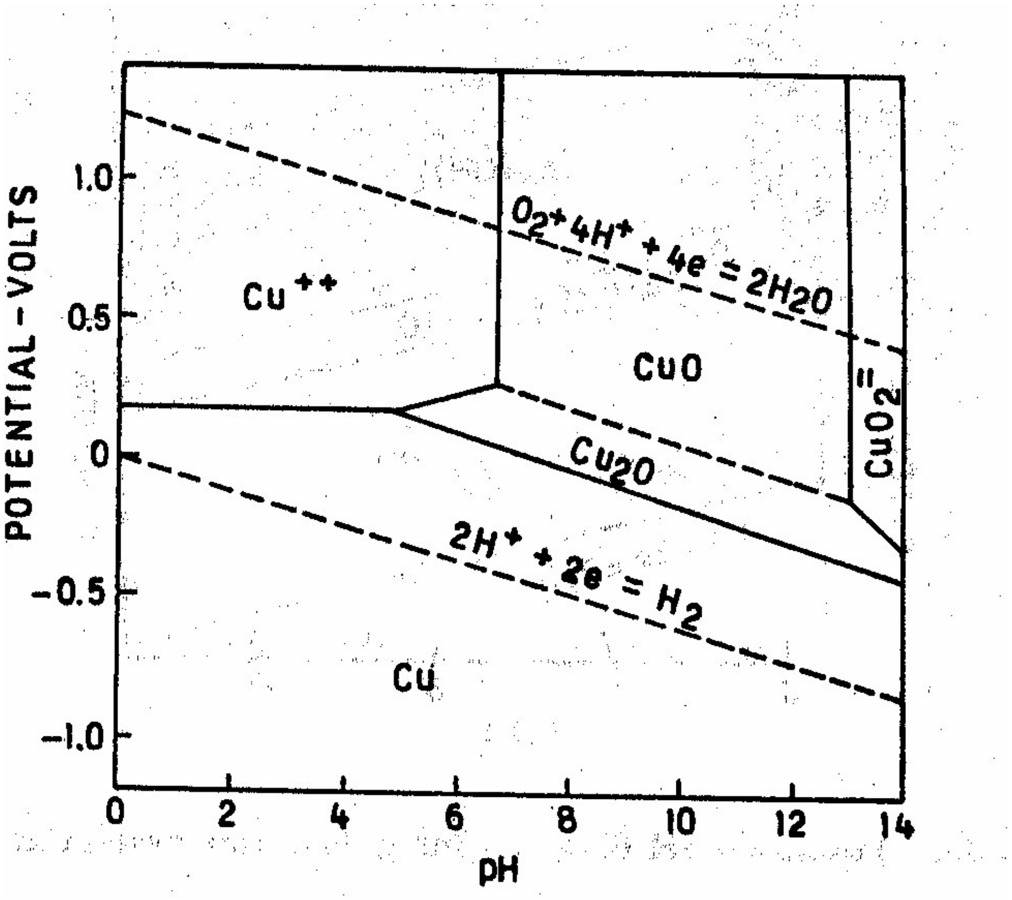
Pourbaix for Water



Pourbaix for Iron

Add A Metal

Eh-pH diagram shows *Cu–H_2O* system



Dotted lines represent water stability region; solid lines represent equilibria between copper species

Two aqueous species, Cu^{2+} and CuO_2^{2-}

Oxidation state of Cu as Cu^0 is 0

Oxidation state of Cu as Cu_2O is +1

Oxidation state of Cu in Cu^{2+}, CuO, and CuO_2^{2-} is +2

Lower oxidation states are stable at bottom, higher oxidation states at top

Activity of solid compounds = 1 when predominant; varies for aqueous species (1 in this case, could be as low as 10^{-6})

Predominance activity determined by purpose, value of metal

More on Metal – H_2O Diagrams

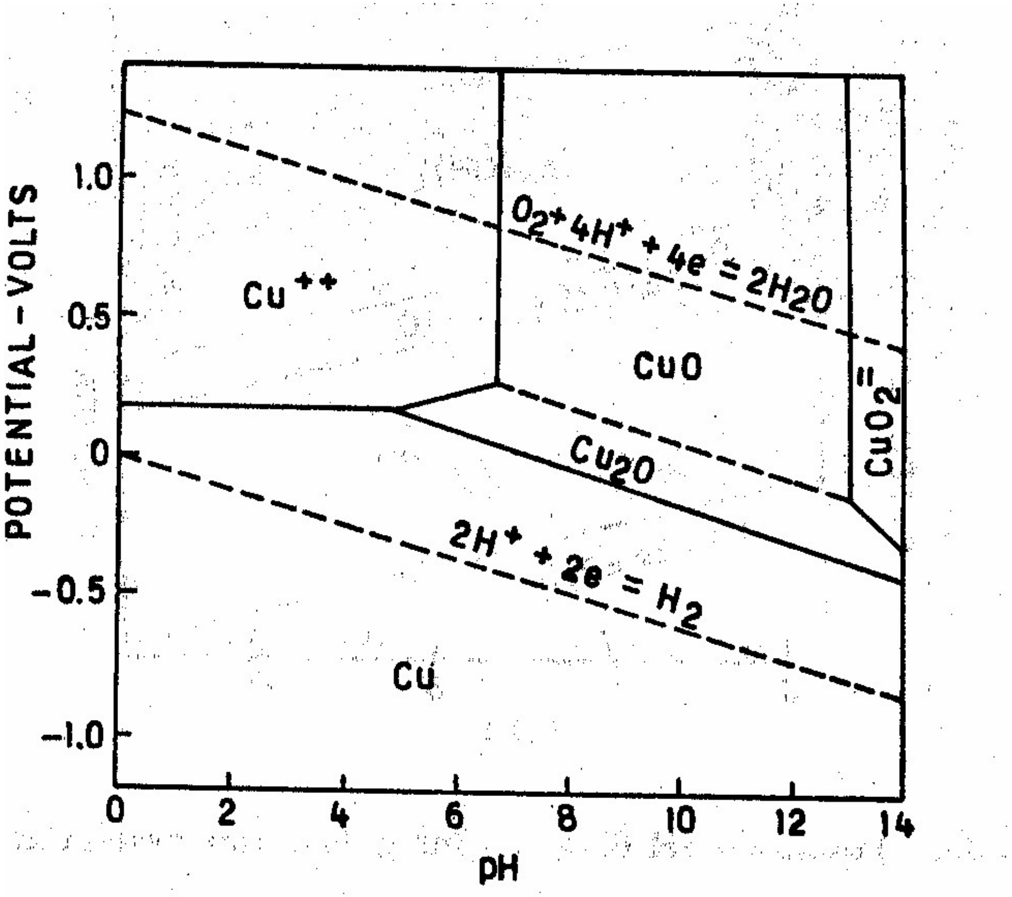
Type of stable ion depends on pH

For $CuO + 2\ H^+ = Cu^{2+} + H_2O$, low pH drives reaction to right

Simple ions like Cu^{2+} are stable at low pH

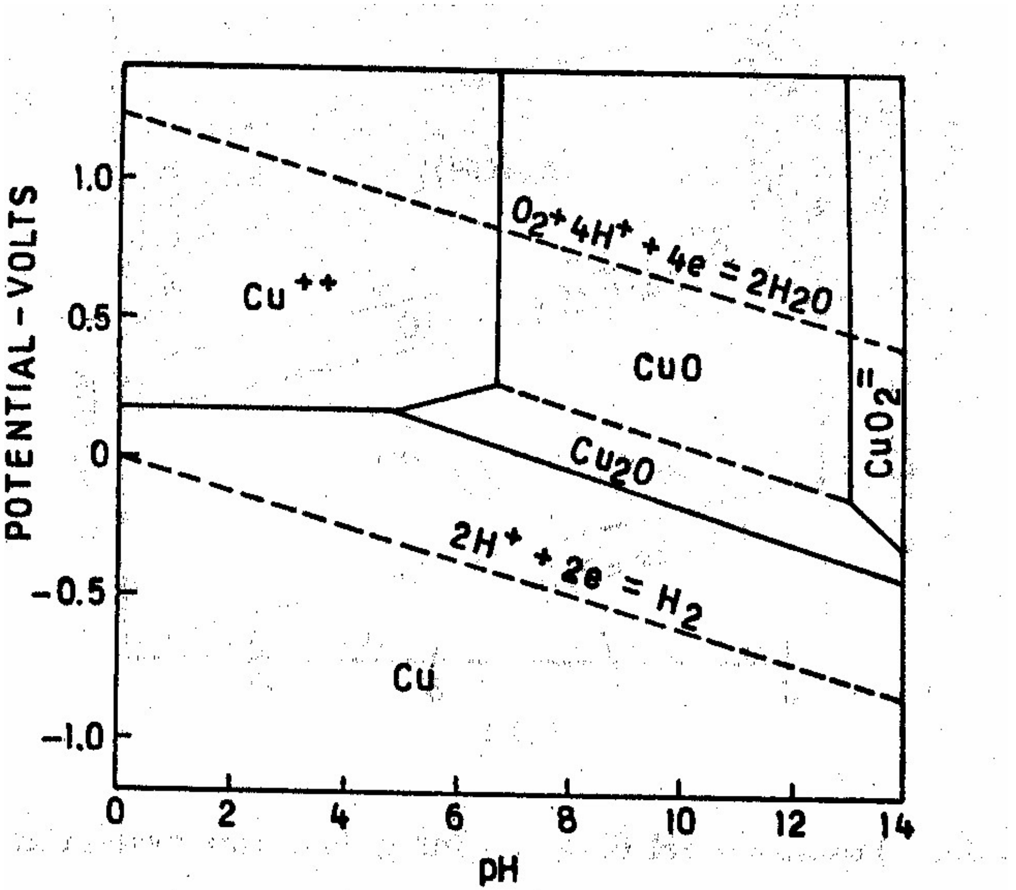
For $CuO + H_2O = 2\ H^+ + CuO_2^{2-}$, high pH drives reaction to right

Oxyions like CuO_2^{2-} are stable at high pH



Solid oxides, hydroxides most stable in center of diagram

More on Metal – H_2O Diagrams



Three kinds of lines separate copper species in this diagram

First is vertical: $CuO + 2\,H^+ = Cu^{2+} + H_2O$; $CuO + H_2O = CuO_2^{2-} + 2\,H^+$

Reactions involve exchange of H^+, but no electrons (no oxidation/reduction); independent of E

Second type of line is horizontal: $Cu^{2+} + 2\,e^- = Cu$

Reaction involves oxidation/reduction, but no H^+; independent of pH

Third type of line is diagonal: $Cu_2O + 2\,H^+ + 2\,e^- = 2\,Cu + H_2O$

Reaction involves both oxidation/reduction and H^+ exchange, so line is a function of E and pH

(No curved lines in most diagrams.)

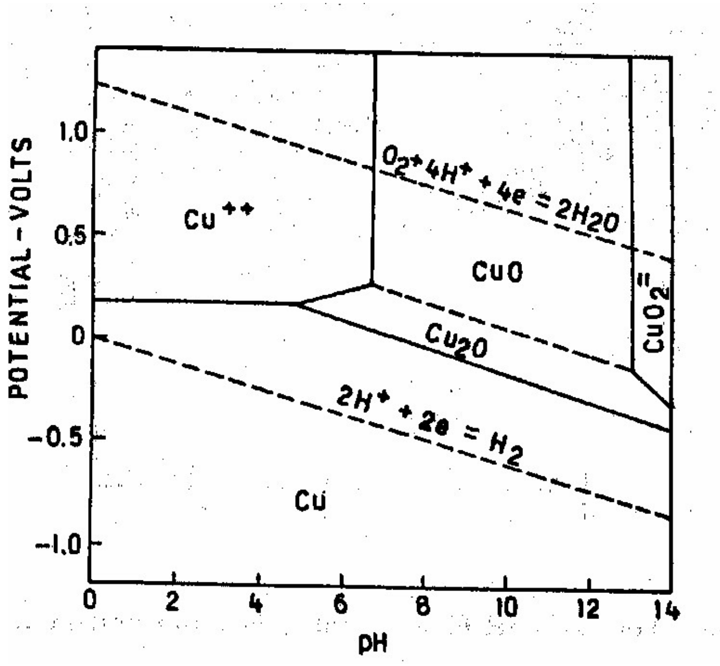
Why Does This Matter? (Part I)

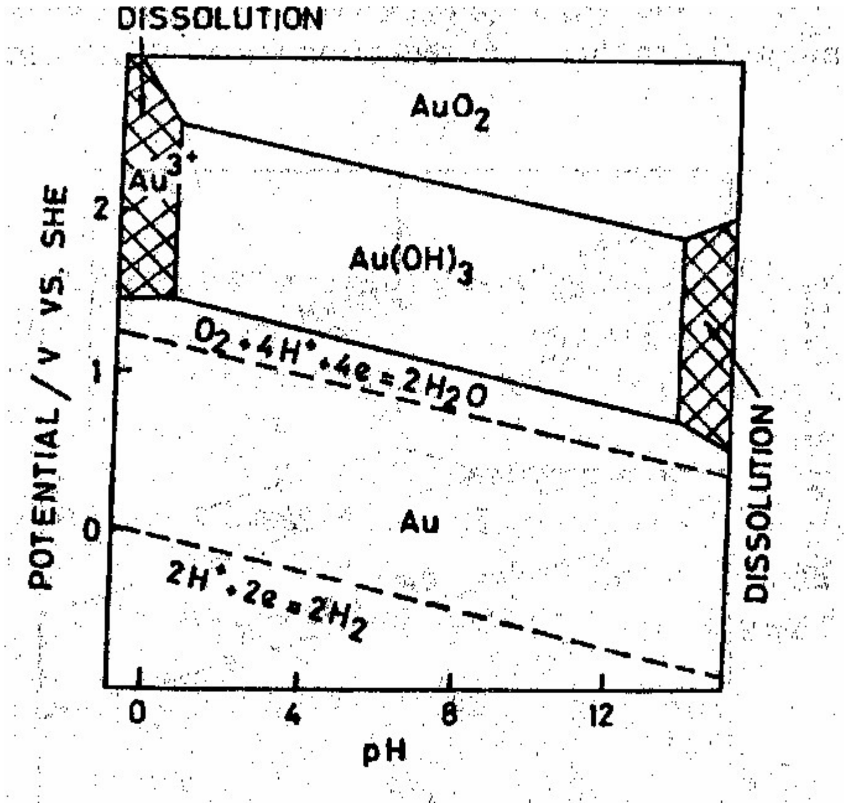
Diagram at bottom left is Cu–H_2O system

Presence of stability region between lines for Cu and ions shows that Cu can be produced hydrometallurgically

Diagram at bottom right is Au–H_2O system

No stability region for gold ions between lines; can’t dissolve Au in aqueous solutions (for now)





Limitations of Eh-pH Diagrams

- Doesn’t include impact of kinetics
- Presumes only one predominant species (sometimes activities of ions are nearly equal)
- Depends on accurate thermodynamic data (not always available for complex compounds)

Factors effecting Corrosion

Nature of the Metal:

- ❑**Position in the galvanic series:** The greater the oxidation potential, when the metal is higher up in the galvanic series, greater is its tendency to become anodic and hence greater is the rate of corrosion.
- ❑**Purity of metal:** Lesser is the percentage purity of a metal, faster is the rate of corrosion. The impurities present in a metal cause heterogeneity and thus tiny electrochemical cells are set up at the exposed part of the impurity and corrosion of metal around the impurity takes place due to local action.
- ❑**Physical state of the metal:** The rate of corrosion is influenced by physical state of metal. The smaller the grain size of the metal or alloy, the greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.
- ❑**Nature of the oxide film:** The ratio of the volumes of the metal oxide to the metal, is known as "specific volume ratio". Greater the specific volume ratio, lesser is the oxidation corrosion rate.
- ❑**Relative areas of the anode and cathode:** When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of the cathodic part and the anodic part. When cathodic area is smaller, the demand for electrons will be less and this result in the decreased rate of dissolution of metal at anodic regions.

- **Solubility of corrosion products:** In the electochemical corrosion, if the corrosion product is soluble in corroding medium, then corrosion proceeds at a faster rate. For example, Pb in H_2SO_4 medium forms $PbSO_4$ which is insoluble in the corroding medium, hence corrosion proceeds at a smaller rate.
- **Volatility of corrosion products:** Rapid and continuous corrosion of metal take place if corrosion product is volatile. This is due to the fact that as soon as corrosion product is formed, it volatilize, thereby leaving the underlying metal surface for further attack.

Nature of the Corroding Environment:

- **Temperature:** With increase of temperature of environment, the reaction as well as diffusion rate increase, thereby corrosion rate is generally enhanced.
- **Humidity of air :** The greater is humidity, the greater is the rate and extent of corrosion. This is due to the fact that moisture acts as a solvent for O_2, H_2S, SO_2 and NaCl etc. to furnish the electrolyte essential for setting up a corrosion cell.
- **Effect of pH:** Corrosions of those metal which are readily attacked by acids can be reduced by increasing the pH of the attacking environment.
- **Presence of impurities in atmosphere:** Corrosion of metals is more in areas near to the industry and sea. This is due to the fact that corrosive gases like H_2S, SO_2, CO_2 and fumes of H_2SO_4 and HCl in the industrial areas and NaCl of sea water leads to increased conductivity of the liquid layer in contact with the metal surface, thereby increase the corrosion rate.
- **Presence of suspended particles in atmosphere:** In case of atmospheric corrosion; (a) if the suspended particles are chemically active in nature [like NaCl, $(NH_4)_2SO_4$], they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion

1-6 Classification of Corrosion

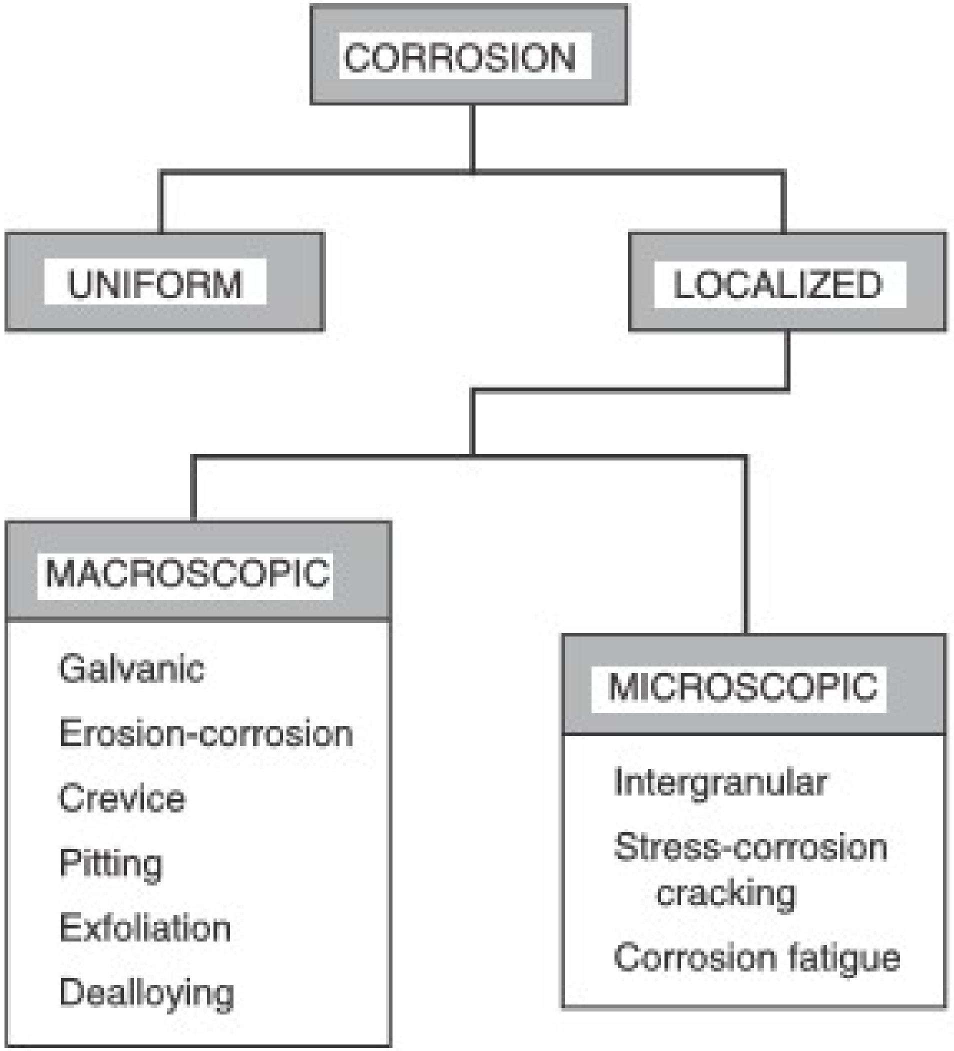
Corrosion has been classified in many different ways. One method divides corrosion into low-temperature and high-temperature corrosion. Another separates corrosion into direct combination (or oxidation) and electrochemical corrosion. The preferred classification here is (1) *wet* corrosion and (2) *dry* corrosion.

Wet corrosion occurs when a liquid is present. This usually involves aqueous solutions or electrolytes and accounts for the greatest amount of corrosion by far. A common example is corrosion of steel by water. Dry corrosion occurs in the absence of a liquid phase or above the dew point of the environment. Vapors and gases are usually the corrodents. Dry corrosion is most often associated with high temperatures. An example is attack on steel by furnace gases.

The presence of even small amounts of moisture could change the corrosion picture completely. For example, dry chlorine is practically noncorrosive to ordinary steel, but moist chlorine, or chlorine dissolved in water, is extremely corrosive and attacks most of the common metals and alloys. The reverse is true for titanium—dry chlorine gas is more corrosive than wet chlorine.

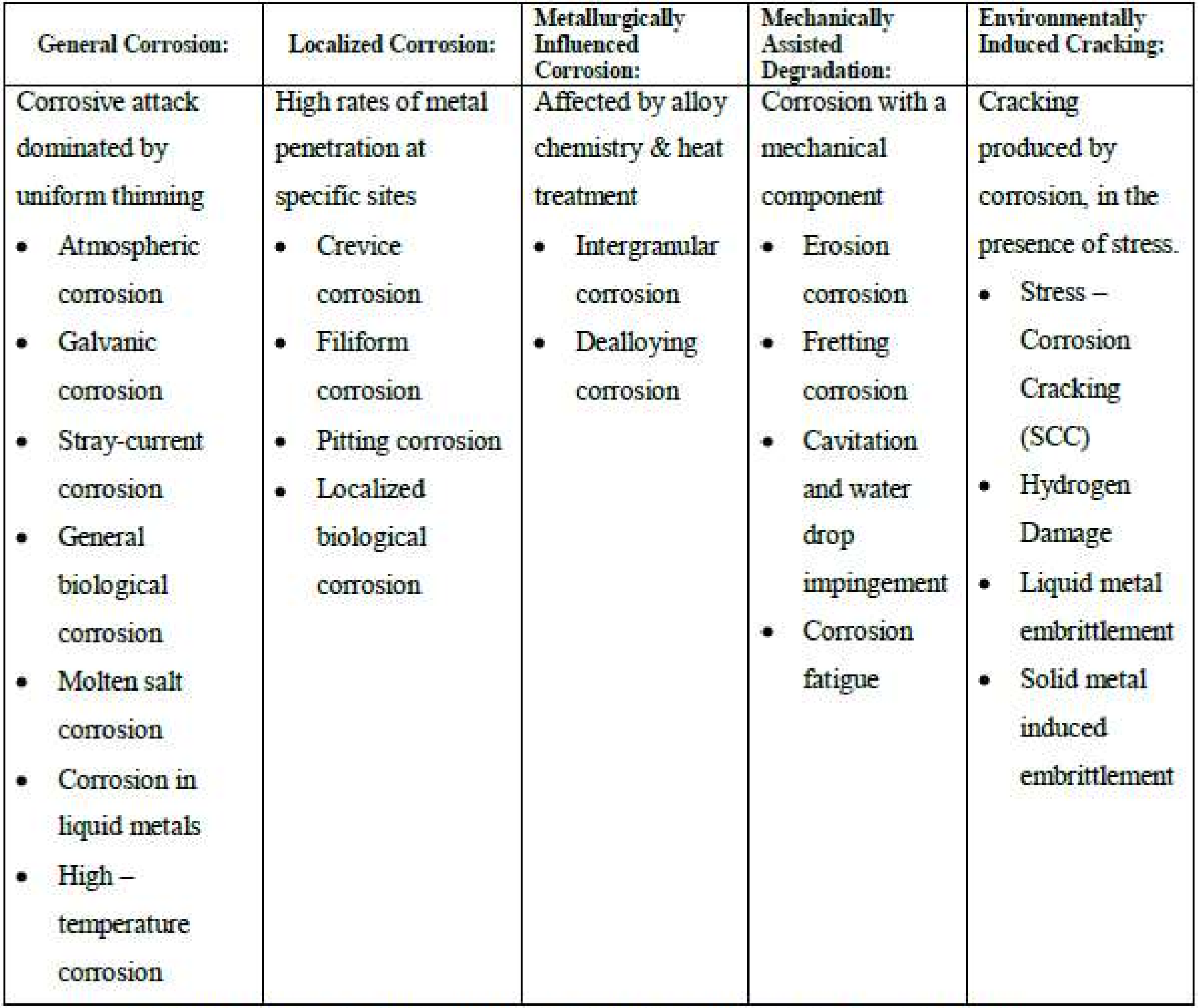
Eight forms of Corrosion

1. Uniform or general Corrosion
2. Galvanic or Two metal Corrosion
3. Crevice Corrosion
4. Pitting Corrosion
5. Intergranular Corrosion
6. Selective Leaching or Parting Corrosion
7. Erosion Corrosion
8. Stress Corrosion



Macroscopic versus microscopic forms of localized corrosion

Table 1.1 ASM classifications of corrosion types



General Corrosion:	Localized Corrosion:	Metallurgically Influenced Corrosion:	Mechanically Assisted Degradation:	Environmentally Induced Cracking:
Corrosive attack dominated by uniform thinning • Atmospheric corrosion • Galvanic corrosion • Stray-current corrosion • General biological corrosion • Molten salt corrosion • Corrosion in liquid metals • High – temperature corrosion	High rates of metal penetration at specific sites • Crevice corrosion • Filiform corrosion • Pitting corrosion • Localized biological corrosion	Affected by alloy chemistry & heat treatment • Intergranular corrosion • Dealloying corrosion	Corrosion with a mechanical component • Erosion corrosion • Fretting corrosion • Cavitation and water drop impingement • Corrosion fatigue	Cracking produced by corrosion, in the presence of stress. • Stress – Corrosion Cracking (SCC) • Hydrogen Damage • Liquid metal embrittlement • Solid metal induced embrittlement

(Ref. Sully J R, Taylor D. W, Electrochemical Methods of Corrosion Testing, Metals Hand Book. Vol 13, 1987.)

ASM: American Society for Metals

Uniform Corrosion

- Chemical or electrochemical reaction that proceeds uniformly over the entire exposed surface or over large area
- An electrochemical reaction at granular level
- Relatively slow and predictable
- Easily corrected with coatings and regular maintenance

Examples

☐ Steel or Zinc immersed in dilute sulphuric acid
☐ Iron in all most all environments
☐ Tarnished Silver

Prevention:

- Protective coating
- Inhibitors
- Cathodic protection

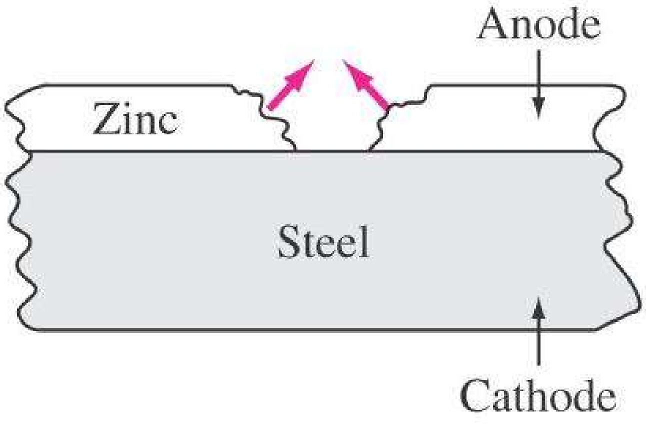
GALVANIC OR TWO-METAL CORROSION

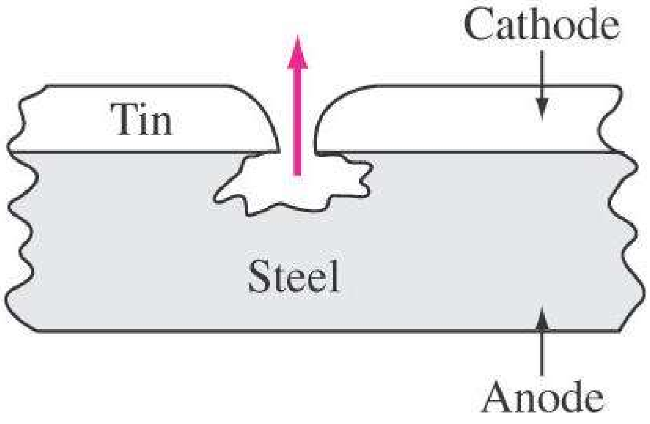
A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron flow between them. Corrosion of the less corrosion-resistant metal is usually increased and attack of the more resistant material is decreased, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes *anodic* and the more resistant metal *cathodic*. Usually the cathode or cathodic metal corrodes very little or not at all in this type of couple. Because of the electric currents and dissimilar metals involved, this form of corrosion is called galvanic, or two-metal, corrosion. It is electrochemical corrosion, but we shall restrict the term *galvanic* to dissimilar-metal effects for purposes of clarity.

The driving force for current and corrosion is the potential developed between the two metals. The so-called dry-cell battery depicted in Fig. 3-2 is a good example of this point. The carbon electrode acts as a noble or corrosion-resistant metal—the cathode—and the zinc as the anode, which corrodes. The moist paste between the electrodes is the conductive (and corrosive) environment that carries the current. Magnesium may also be used as the anodic material or outer case.

Galvanic Corrosion

- Occurs when two metals or alloys having different compositions are electrically coupled while exposed to an electrolyte.
- Examples:
  - Galvanized steel, steel coated with Zn; Zn is sacrificed to protect steel
  - Tin can (food container), steel coated with Sn; Sn is sacrificed to protect steel





Solutions:

Choose metals close in galvanic series

Have large anode/cathode ratios

Insulate dissimilar metals

Use "Cathodic protection"

Tin plating is used to protect the inside of steel food cans from rusting. The layer of tin stops air and water reaching the iron.

Applications of Cathodic Protection

- Galvanized Steel
  - Zinc coating

- Sacrificial Anodes
  - Ship Hulls
  - Subs (free flooding areas)

Table 3-2 Galvanic series of some commercial metals and alloys in seawater

↑	Platinum
	Gold
Noble or cathodic	Graphite
	Titanium
	Silver
	Chlorimet 3 (62 Ni, 18 Cr, 18 Mo Hastelloy C (62 Ni, 17 Cr, 15 Mo)
	18-8 Mo stainless steel (passive) 18-8 stainless steel (passive) Chromium stainless steel 11-30% Cr (passive)
	Inconel (passive) (80 Ni, 13 Cr, 7 Fe) Nickel (passive)
	Silver solder
	Monel (70 Ni, 30 Cu) Cupronickels (60-90 Cu, 40-10 Ni) Bronzes (Cu-Sn) Copper Brasses (Cu-Zn)
	Chlorimet 2 (66 Ni, 32 Mo, 1 Fe) Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 M
	Inconel (active) Nickel (active)
	Tin
	Lead
	Lead-tin solders
	18-8 Mo stainless steel (active) 18-8 stainless steel (active)
	Ni-Resist (high Ni cast iron)
	Chromium stainless steel, 13% Cr (active)
	Cast iron Steel or iron
	2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)
Active or anodic	Cadmium
	Commercially pure aluminum (1100)
↓	Zinc
	Magnesium and magnesium alloys

Another interesting feature of the galvanic series is the brackets shown in Table 3-2. The alloys grouped in these brackets are somewhat similar in base composition—for example, copper and copper alloys. The bracket indicates that in most practical applications there is little danger of galvanic corrosion if metals in a given bracket are coupled or in contact with each other. This is because these materials are close together in the series and the potential generated by these couples is not great. The farther apart in the series, the greater the potential generated.

Galvanic corrosion sometimes occurs in unexpected places. For example, corrosion was noted on the leading edges of inlet cowlings on jet engines. This attack was caused by the fabric used on the engine inlet duct plugs. This was a canvas fabric treated with a copper salt to prevent mildew. Treatment of fabric is common practice for preventing mildew, for flameproofing, and for other reasons. The copper salt deposited copper on the alloy steel, resulting in galvanic attack of the steel. This problem was solved by using a vinyl-coated nylon containing no metal.

These examples emphasize the fact that design engineers should be particularly aware of the possibilities of galvanic corrosion, since they specify the detailed materials to be used in equipment. It is sometimes economical to use dissimilar materials in contact—for example, water heaters with copper tubes and cast iron or steel tube sheets. If galvanic corrosion occurs, it accelerates attack on the heavy tube sheet (instead of the thin copper tubes), and long life is obtained because of the thickness of the tube sheets. Accordingly, expensive bronze tube sheets are not required. For more severe corrosion conditions, such as dilute acidic solutions, bronze tube sheets would be necessary.

The potential generated by a galvanic cell consisting of dissimilar metals can change with time. The potential generated causes a flow of current and corrosion to occur at the anodic electrode. As corrosion progresses, reaction products or corrosion products may accumulate at either the anode or cathode, or both. This reduces the speed at which corrosion proceeds.

3-5 Prevention

A number of procedures or practices can be used for combating or minimizing galvanic corrosion. Sometimes one is sufficient, but a combination of one or more may be required. These practices are as follows:

1. Select combinations of metals as close together as possible in the galvanic series.
2. Avoid the unfavorable area effect of a small anode and large cathode. Small parts such as fasteners sometimes work well for holding less resistant materials.
3. Insulate dissimilar metals wherever practicable. It is important to insulate *completly* if possible. A common error in this regard concerns bolted joints such as two flanges, like a pipe to a valve, where the pipe might be steel or lead and the valve a different material. Bakelite washers under the bolt heads and nuts are assumed to insulate the two parts, yet the shank of the bolt touches both flanges! This problem is solved by putting plastic tubes over the bolt shanks, plus the washers, so the bolts are isolated completely from the flanges. Figure 3-5 shows proper insulation for a bolted joint. Tape and paint to increase resistance of the circuit are alternatives.

4. Apply coatings with caution. Avoid situations similar to one described in connection with Fig. 3-4. Keep the coatings in good repair, particularly the one on the anodic member.
5. Add inhibitors, if possible, to decrease the aggressiveness of the environment.
6. Avoid threaded joints for materials far apart in the series. As shown in Fig. 3-5, much of the effective wall thickness of the metal is cut away during the threading operation. In addition, spilled liquid or condensed moisture can collect and remain in the thread grooves. Brazed joints are preferred, using a brazing alloy more noble than at least one of the metals to be joined. Welded joints using welds of the same alloy are even better.
7. Design for the use of readily replaceable anodic parts or make them thicker for longer life.
8. Install a third metal that is anodic to *both* metals in the galvanic contact.

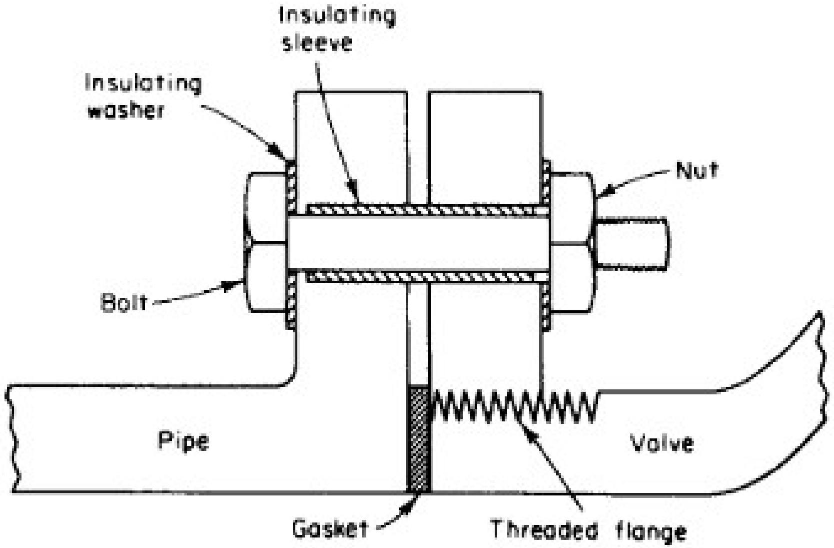


Figure 3-5 Proper insulation of a flanged joint.

3-6 Beneficial Applications

Galvanic corrosion has several beneficial or desirable applications. As noted before, dry cells and other primary batteries derive their electric power by galvanic corrosion of an electrode. It is interesting to note that if such a battery is used to the point where the zinc case is perforated and leakage of the corrosive electrolyte occurs, it becomes a galvanic corrosion problem! Some other beneficial applications are briefly described below:

Cathodic protection The concept of cathodic protection is introduced at this point because it often utilizes the principles of galvanic corrosion. This subject is discussed in more detail in Chap. 6. Cathodic protection is simply the protection of a metal structure by making it the cathode of a galvanic cell. Galvanized (zinc-coated) steel is the classic example of cathodic protection of steel. The zinc coating is put on the steel, not because it is corrosion resistant but because it is not. The zinc corrodes preferentially and protects the steel, as shown by Table 3-3 and Fig. 3-6. Zinc acts as a sacrificial anode. In contrast, tin, which is more corrosion resistant than zinc, is sometimes undesirable as a coating because it is usually cathodic to steel. At perforations in the tin coating, the corrosion of the steel is accelerated by galvanic action. Magnesium is often connected to underground steel pipes to suppress their corrosion (the magnesium preferentially corrodes). Cathodic protection is also obtained by impressing a current from an external power source through an inert anode (see Chap. 6).

Cleaning silver Another useful application concerns the use of galvanic corrosion for cleaning silverware in the home. Most household silver is cleaned by rubbing with an abrasive. This removes silver and is particularly bad for silver plate because the plating is eventually removed. Many of the stains on silverware are due to silver sulfide. A simple electrochemical cleaning method consists of placing the silver in an *aluminum* pan containing water and baking soda (do not use sodium chloride). The current generated by the contact between silver and aluminum causes the silver sulfide to be reduced back to silver. No silver is actually removed. The silver is then rinsed and washed in warm soapy water. It does not look quite as nice as a polished surface but it saves wear and tear on the silver and also on the individual who has to do the job. Simultaneous use of ultrasonic cleaning is faster and better, but this equipment is not generally available.

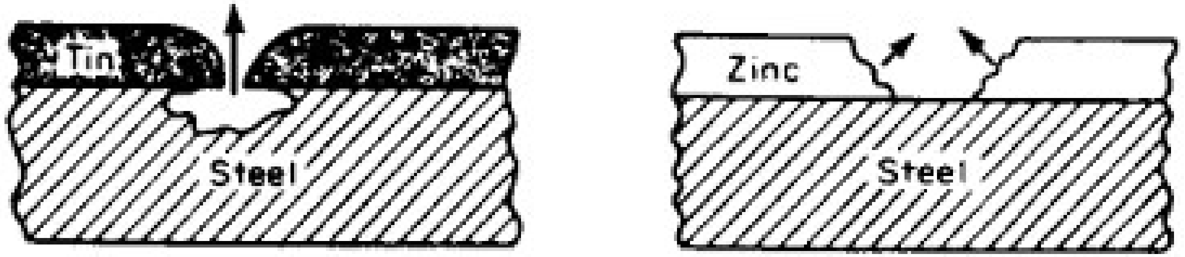
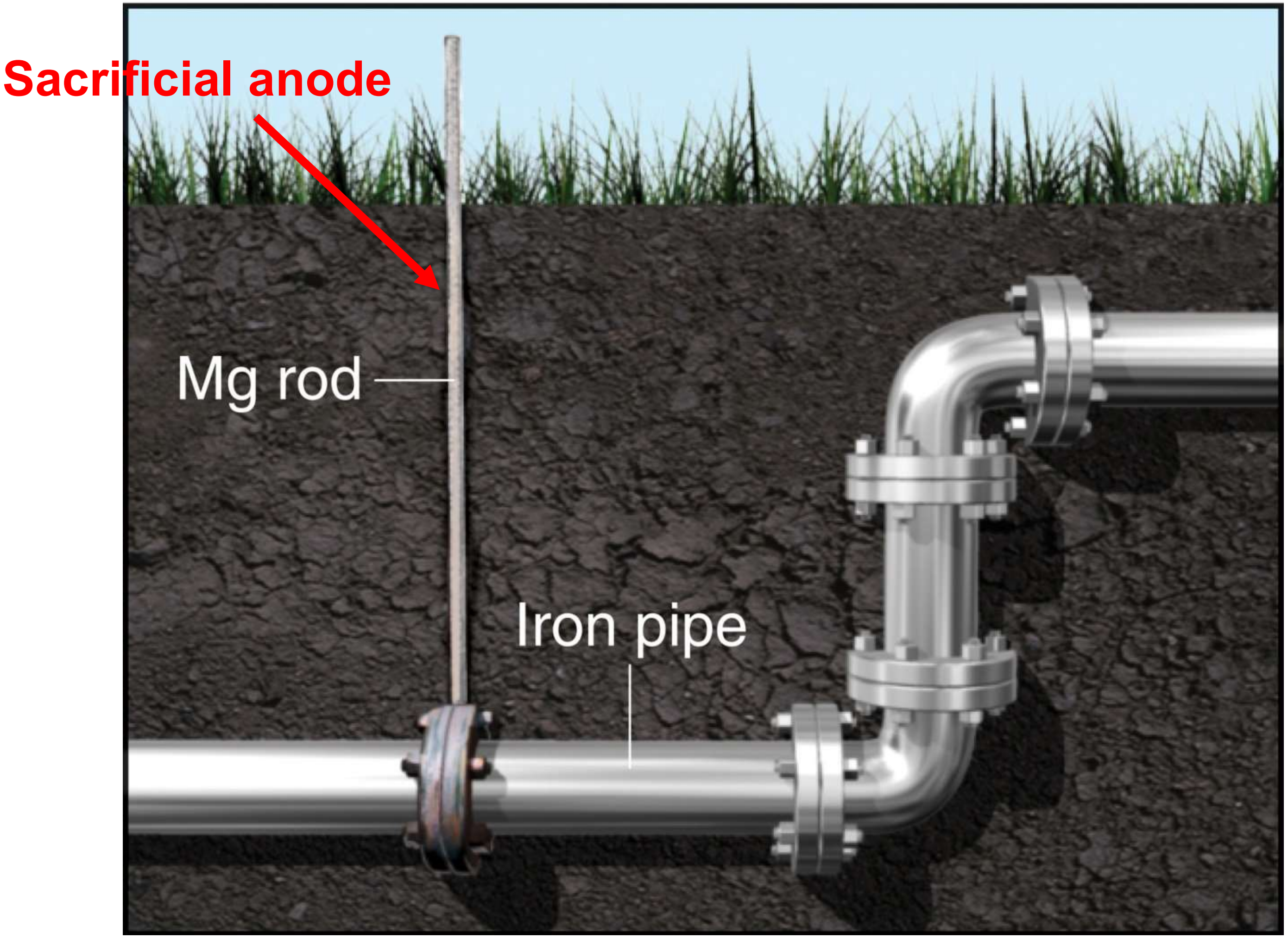


Figure 3-6 Galvanic corrosion at perforation in tin- and zinc-coated steel. Arrows indicate corrosive attack.

One will sometimes see for sale a piece of "magic metal" that will do the same thing. The directions call for placing it in an *enameled* pan. The so-called magic metal is usually a piece of magnesium or aluminum.

The use of Sacrificial Anodes to prevent iron Corrosion



In cathodic protection, an active metal, such as zinc, magnesium, or aluminum, acts as the anode and is sacrificed instead of the iron.

Corrosion Control by Anodic Protection

The technique of cathodic protection is well known and has been widely applied to a number of corrosion problems. It is not so well known that corrosion can also be prevented in suitable cases by anodic protection, using a platinum electrode system. The author shows that, with adequate laboratory work beforehand and proper instrumentation, the use of anodic protection can make an effective contribution to the life of a chemical plant.

In practice we can achieve immunity by doing one or more of the following:

(1) Using a suitably noble metal

(2) Removing unnecessary oxidising agents (e.g. air)

(3) Adding a cathodic inhibitor (lessening the effectiveness of the oxidising agents)

(4) Applying cathodic protection

Anodic protection refers to prevention of corrosion through impressed anodic current. This method of protection tested and demonstrated by Edeleanu in 1954 however can be applied only to metals and alloys that exhibit active-passive behavior. The interface potential of the structure is increased to passive domain.

If an active-passive alloy such as stainless steel is maintained in the passive region through an applied potential (or current) from a potentiostat, its initial corrosion rate (i_{corr}) can be shifted to a low value at i_{pass} as shown in Fig. 23.1.

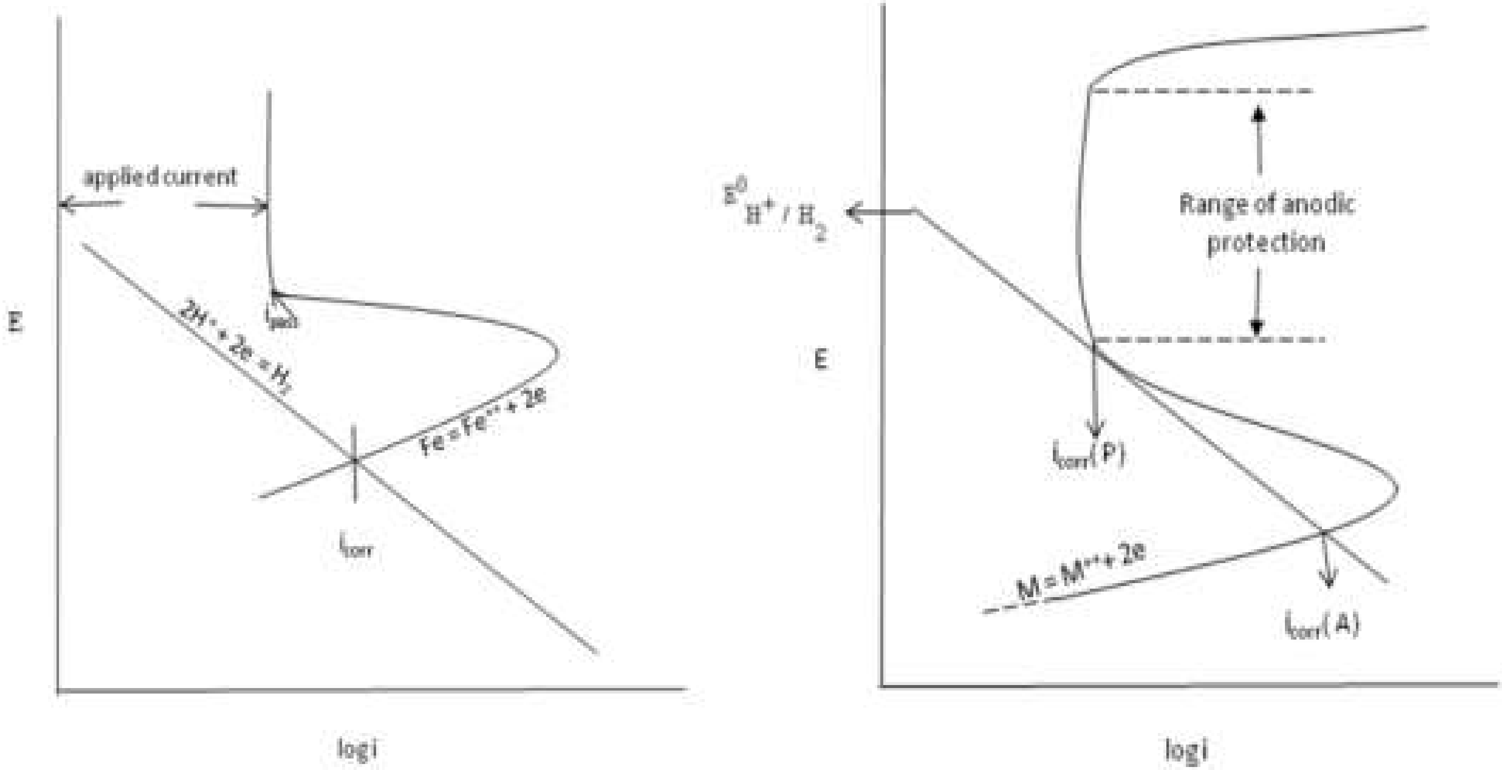
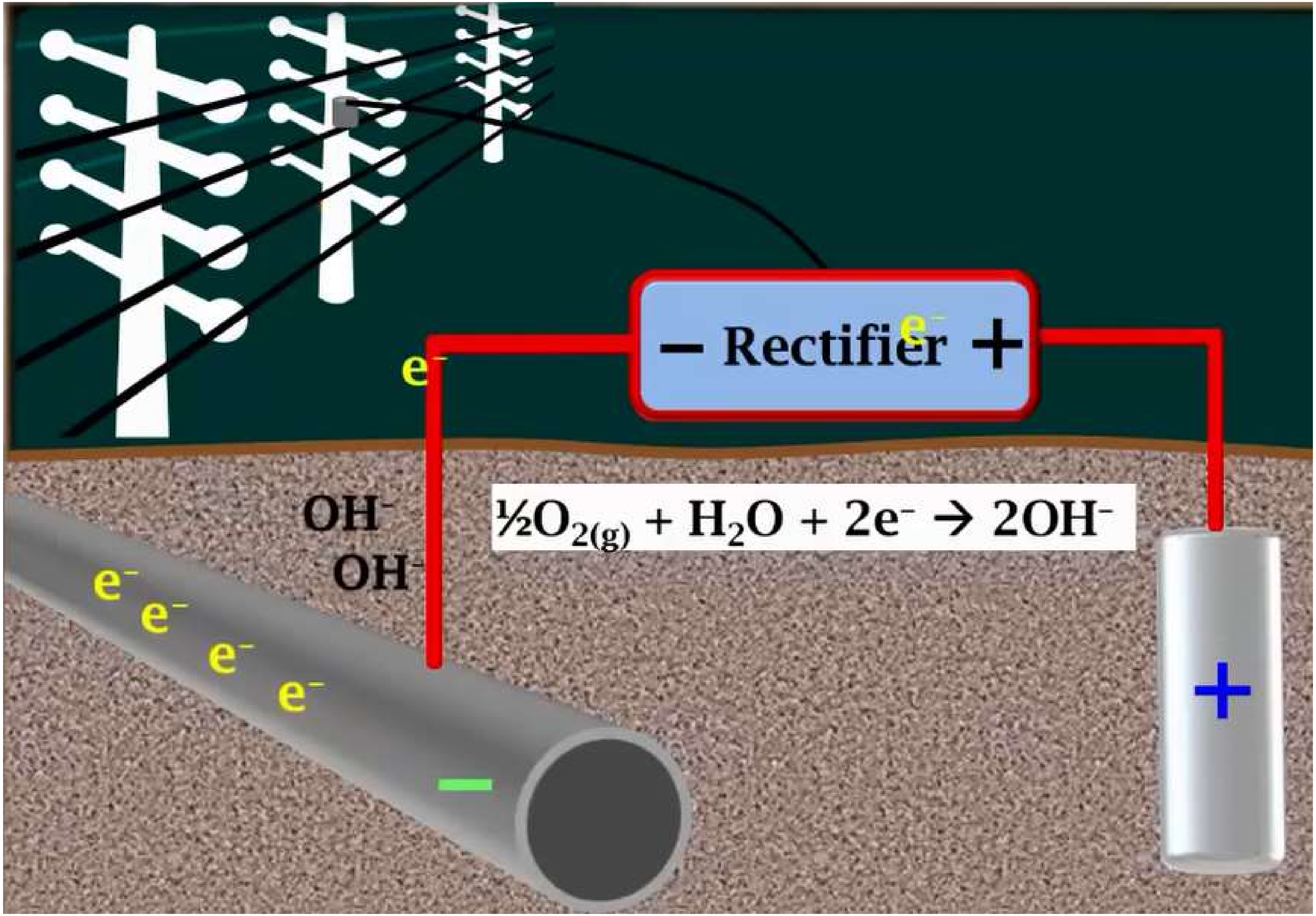


Fig 23.1 Polarization curves depicting principles of anodic protection

Anodic protection is more effective in acid solutions than cathodic protection. Current requirements for cathodic protection in acid solutions are several orders of magnitude higher than that necessary for complete anodic protection. Cathodic protection currents in acid solution can also lead to hydrogen liberation and embrittlement of steels.

Anodic protection unlike cathodic protection is ideally suited for protection of active-passive alloys in aggressive environments such as high acidity and corrosive chemicals. Hence anodic protection is the most preferred choice for protection of chemical process equipment.

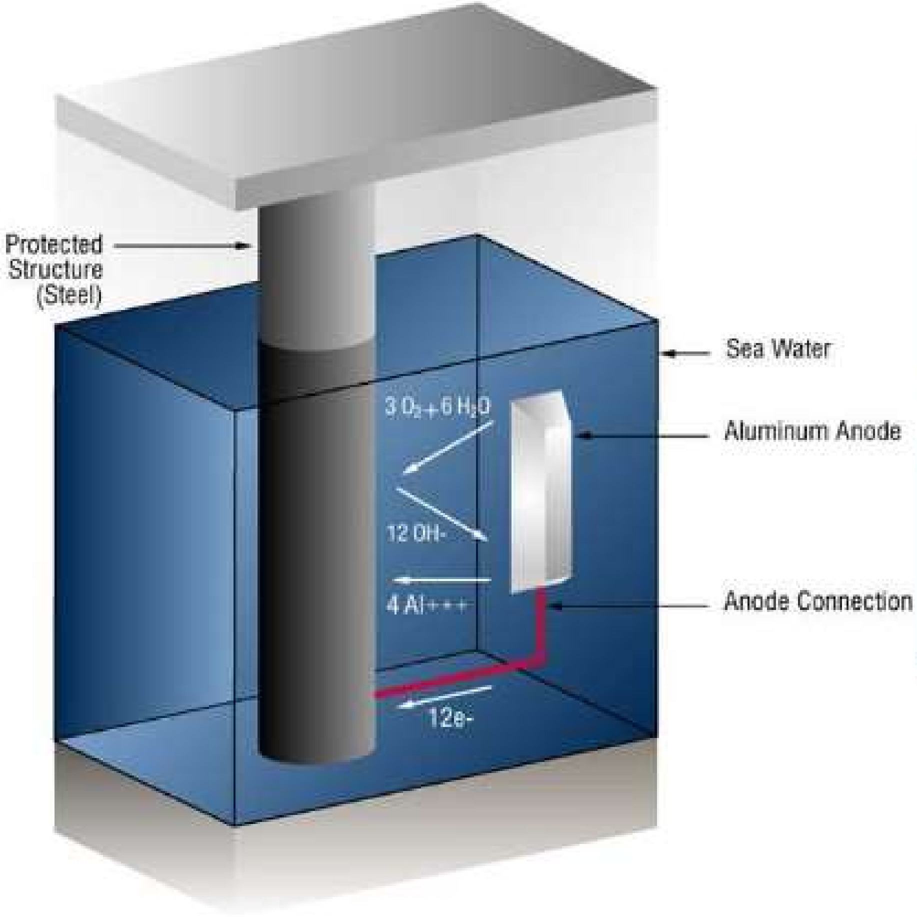
Impressed current cathodic protection



Pipe has always excess electrons so that it will not corrode

Cathodic protection

Sacrificial anode system in seawater



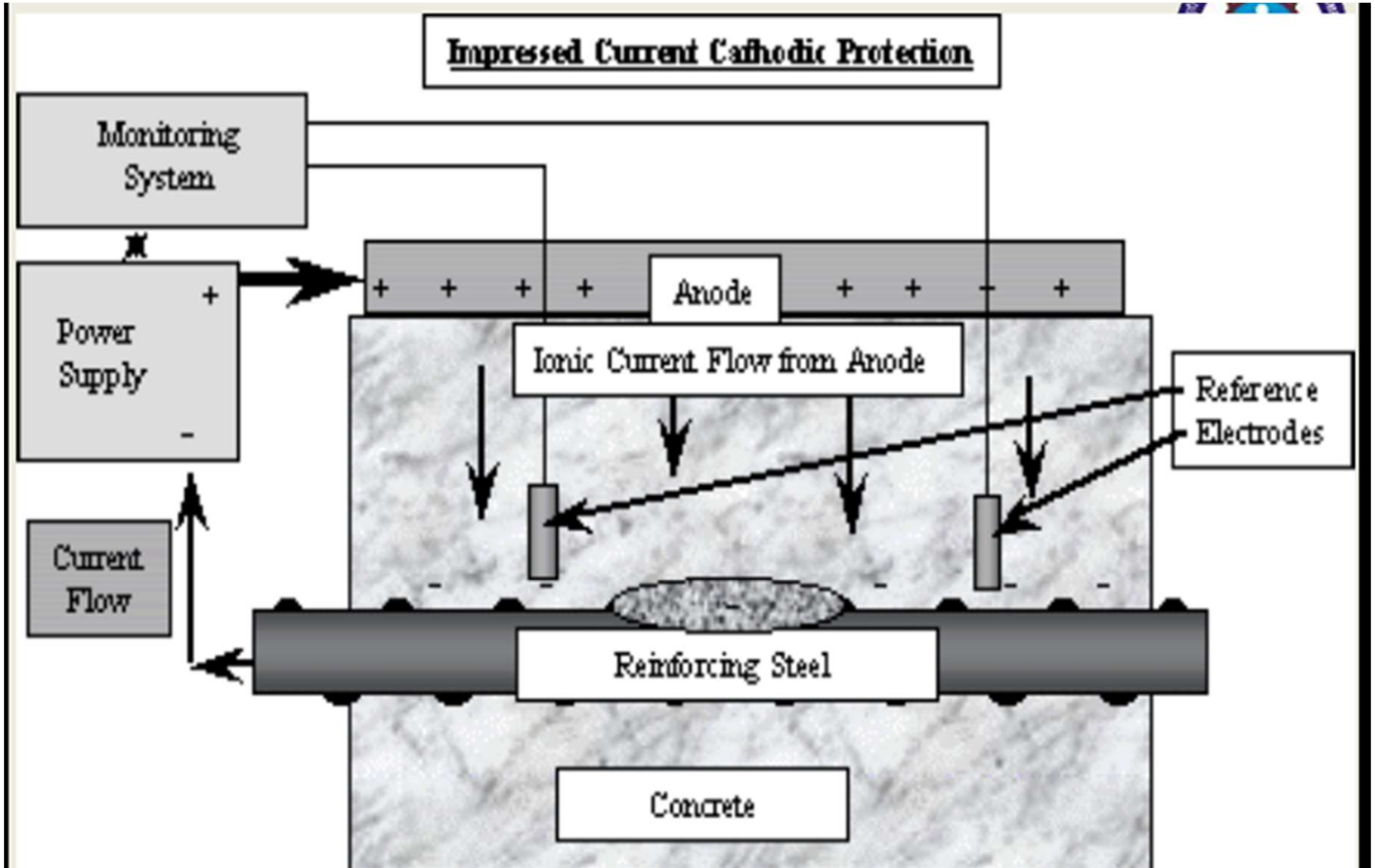
Protected surface (cathode):

$3O_2 + 12e^- + 6H_20 \rightarrow 12OH^-$

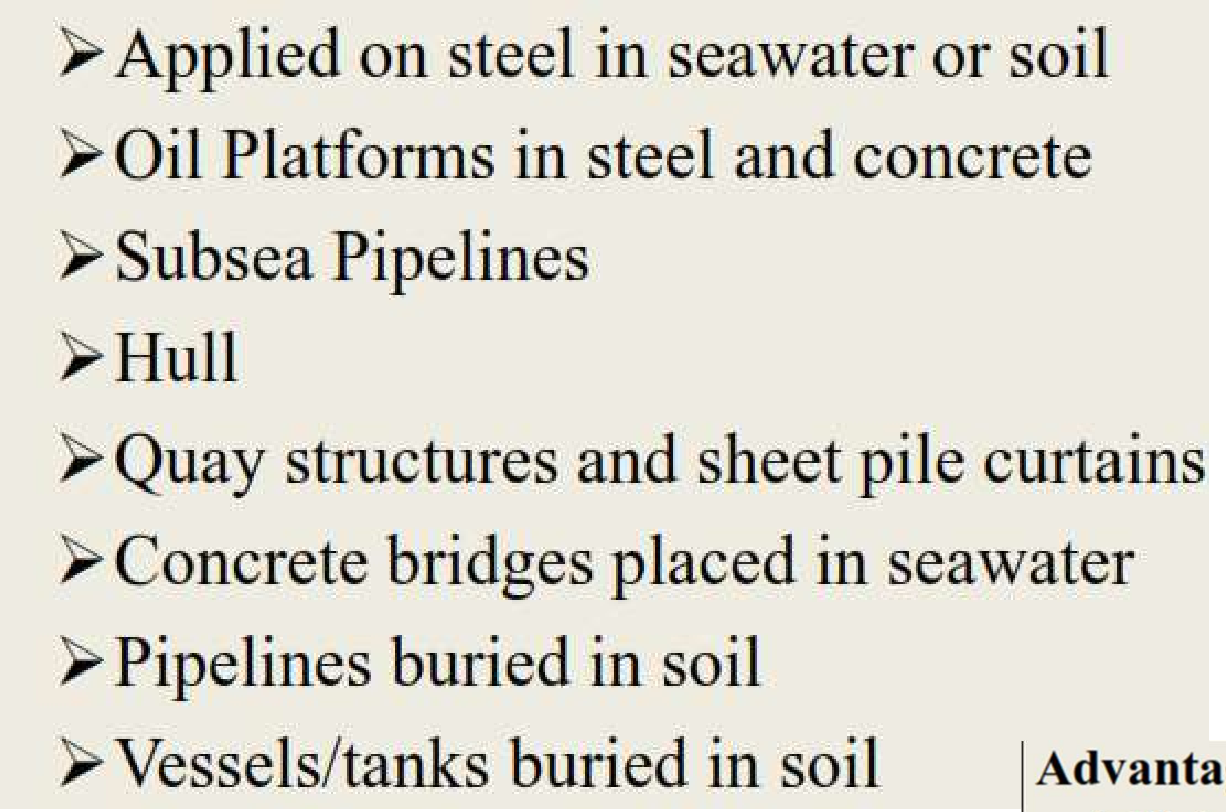
Sacrificial anode:

$4Al \rightarrow 4AL^{+++} + 12\ e^-$

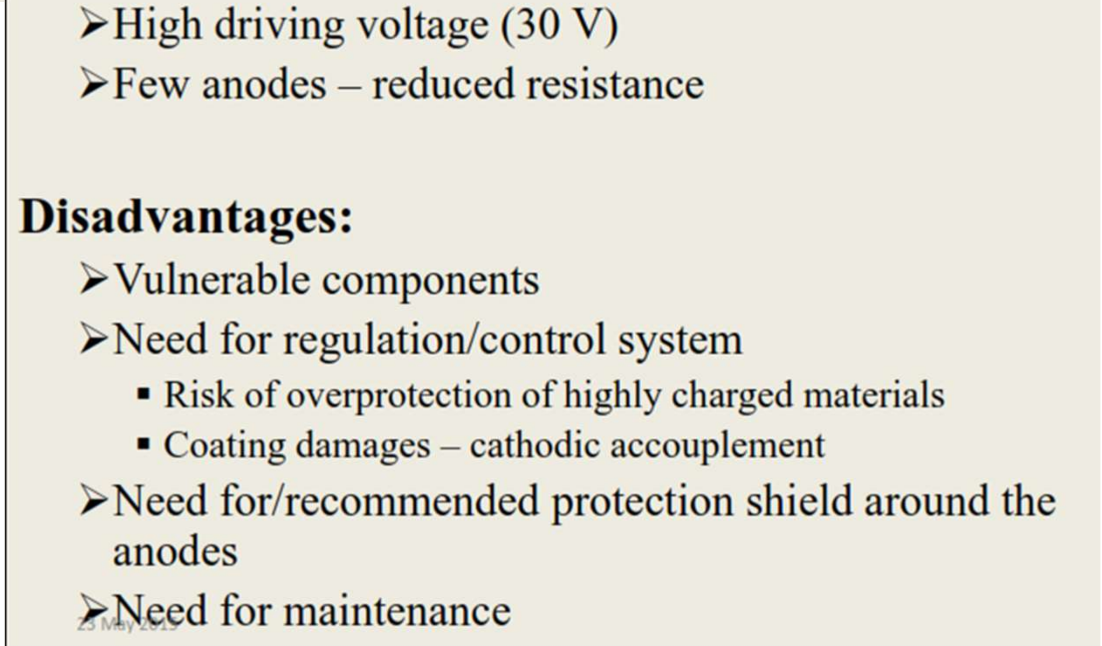
- ❑ **Electrical cathodic protection:** In this method an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. The current is derived from direct sources like battery of rectifier on A.C. line with an insoluble anode (graphite, stainless steel or scrap iron buried in soil.
- ❑ The negative terminal of DC is connected to pipeline to be protected. The anode is kept in back fill to increase the electrical contact with the surrounding soil.
- ❑ This technique is used for long term operations



Applications of Impressed current



- Applied on steel in seawater or soil
- Oil Platforms in steel and concrete
- Subsea Pipelines
- Hull
- Quay structures and sheet pile curtains
- Concrete bridges placed in seawater
- Pipelines buried in soil
- Vessels/tanks buried in soil



Advantages:

- High driving voltage (30 V)
- Few anodes – reduced resistance

Disadvantages:

- Vulnerable components
- Need for regulation/control system
  - Risk of overprotection of highly charged materials
  - Coating damages – cathodic accouplement
- Need for/recommended protection shield around the anodes
- Need for maintenance

CATHODES FOR ANODIC PROTECTION

- Should be permanent and can be used as current collector without any significant degradation.
- Having large surface area in order to suppress cathodic overpotential.
- Low cost.

Platinum clad brass can be used for anodic protection cathodes because this cathode has low overpotential and its degradation rate is very low, however it is very expensive.

ANODIC PROTECTION

This is an electrochemical method of corrosion control in which an external potential control system, called potentiostat, is used to produce and maintain a thin non corroding, passive film on a metal or an alloy. The use of potentiostat is to shift corrosion potential into passive potential so that the corrosion of the metal is stopped.

The potential of the object (say acid storage tank) to be protected is controlled by potential controller (potentiostat) so that under certain potential range, the object becomes passive and prevents further corrosion. This potential range depends upon the relationship between the metal and the environment.

Applications:

1. Used in acid coolers in dilute sulphuric acid plants
2. used in storage tanks for sulphuric acid
3. used in chromium in contact with hydrofluoric acid
4. **Anodic protection has been applied to protect storage tanks, reactors, heat exchangers, transportation vessels for corrosive solutions**
5. **Anodic protection decreases corrosion rate of the stainless steel, initially from 5 mm/year down to 0.025 mm/year and therefore less contaminated sulfuric acid can be obtained.**

Limitations:

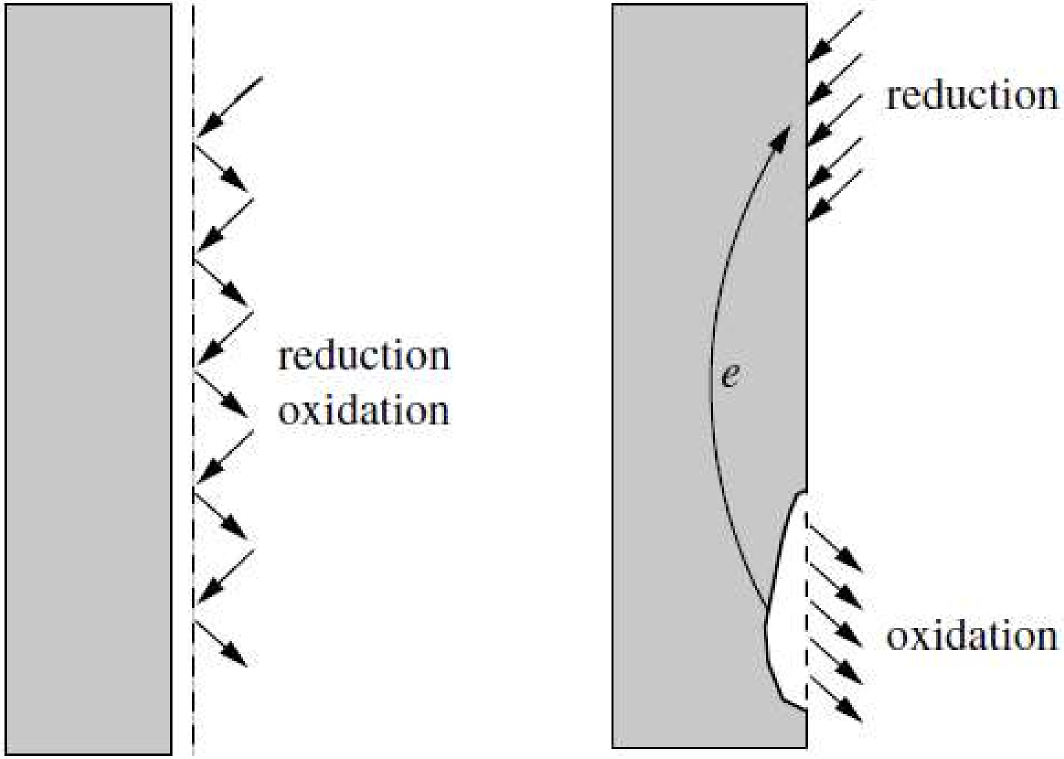
1. This method cannot be applied in the case of corrosive medium containing aggressive chloride.
2. This cannot be applied if protection breaks down at any point, it is difficult to reestablish.

Cathodes used in recent anodic protection systems

Cathode metal	Environment
Platinum-clad brass	Sulfuric acid of various concentrations
Steel	Kraft pulping liquor
Chromium nickel steel	H_2SO_4 (78–105%)
Silicon cast iron	H_2SO_4 (89–105%)
Copper	Hydroxylamine sulfate
S30400	Liquid fertilizers (nitrate solutions)
	Sulfuric acid
Nickel-plated steel	Chemical nickel plating solutions
Hastelloy C	Liquid fertilizers (nitrate solutions)
	Sulfuric acid of various concentrations
	Kraft digester liquid

Table. 23.1 Comparison of cathodic and anodic protection methods

Factors	**Cathodic protection**	**Anodic protection**
Suitability	To all metals in general.	Only to those exhibiting active-passive behavior
Environment	Only for moderate corrosion environment.	Even aggressive chemical corrosives.
Cost benefit	Low investment, but higher operative costs..	Higher investment, but low operative costs.
Operation	Protective currents to be established through initial design and field trials	More precise electrochemical estimation of protection range possible.



uniform corrosion   localized corrosion

Figure 1.7 Uniform and localized corrosion of a metal surface.

Erosion Corrosion

Is the deterioration of metals and alloys due to relative movement between Surfaces and corrosive fluids. Depending on the rate of this movement, abrasion takes place.

Causes:

Abrasive fluids impinging on surfaces

Commonly found in piping, propellers, turbine blades, valves and pumps

Abrasion of zinc coatings

Solutions:

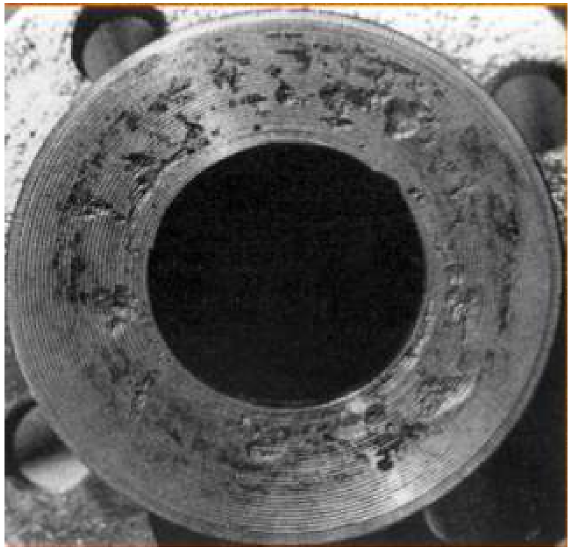
- Change design to minimize or eliminate fluid turbulence and impingement effects.
- Use other materials that resist erosion
- Remove particulates from fluids

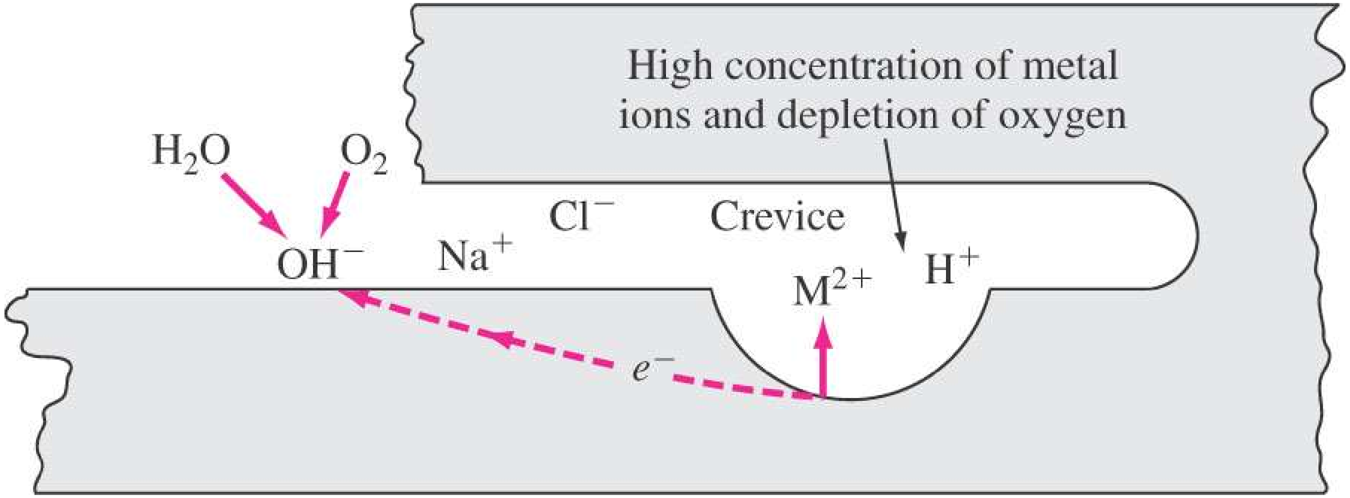
Results wear & abrasion
Characterized by the appearance on the metal surface of grooves, valley, pits, rounded holes. (Ex: stainless alloy pump impeller, condenser tube walls etc)

Crevice Corrosion

- Intensive localized corrosion within crevices & shielded areas on metal surfaces
- Small volumes of stagnant corrosive caused by holes, gaskets, surface deposits, lap joints
- narrow crevice filled with ionized solution
- Oxygen-rich on the outside, oxygen-poor on the inside
- metals oxidize with salt anions $FeCl_2$ and pH rises in cathodic zone
- H^+ may destroy passivity

Examples of such geometries include flanges, gaskets, disbonded linings/coatings, fasteners





Examples of deposits that may produce crevice are sand, dirt, corrosion products, and other solids. The deposit acts as a shield and creates a stagnant condition thereunder. The deposit could also be a permeable corrosion product.

Contact between metal and nonmetallic surfaces can cause crevice corrosion in the case of a gasket. Wood, plastics, rubber, glass, concrete, asbestos, wax and fabrics are materials that can cause this type of corrosion.

Mechanism

it is simply from differences in metal ion or oxygen concentration between the crevice and its surroundings. This crevice corrosion is also called as "**Concentration cell corrosion**"

Dissolution of metal M and the reduction of oxygen to hydroxide ions

$$\text{Oxidation} \qquad M \rightarrow M^{+} + e \qquad (3.1)$$

$$\text{Reduction} \qquad O_2 + 2H_2O + 4e \rightarrow 4OH^{-} \qquad (3.2)$$

After a short interval, the O2 within the crevice is depleted because of the restricted convection. After oxygen is depleted, no further O2 reduction occurs, although the dissolution of metal M continues. This tends to produce an excess of positive charge in the solution (M+), which is necessarily balanced by the migration of chloride ions into the crevice. This results in an increased concentration of metal chloride within the crevice.

$$M^{+}Cl^{-} + H_2O = MOH\downarrow + H^{+}Cl^{-} \qquad (3.3)$$

Both chloride and hydrogen ions accelerate the dissolution rates of most metals and alloys.

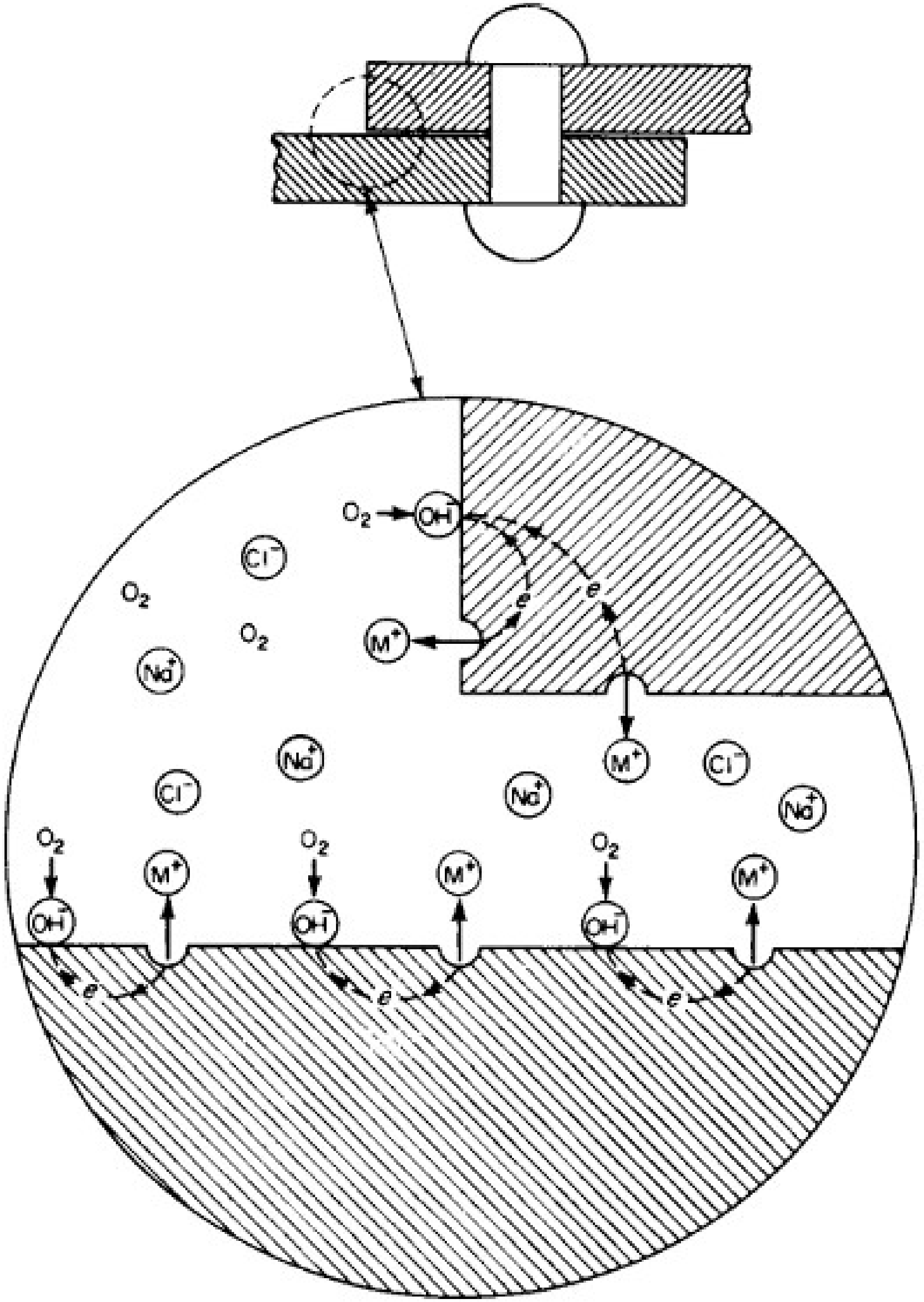


Figure 3-9 Crevice corrosion—initial stage.

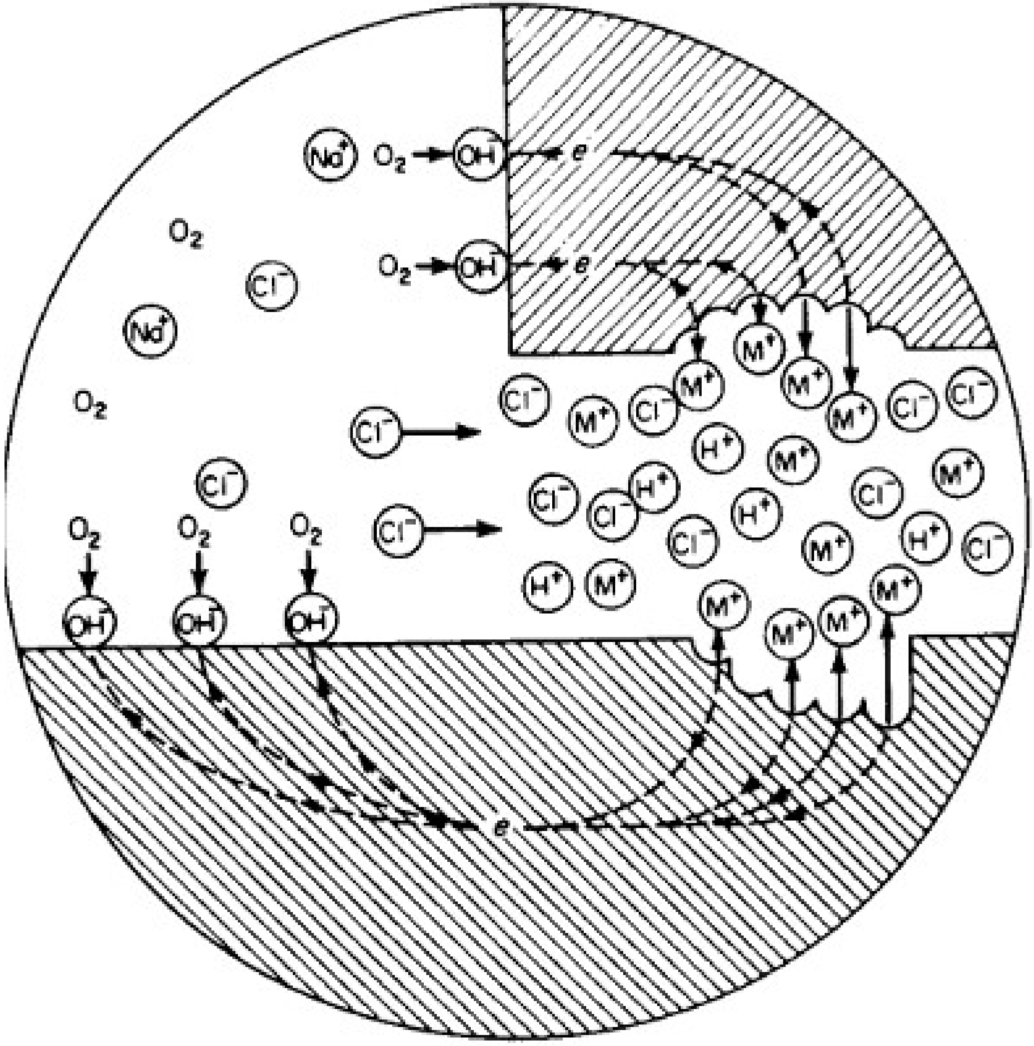


Figure 3-10 Crevice corrosion—later stage.

3-9 Combating Crevice Corrosion

Methods and procedures for combating or minimizing crevice corrosion are as follows:

1. Use welded butt joints instead of riveted or bolted joints in new equipment. Sound welds and complete penetration are necessary to avoid porosity and crevices on the inside (if welded only from one side).
2. Close crevices in existing lap joints by continuous welding, caulking, or soldering.
3. Design vessels for complete drainage; avoid sharp corners and stagnant areas. Complete draining facilitates washing and cleaning and tends to prevent solids from settling on the bottom of the vessel.
4. Inspect equipment and remove deposits frequently.
5. Remove solids in suspension early in the process or plant flow sheet, if possible.
6. Remove wet packing materials during long shutdowns.
7. Provide uniform environments, if possible, as in the case of backfilling a pipeline trench.
8. Use "solid," nonabsorbent gaskets, such as Teflon, wherever possible.
9. Weld instead of rolling in tubes in tube sheets.

3-10 Filiform Corrosion

Although not immediately apparent, *filiform corrosion* (filamentary corrosion occuring on metal surfaces) is a special type of crevice corrosion. In most instances it occurs under protective films, and for this reason it is often referred to as *underfilm corrosion*. This type of corrosion is quite common; the most frequent example is the attack of enameled or lacquered surfaces of food and beverage cans that have been exposed to the atmosphere. The red-brown corrosion filaments are readily visible.

Filiform corrosion has been observed on steel, magnesium, and aluminum surfaces covered by tin, silver, gold, phosphate, enamel, and lacquer coatings. It has also been observed on paper-backed aluminum foil, corrosion occuring at the paper-aluminum interface.

Filiform corrosion is an unusual type of attack, since it does not weaken or destroy metallic components but only affects surface appearance. Appearance is very important in food packaging, and this peculiar form of corrosion is a major problem in the canning industry. Although filiform attack on the exterior of a food can does not affect its contents, it does affect the sale of such cans.

Under transparent surface films, the attack appears as a network of corrosion product trails. The filaments consist of an active head and a red-brown corrosion product tail as illustrated in Fig. 3-11. The filaments are $\frac{1}{10}$ in. or less wide, and corrosion occurs only in the filament head. The blue-green color of the active head is the characteristic color of ferrous ions, and the red-brown coloration of the inactive tail is due to the presence of ferric oxide or hydrated ferric oxide.

Pitting Corrosion

❑ Local corrosion attack resulting from the formation of small anodes on a metal surface that produces holes or pits (extremely localized attack that results in holes the metal (relatively small)

❑ Pitting corrosion results in the formation of pinholes, pits and cavities in the metal. Pitting is, usually, the result of the breakdown or cracking of the protective film on the metal at specific points. This gives rise to the formation of small anodic and large cathodic areas.

❑ It is often difficult to detect pits because of their small size and because of the varying depths and numbers of pits that may occur under identical conditions.

Causes:

Concentration gradients in electrolyte cause some areas high in ion concentrations that accelerate oxidation

Prevention:

Weld – don't rivet

Use non-absorbing gaskets

Polish surfaces

Add drains – avoid stagnant water

Adjust composition; e.g., add Mo to SS

Autocatalytic nature of pitting

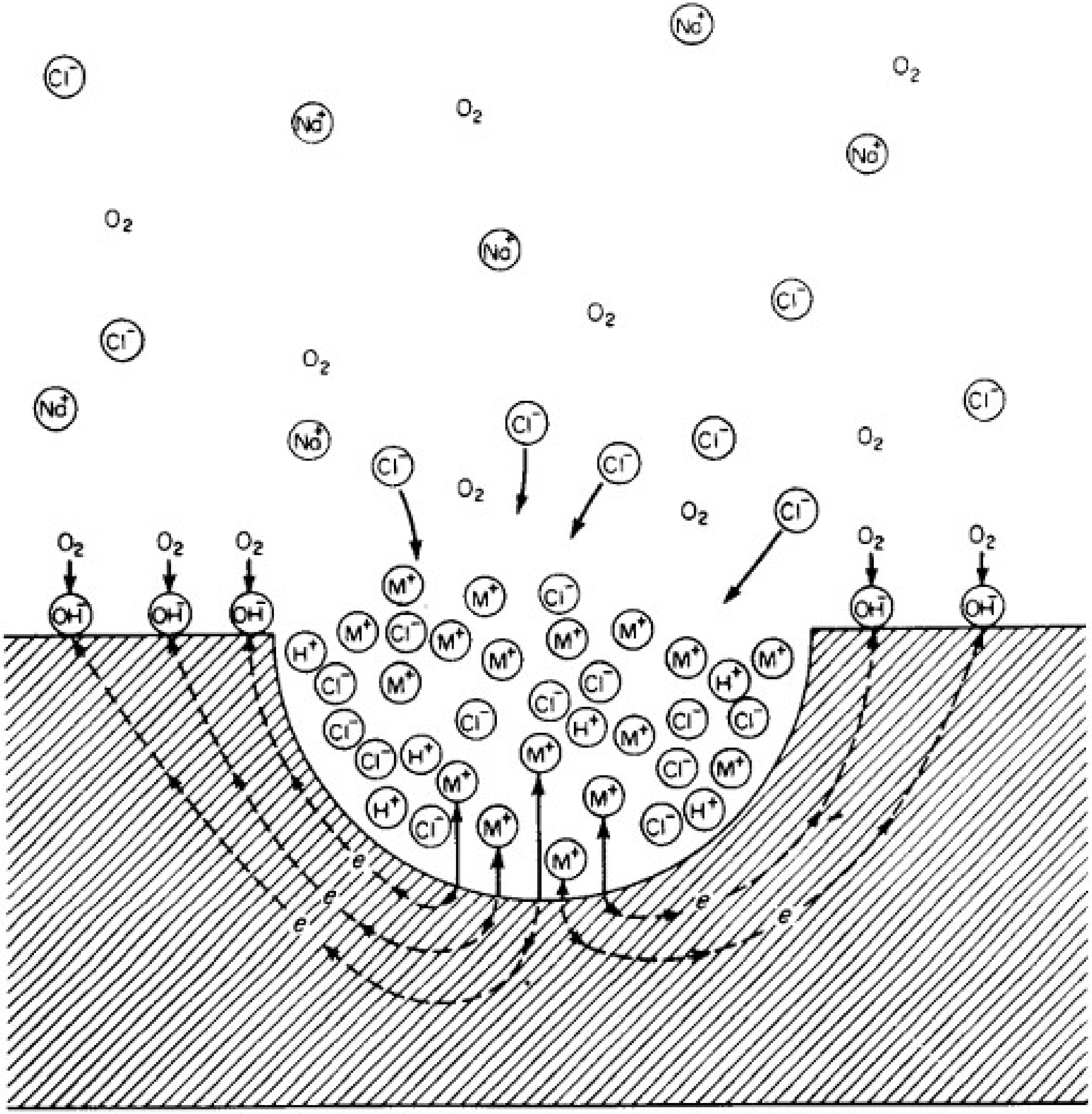
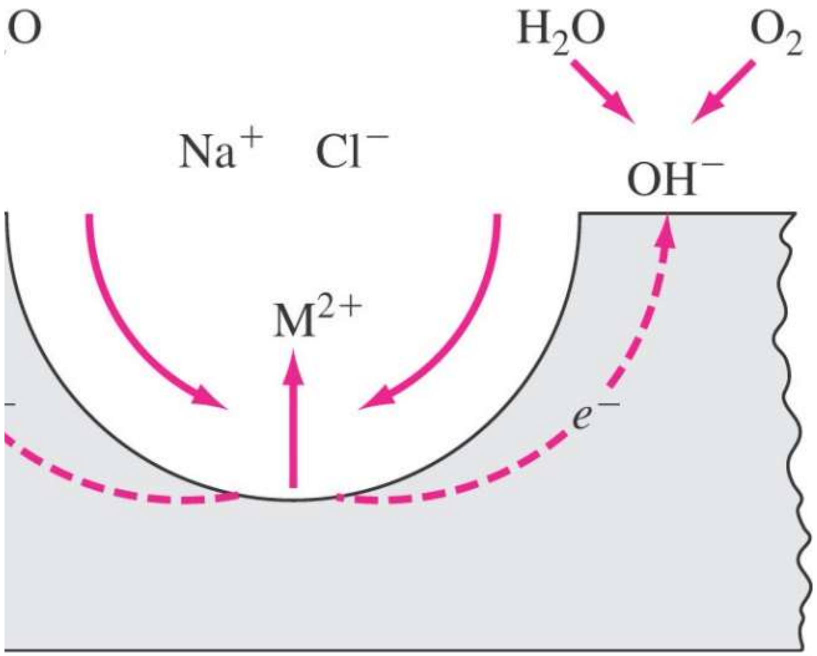
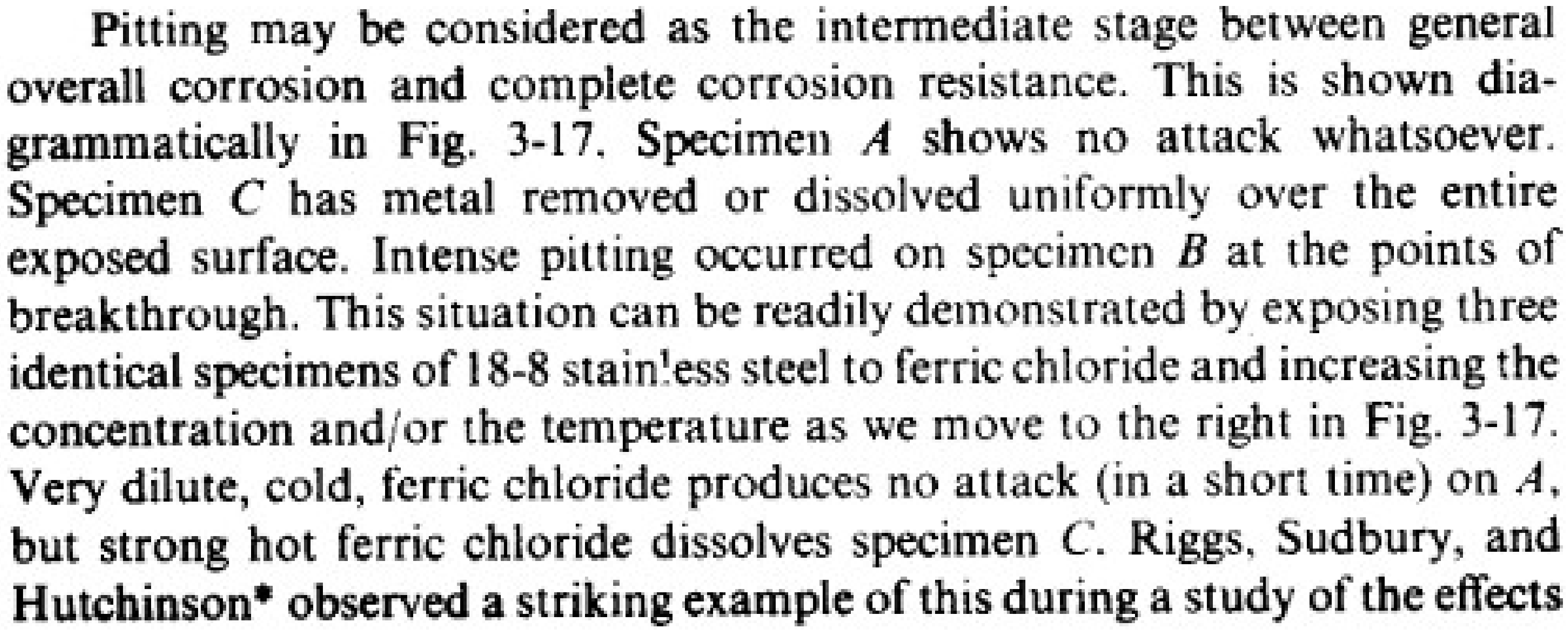
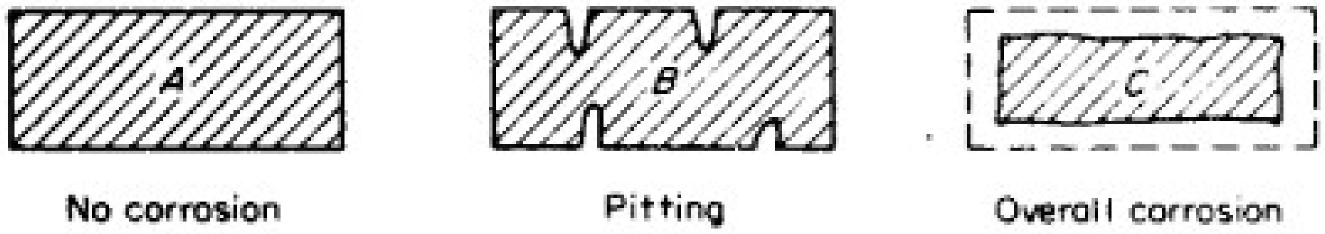


Figure 3-19 Autocatalytic processes occurring in a corrosion pit.





Pitting may be considered as the intermediate stage between general overall corrosion and complete corrosion resistance. This is shown diagrammatically in Fig. 3-17. Specimen *A* shows no attack whatsoever. Specimen *C* has metal removed or dissolved uniformly over the entire exposed surface. Intense pitting occurred on specimen *B* at the points of breakthrough. This situation can be readily demonstrated by exposing three identical specimens of 18-8 stainless steel to ferric chloride and increasing the concentration and/or the temperature as we move to the right in Fig. 3-17. Very dilute, cold, ferric chloride produces no attack (in a short time) on *A*, but strong hot ferric chloride dissolves specimen *C*. Riggs, Sudbury, and Hutchinson* observed a striking example of this during a study of the effects



No corrosion Pitting Overall corrosion

Figure 3-17 Diagrammatic representation of pitting corrosion as an intermediate stage.

This process is self stimulating and self propagating. Both hydrogen and chloride ions stimulate the dissolution of most metals and alloys and the entire process accelerates with time

Table 3-7 Effects of alloying on pitting resistance of stainless steel alloys

Element	Effect on pitting resistance
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Silicon	Decreases; increases when present with molybdenum
Titanium and columbium	Decreases resistance in $FeCl_3$; other mediums no effect
Sulfur and selenium	Decreases
Carbon	Decreases, especially in sensitized condition
Nitrogen	Increases

3-17 Prevention

The methods suggested for combating crevice corrosion generally apply also for pitting. Materials that show pitting, or tendencies to pit, during corrosion tests should not be used to build the plant or equipment under consideration. Some materials are more resistant to pitting than others. For example, the addition of 2% molybdenum to 18-8S (type 304) to produce 18-8SMo (type 316) results in a very large increase in resistance to pitting. The addition apparently results in a more protective or more stable passive surface. These two materials behave so differently that one is considered unsuitable for seawater service but the other is sometimes recommended. The best procedure is to use materials that are known not to pit in the environment under consideration. As a general guide, the following list of metals and alloys may be used as a qualitative guide to suitable materials. However, tests should be conducted before final selection is made.

Increasing pitting resistance ↓	
	Type 304 stainless steel
	Type 316 stainless steel
	Hastelloy F, Nionel, or Durimet 20
	Hastelloy C or Chlorimet 3
	Titanium

Adding inhibitors is sometimes helpful, but this may be a dangerous procedure unless attack is stopped *completely*. If it is not, the intensity of the pitting may be increased.*

INTERGRANULAR CORROSION

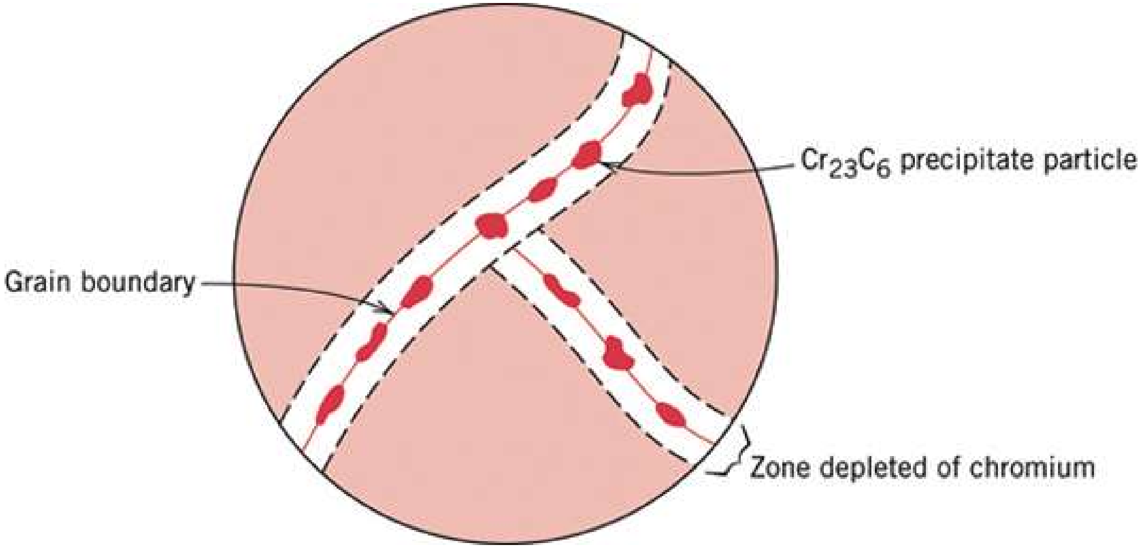
The more reactive nature of grain boundaries was discussed in Chap. 2. Grain boundary effects are of little or no consequence in most applications or uses of metals. If a metal corrodes, uniform attack results since grain boundaries are usually only slightly more reactive than the matrix. However, under certain conditions, grain interfaces are very reactive and intergranular corrosion results. Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains, is *intergranular corrosion*. The alloy disintegrates (grains fall out) and/or loses its strength.

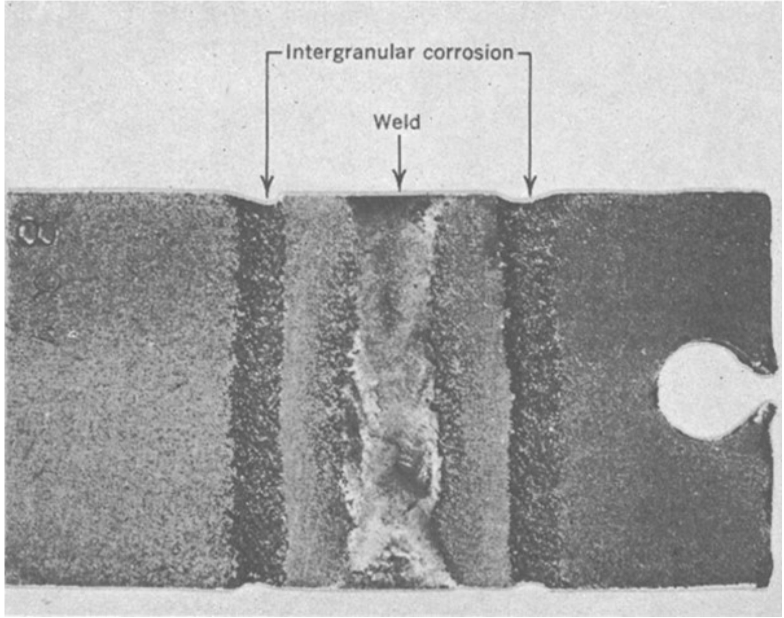
Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain-boundary areas. Small amounts of iron in aluminum, wherein the solubility of iron is low, have been shown to segregate in the grain boundaries and cause intergranular corrosion. It has been shown that based on surface tension considerations the zinc content of a brass is higher at the grain boundaries. Depletion of chromium in the grain-boundary regions results in intergranular corrosion of stainless steels.

Intergranular Corrosion

Occurs in specific alloys – precipitation of corrosive specimens along grain boundaries and in particular environments

E.g. : Chromium carbide forming in SS, leaving adjacent areas depleted in Cr



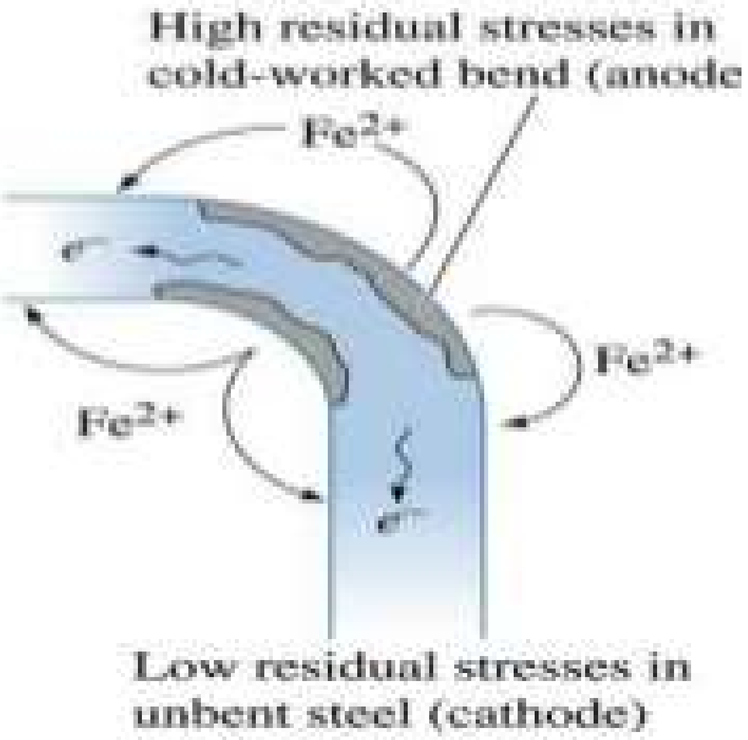


Solutions:

High temp heat treat to re-dissolve carbides

Lower carbon content (in SS) to minimize carbide formation.
Alloy with a material that has stronger carbide formation (e.g., Ti or Nb)

Stress Corrosion



- The metallic substances are subjected to uneven stresses during manufacturing operations such as bending, welding, pressing and hammering
- Parts have not been cooled properly (non-uniform cooling) during fabrication causes stress
- The areas which are more stressed become anode and corroded faster
- It occurs due to combined effect of tensile stress & corroding environment
- Ex: Brass undergoes stress corrosion in presence of ammonia

Cracks grow along grain boundaries as a result of residual or applied stress or trapped gas or solid corrosion products

Stress levels may be very low tensile stress and corrosive environments

cracks are initiated at corrosion areas

tensile stresses propagate the crack

corrosion further deteriorate crack

- e.g., brasses are sensitive to ammonia

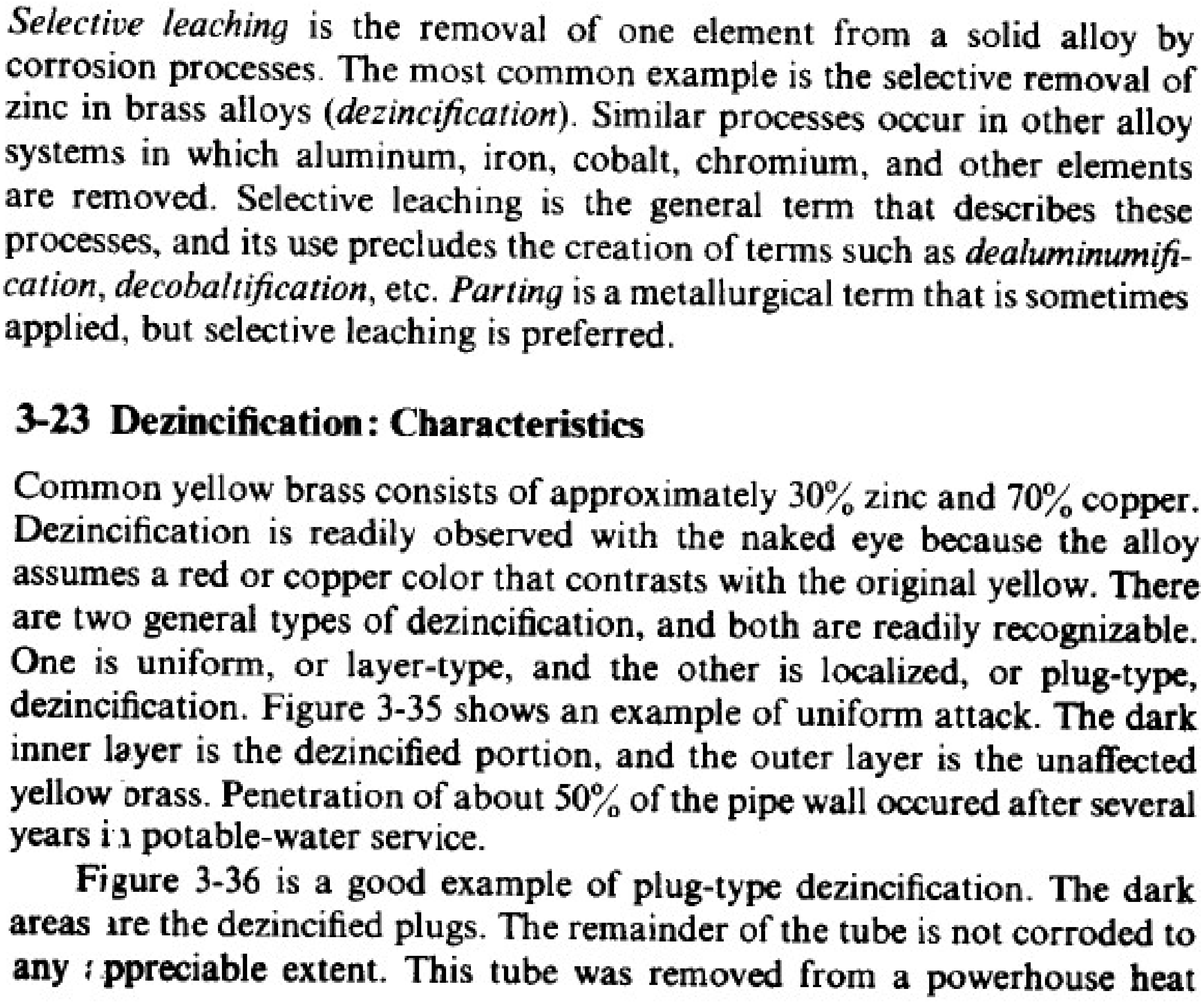
Solutions:

Reduce stress levels

Heat treatment

Atmosphere control

Selective Leaching



Selective leaching is the removal of one element from a solid alloy by corrosion processes. The most common example is the selective removal of zinc in brass alloys (*dezincification*). Similar processes occur in other alloy systems in which aluminum, iron, cobalt, chromium, and other elements are removed. Selective leaching is the general term that describes these processes, and its use precludes the creation of terms such as *dealuminumification*, *decobaltification*, etc. *Parting* is a metallurgical term that is sometimes applied, but selective leaching is preferred.

3-23 Dezincification: Characteristics

Common yellow brass consists of approximately 30% zinc and 70% copper. Dezincification is readily observed with the naked eye because the alloy assumes a red or copper color that contrasts with the original yellow. There are two general types of dezincification, and both are readily recognizable. One is uniform, or layer-type, and the other is localized, or plug-type, dezincification. Figure 3-35 shows an example of uniform attack. The dark inner layer is the dezincified portion, and the outer layer is the unaffected yellow brass. Penetration of about 50% of the pipe wall occured after several years in potable-water service.

Figure 3-36 is a good example of plug-type dezincification. The dark areas are the dezincified plugs. The remainder of the tube is not corroded to any appreciable extent. This tube was removed from a powerhouse heat

3-24 Dezincification: Mechanism

Two theories have been proposed for dezincification. One states that zinc is dissolved, leaving vacant sites in the brass lattice structure. This theory is not proven. A strong argument against it is that dezincification to appreciable depths would be impossible or extremely slow because of difficulty of diffusion of solution and ions through a labyrinth of small vacant sites.

The commonly accepted mechanism consists of three steps, as follows: (1) the brass dissolves, (2) the zinc ions stay in solution, and (3) the copper plates back on. Zinc is quite reactive, whereas copper is more noble. Zinc can corrode slowly in pure water by the cathodic ion reduction of H_2O into hydrogen gas and hydroxide ions. For this reason dezincification can proceed in the absence of oxygen. Oxygen also enters into the cathodic reaction and hence increases the rate of attack when it is present. Analyses of dezincified areas show 90 to 95% copper with some of it present as copper oxide. The amount of copper oxide is related to oxygen content of the environment. The porous nature of the deposit permits easy contact between the solution and the brass.

3-25 Dezincification: Prevention

Dezincification can be minimized by reducing the aggressiveness of the environment (i.e., oxygen removal) or by cathodic protection, but in most cases these methods are not economical. Usually a less susceptible alloy is used. For example, red brass (15% Zn) is almost immune.

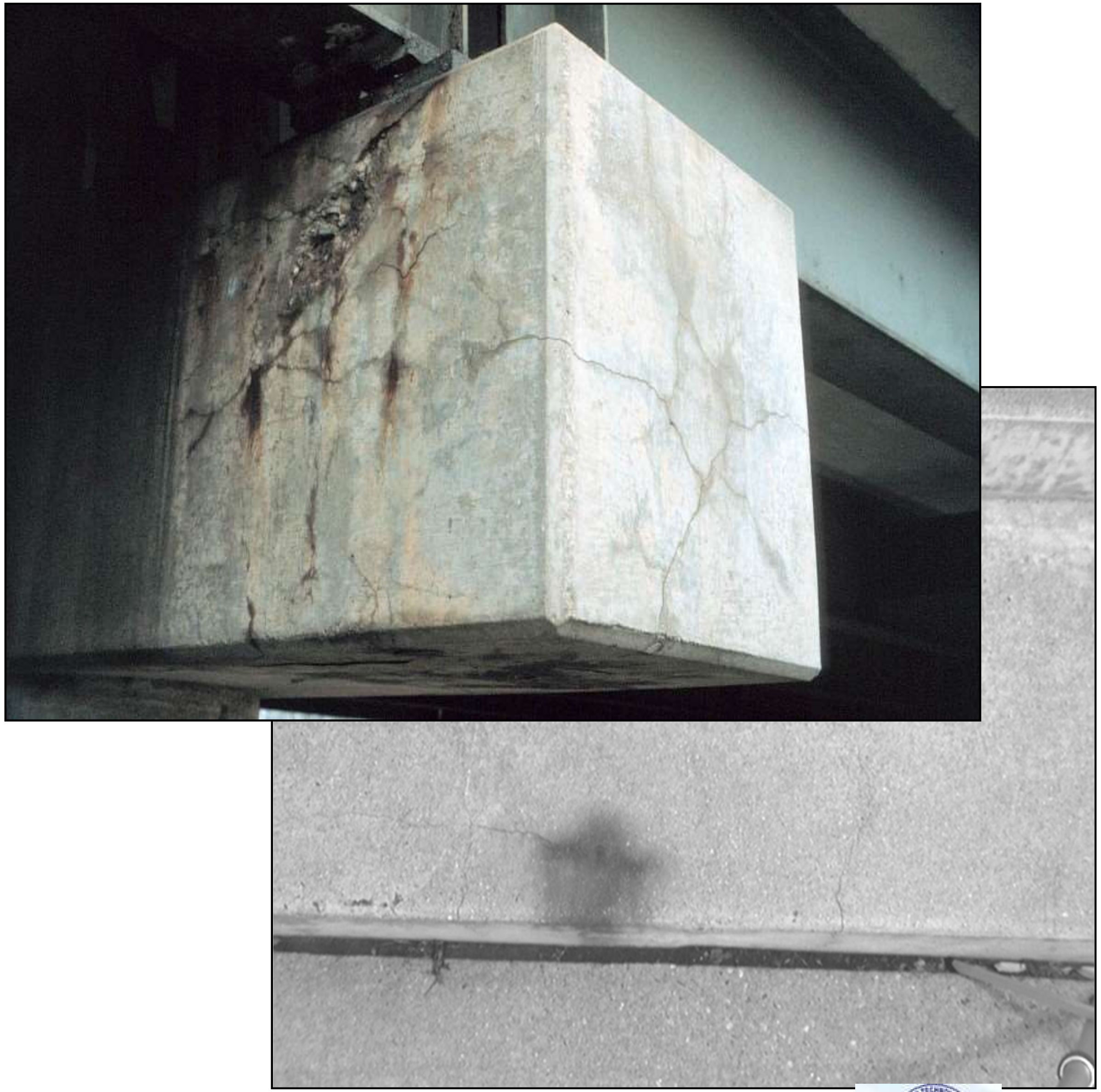
One of the first steps in the development of better brasses was the addition of 1% tin to a 70-30 brass (Admiralty Metal). Further improvement was obtained by adding small amounts of arsenic, antimony, or phosphorus as "inhibitors." For example, arsenical Admiralty Metal contains about 70% Cu, 29% Zn, 1% Sn, and 0.04% As. Apparently these inhibiting elements are redoposited on the alloy as a film and thereby hinder deposition of copper. Arsenic is also added to aluminum (2% Al) brasses.

For severely corrosive environments where dezincification occurs, or for critical parts, cupronickels (70–90% Cu, 30–10% Ni) are utilized.

3-26 Graphitization

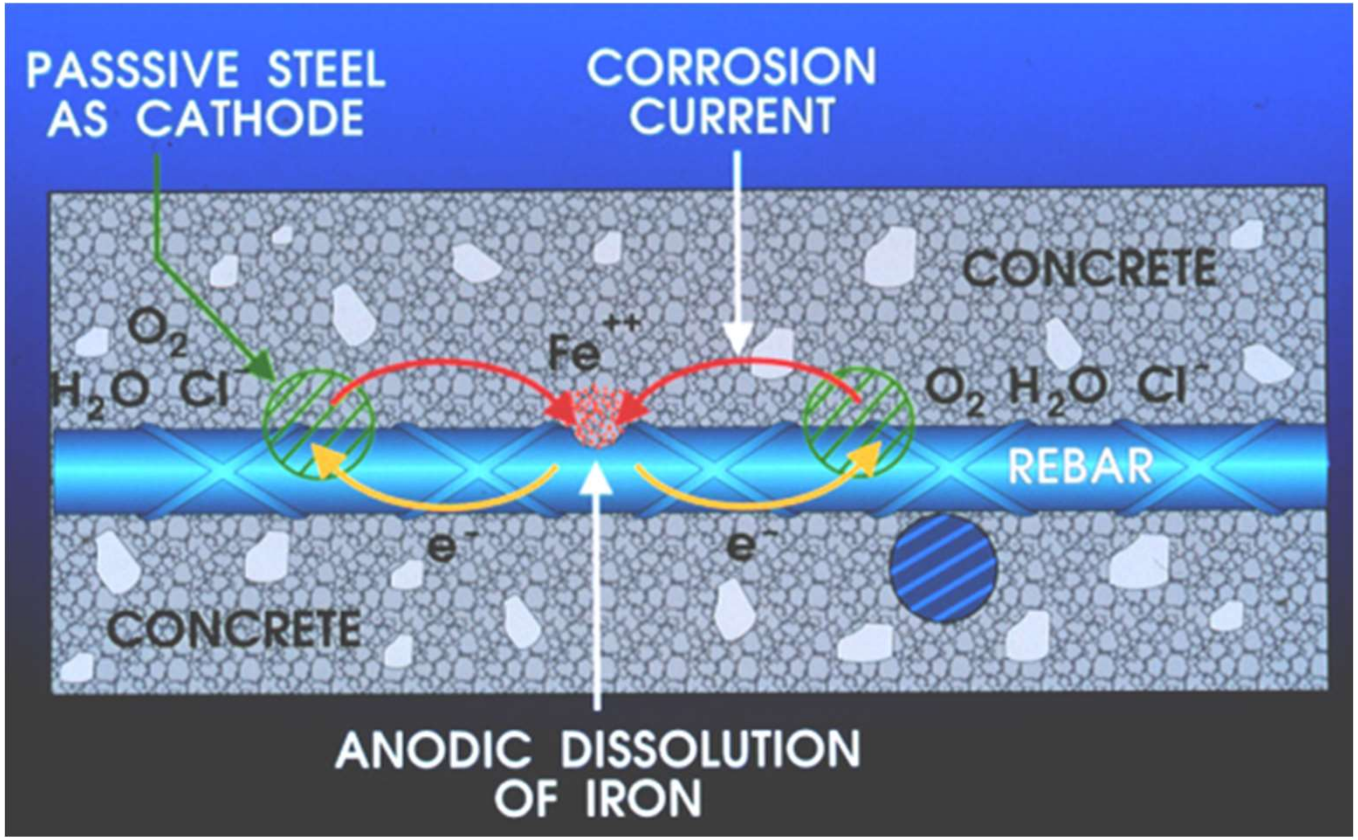
Gray cast iron sometimes shows the effects of selective leaching particularly in relatively mild environments. The cast iron appears to become "graphitized" in that the surface layer has the appearance of graphite and can be easily cut with a penknife. Based on this appearance and behavior, this phenomenon was christened "graphitization." This is a misnomer because the graphite is present in the gray iron before corrosion occurs. It is also called *graphitic corrosion*.

Reinforcement Corrosion



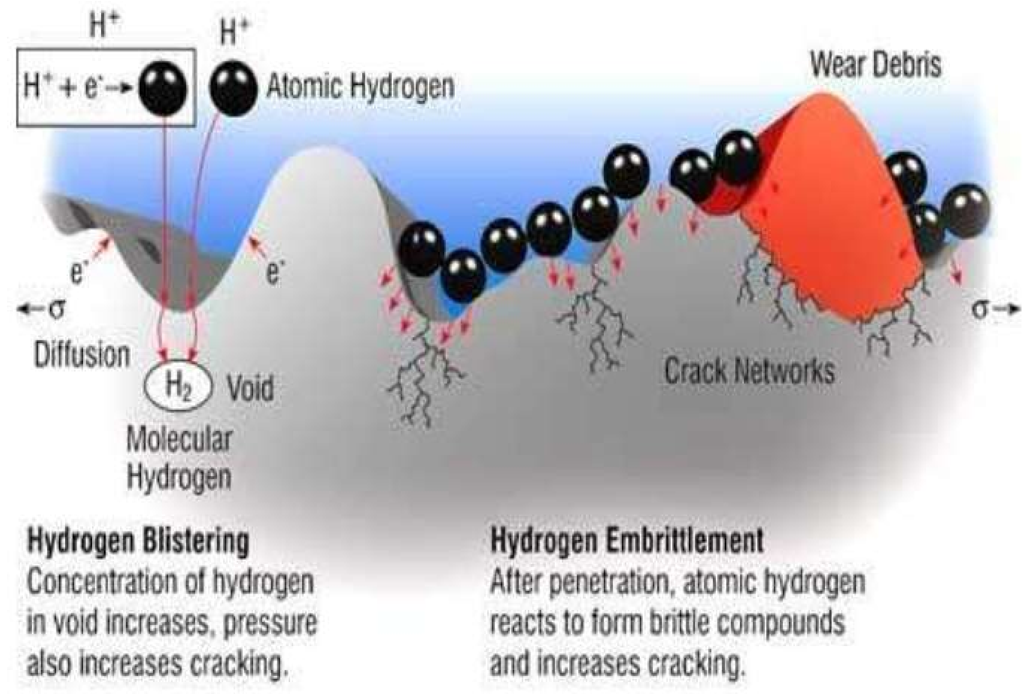
- Concrete is Normally Highly Alkaline
  - Protects Steel from Rusting if Properly Embedded
- If Corrosion Occurs, the Reaction Products are Greater in Volume Than the Original Steel

Corrosion Initiation and Rate Depends On amount of Concrete Cover, Quality of Concrete, Details of Construction, & Exposure to Chlorides

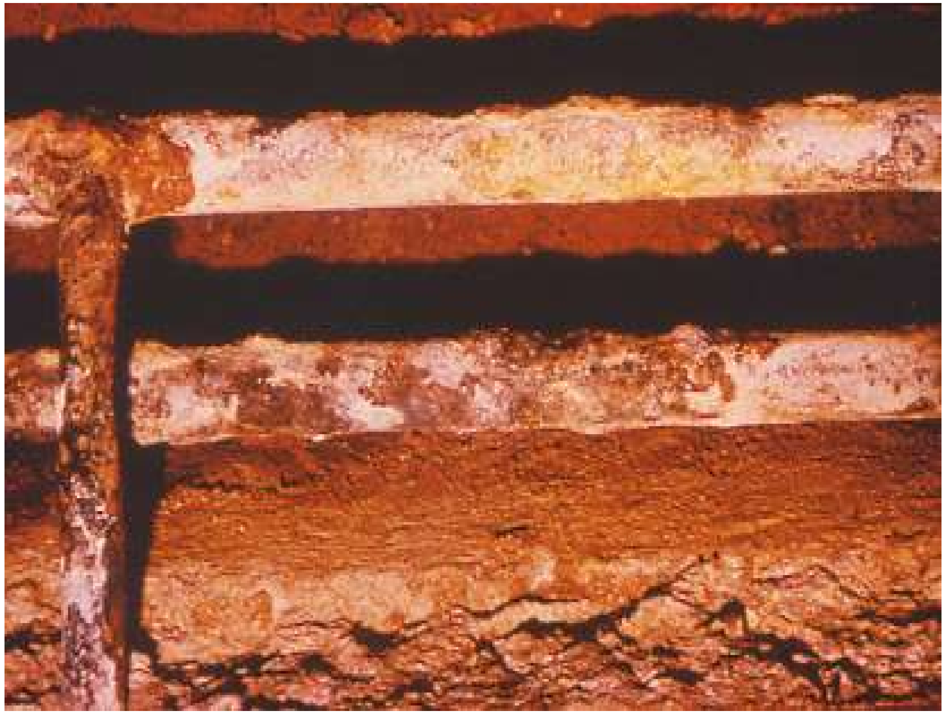


Hydrogen Embrittlement

- Metals loose strength when Hydrogen is absorbed through surface, especially along grain boundaries and dislocations
- Often occurs as a result of decorative plating
- High strength steels particularly susceptible
- Can be removed by "baking" the alloy



Underground corrosion



Buried gas or water supply pipes can suffer severe corrosion which is not detected until an actual leakage occurs, by which time considerable damage may be done.

Electronic components

In electronic equipment it is very important that there should be no raised resistance at low current connections. Corrosion products can cause such damage and can also have sufficient conductance to cause short circuits. These resistors form part of a radar installation.

“Corrosion” of Ship

Sea water is a highly corrosive electrolyte towards mild steel. This ship has suffered severe damage in the areas which are most buffeted by waves, where the protective coating of paint has been largely removed by mechanical action.

Stray currents are currents flowing from external sources. Any metallic structure, such as a buried pipeline represents a low resistant current path and is thus vulnerable to the effect of stray currents.

Stray-current effects are encountered in several impressed current cathodic protection systems. This is very common in industrial protected systems, such as oil production industries having innumerable buried pipe lines. Current leakage from auxiliary anodes associated with cathodic protection systems can enter unintentionally to a near-by unprotected structure and leave from the surfaces creating severe corrosion (see Fig. 19.1).

Stray Current Corrosion

If there is a current path due to a low resistance metallic object (for example, a pipe line or another metallic structure), current leakage from an impressed current protected system will enter such unprotected structure before returning to the protected object. Regions from where current leaves are susceptible to stray-current corrosion.

A solution to such a problem is through electrical bonding of the near-by structure. Simultaneously additional anodes and increasing DC power capacity can accord full protection to all structures in the vicinity. Properly insulated couplings can help reduce the problem (see Fig. 19.2).

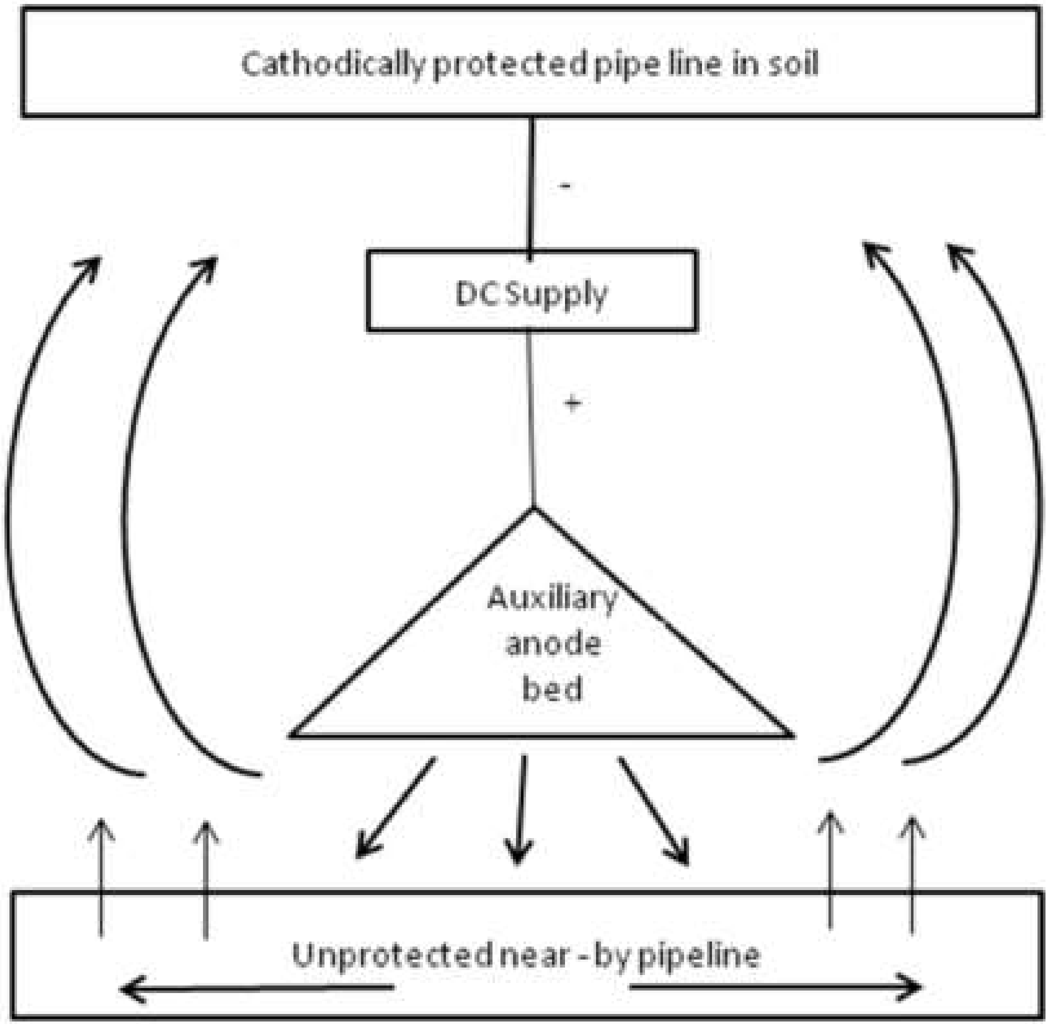


Fig 19.1 Stray current leakage from a cathodic protection system to a nearby pipeline.

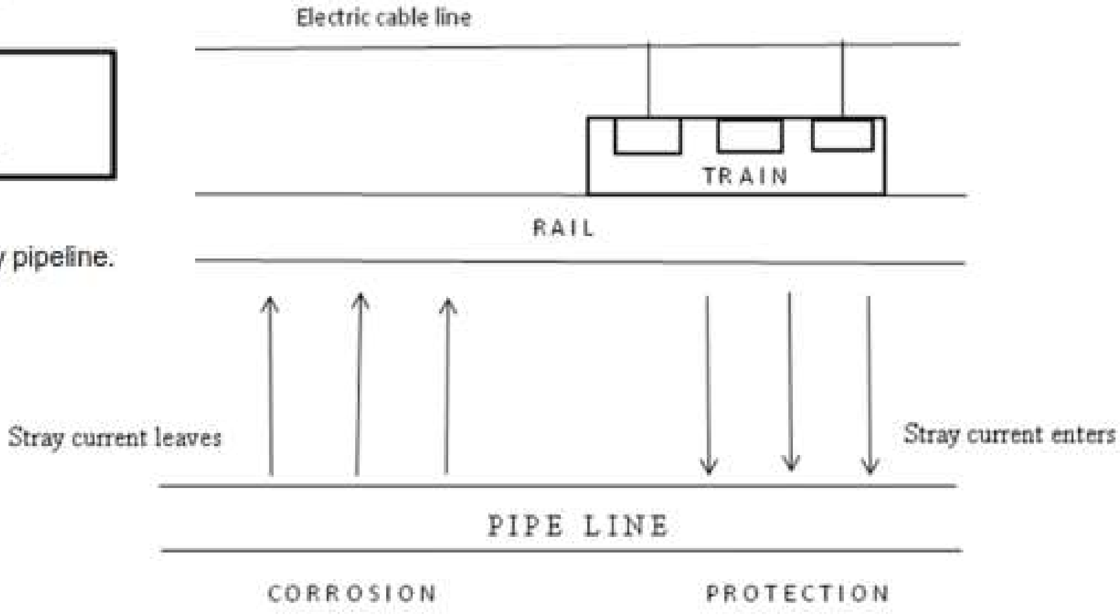


Fig 19.3 Stray current corrosion of a pipeline from a DC rail transit system.

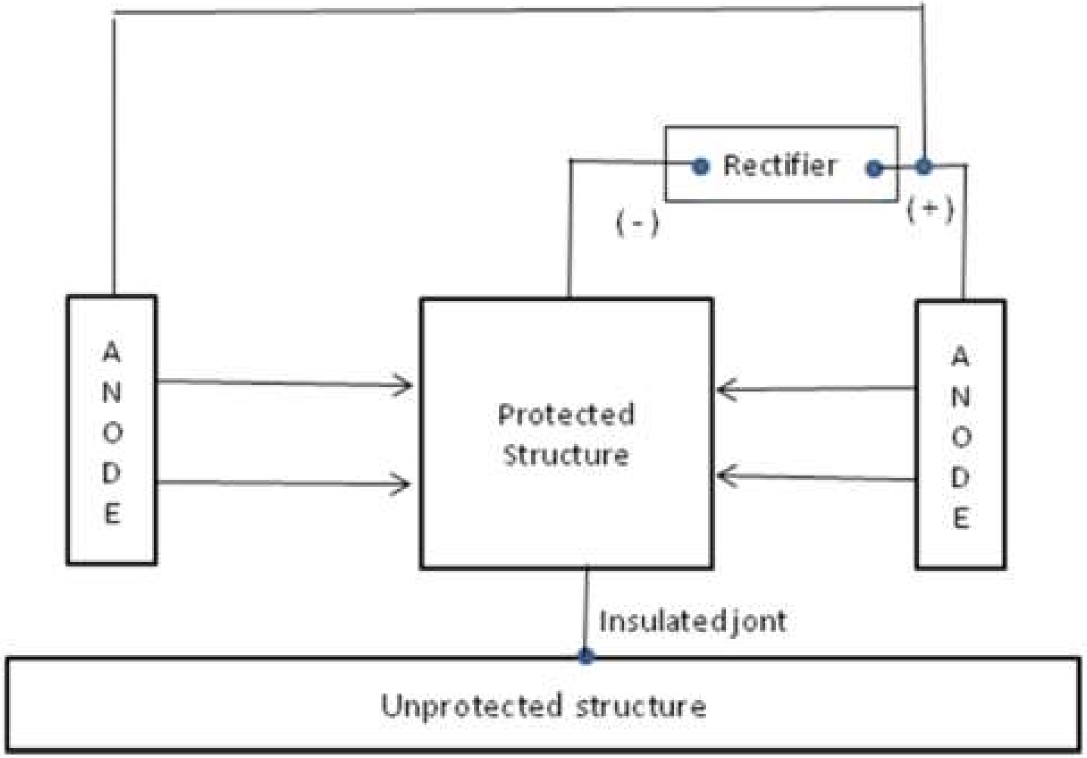


Fig 19.2 Proper design through additional anodes to prevent stray current corrosion.

Direct stray currents can cause anodic, cathodic or a combined interference. Anodic interference is generally found in close proximity to a buried anode. The pipeline will pick up current and will be discharged at a distance farther away from the anode. In the current pickup site, the potential of the pipe will shift in negative direction and is thus beneficial as cathodic protection. Sometimes, overprotection could be created by such potential shifts. On the other hand, cathodic interference is produced in close proximity to a polarized cathode; the potential shifting in a positive direction where current leaves the structure (causing corrosion damage). In combined interference, current pickup occurs close to anode and discharge occurs closer to cathodically polarized areas. The damage could be higher in this case since current pickup (overprotection) and discharge (corrosion) are both detrimental.

FORMS OF CORROSION

- Uniform Attack

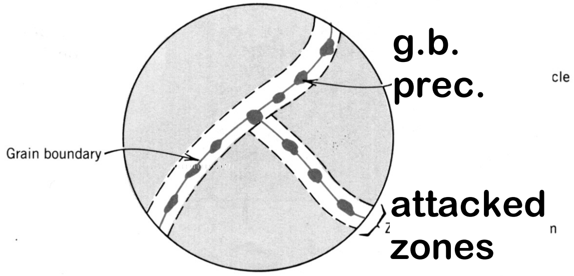
Oxidation & reduction occur uniformly over surface.

- Selective Leaching

Preferred corrosion of one element/constituent (e.g., Zn from brass (Cu-Zn)).

- Intergranular

Corrosion along grain boundaries, often where special phases exist.



- Stress corrosion

Stress & corrosion work together at crack tips.

Forms of corrosion

- Galvanic

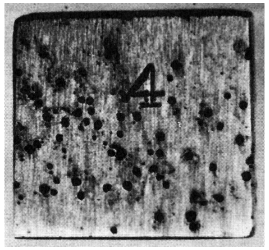
Dissimilar metals are physically joined. The more anodic one corrodes. Zn & Mg very anodic.

- Erosion-corrosion

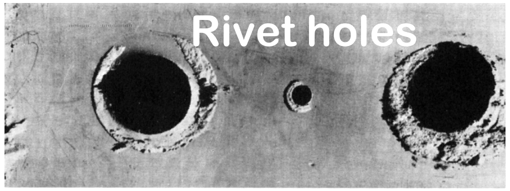
Break down of passivating layer by erosion (pipe elbows).

- Pitting

Downward propagation of small pits & holes.



- Crevice Between two pieces of the same metal.



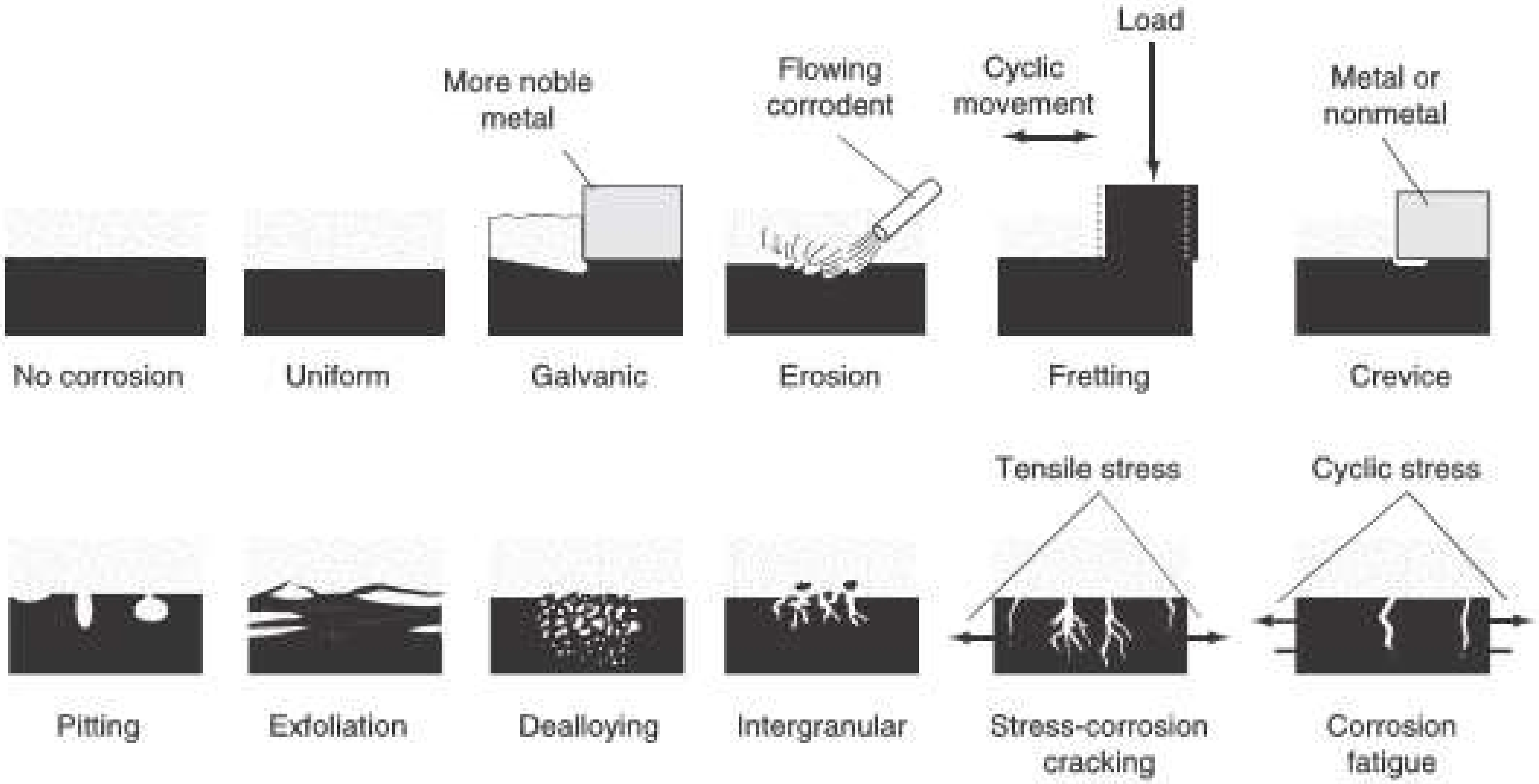


Fig. 2 Schematics of the common forms of corrosion

Stainless Steel

Highly reflective stainless steel 316L from Outokumpu helps to lend Anish Kapoor's Cloud Gate sculpture in Chicago's Millennium Park the appearance of mercury.

Alloying of Fe with Cr

- ❑ A protective Cr_2O_3 layer forms on the surface of Fe

  $$\sigma(Cr_2O_3) = 0.001\ \ \sigma(Fe_2O_3)$$

- ❑ Upto 10 % Cr alloyed steel is used in oil refinery components
- ❑ Cr > 12% → stainless steels → oxidation resistance upto 1000^oC

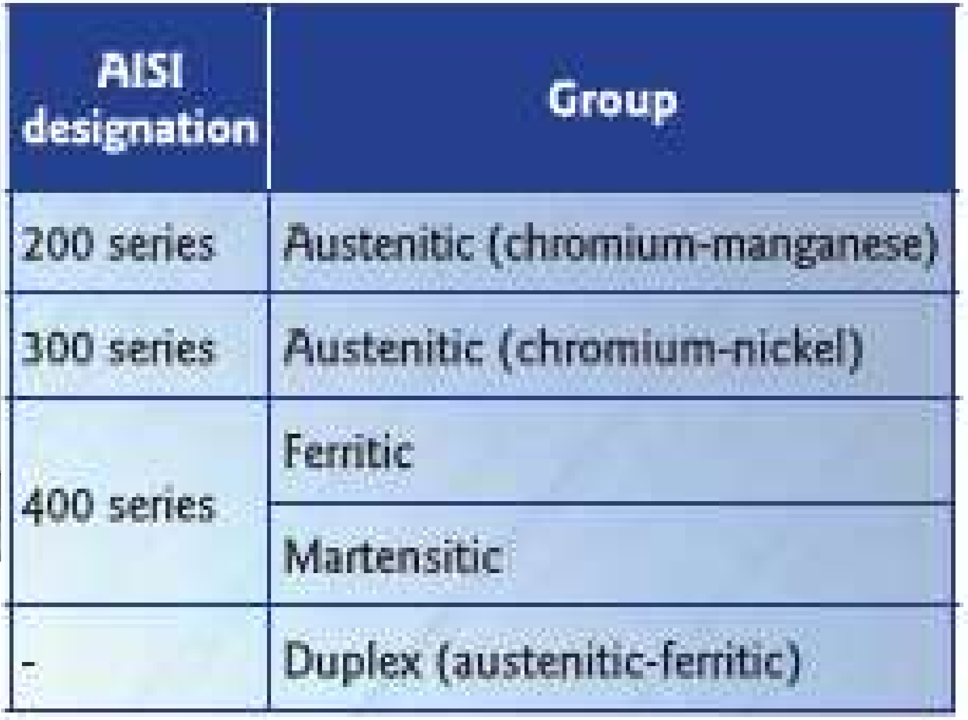
  → turbine blades, furnace parts, valves for IC engines
- ❑ Cr > 17% → oxidation resistance above 1000^oC
- ❑ 18-8 stainless steel (18%Cr, 8%Ni) → excellent corrosion resistance
- ❑ Kanthal (24% Cr, 5.5%Al, 2%Co) → furnace windings (1300^oC)

Other oxidation resistant alloys

- ❑ Nichrome (80%Ni, 20%Cr) → excellent oxidation resistance
- ❑ Inconel (76%Ni, 16%Cr, 7%Fe)

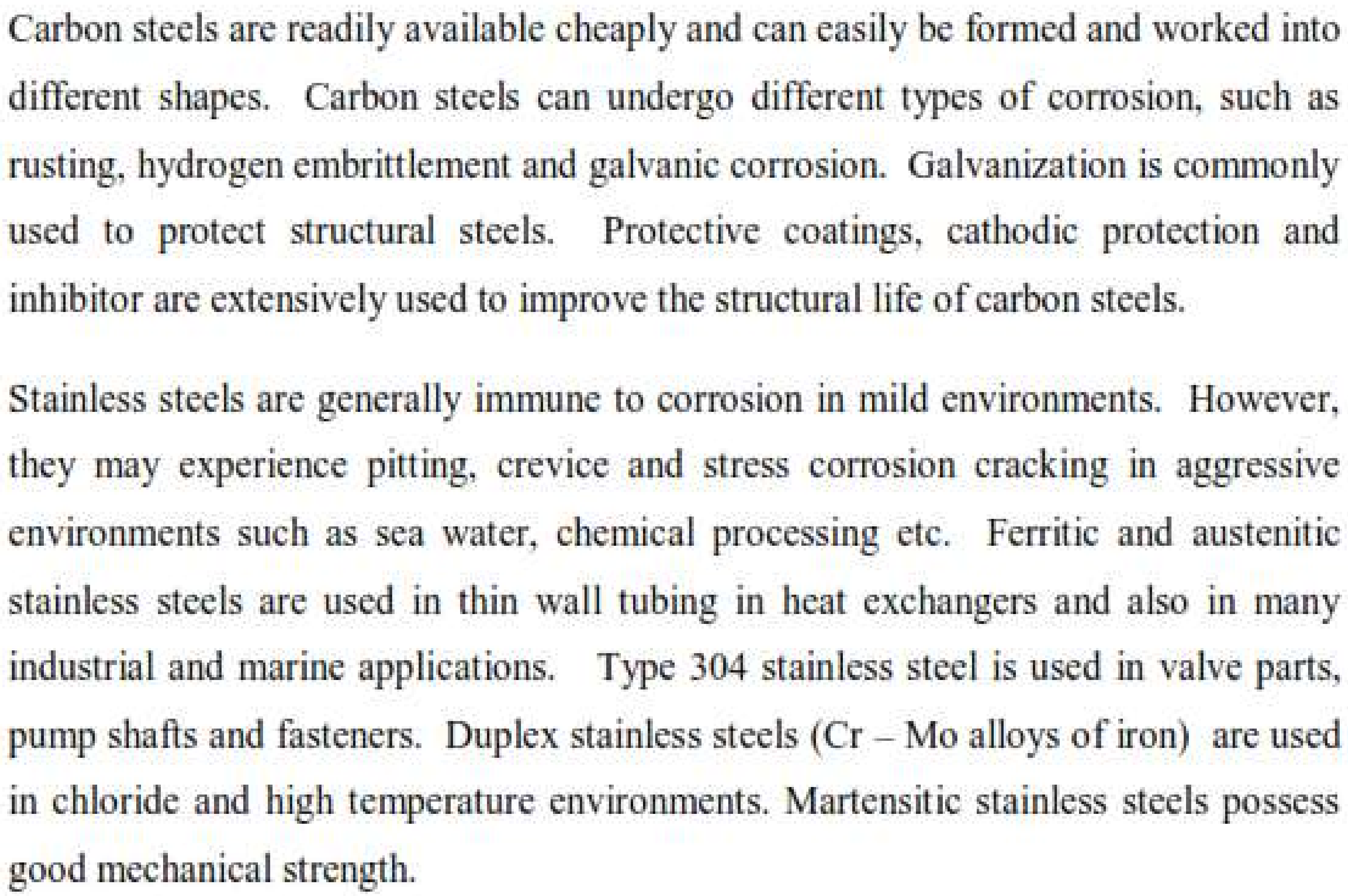
Iron (Fe) and 10.5% Chromium (Cr) combination is called Stainless Steel. Ni, Mo, Mn, Cu, Ti, N, etc were also added to get different properties. More than 100 verities of Steel are available.

Inconel alloy 625 is suitable for seawater applications because of its excellent corrosion resistance and resistance to chloride-ion stress-corrosion cracking. Depicted here, a shell and tube heat exchanger in alloy 625. Photo: Titan.



AISI designation	Group
200 series	Austenitic (chromium-manganese)
300 series	Austenitic (chromium-nickel)
400 series	Ferritic
	Martensitic
-	Duplex (austenitic-ferritic)

(American Iron and Steel Institute)



Carbon steels are readily available cheaply and can easily be formed and worked into different shapes. Carbon steels can undergo different types of corrosion, such as rusting, hydrogen embrittlement and galvanic corrosion. Galvanization is commonly used to protect structural steels. Protective coatings, cathodic protection and inhibitor are extensively used to improve the structural life of carbon steels.

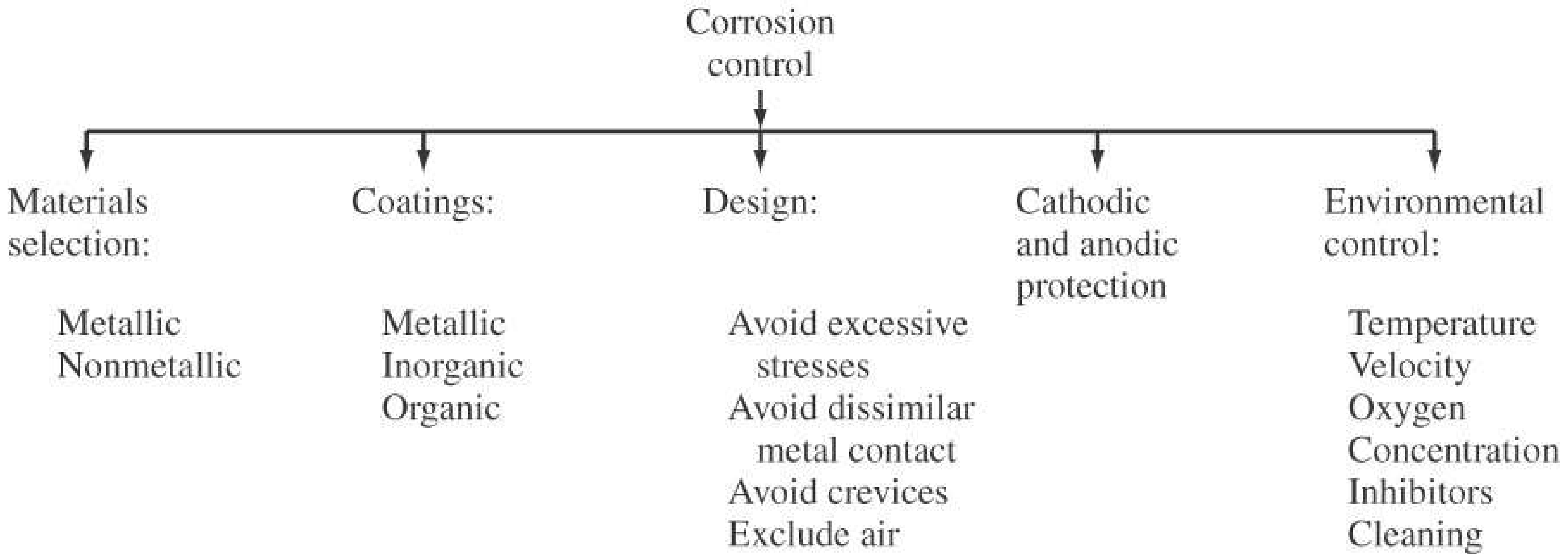
Stainless steels are generally immune to corrosion in mild environments. However, they may experience pitting, crevice and stress corrosion cracking in aggressive environments such as sea water, chemical processing etc. Ferritic and austenitic stainless steels are used in thin wall tubing in heat exchangers and also in many industrial and marine applications. Type 304 stainless steel is used in valve parts, pump shafts and fasteners. Duplex stainless steels (Cr – Mo alloys of iron) are used in chloride and high temperature environments. Martensitic stainless steels possess good mechanical strength.

Stainless Steel is badly attacked in hours by Polythionic Acid

Corrosion Control

There are no of methods to control corrosion.

- **Material Selection**
- **Design**
- **Protective Coatings**
- **Inhibitors and environmental alterations**
- **Corrosion allowances**



Corrosion control

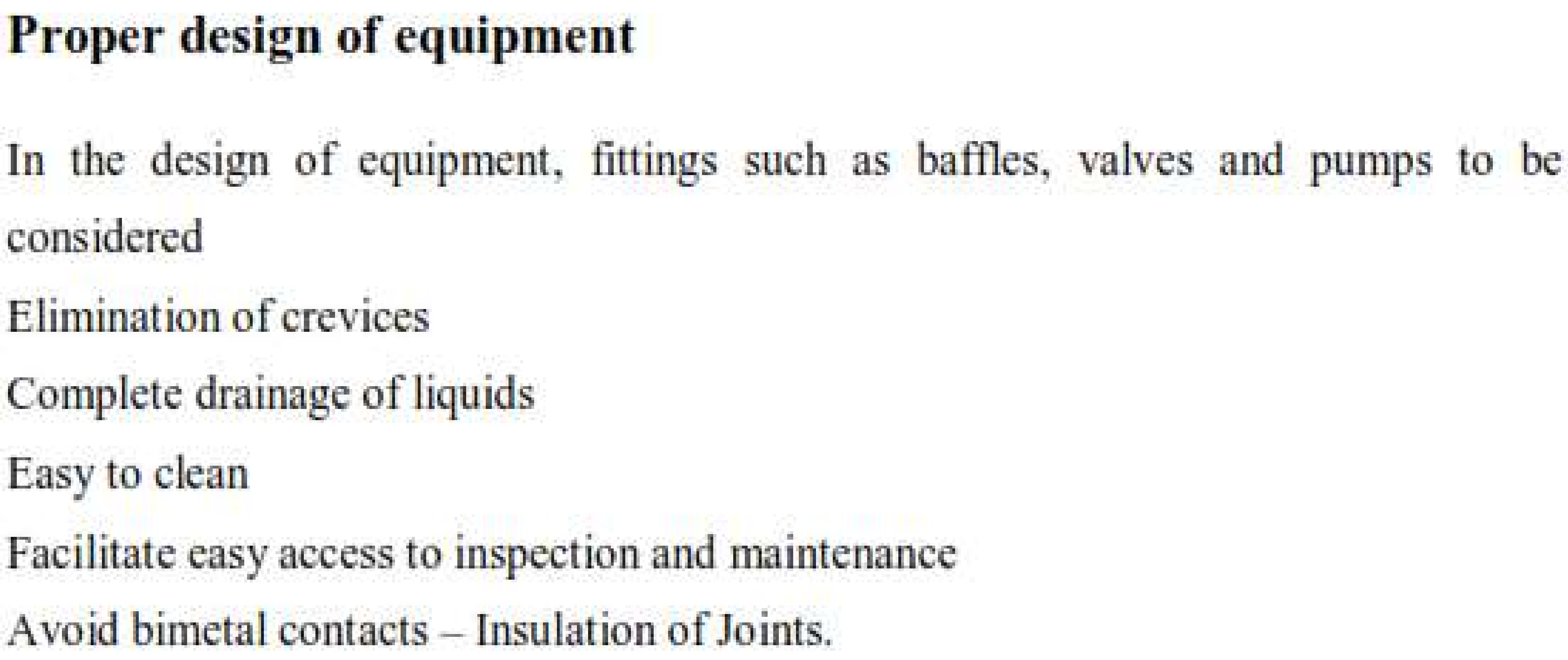
Materials selection:
- Metallic
- Nonmetallic

Coatings:
- Metallic
- Inorganic
- Organic

Design:
- Avoid excessive stresses
- Avoid dissimilar metal contact
- Avoid crevices
- Exclude air

Cathodic and anodic protection

Environmental control:
- Temperature
- Velocity
- Oxygen
- Concentration
- Inhibitors
- Cleaning



Proper design of equipment

In the design of equipment, fittings such as baffles, valves and pumps to be considered

Elimination of crevices

Complete drainage of liquids

Easy to clean

Facilitate easy access to inspection and maintenance

Avoid bimetal contacts – Insulation of Joints.

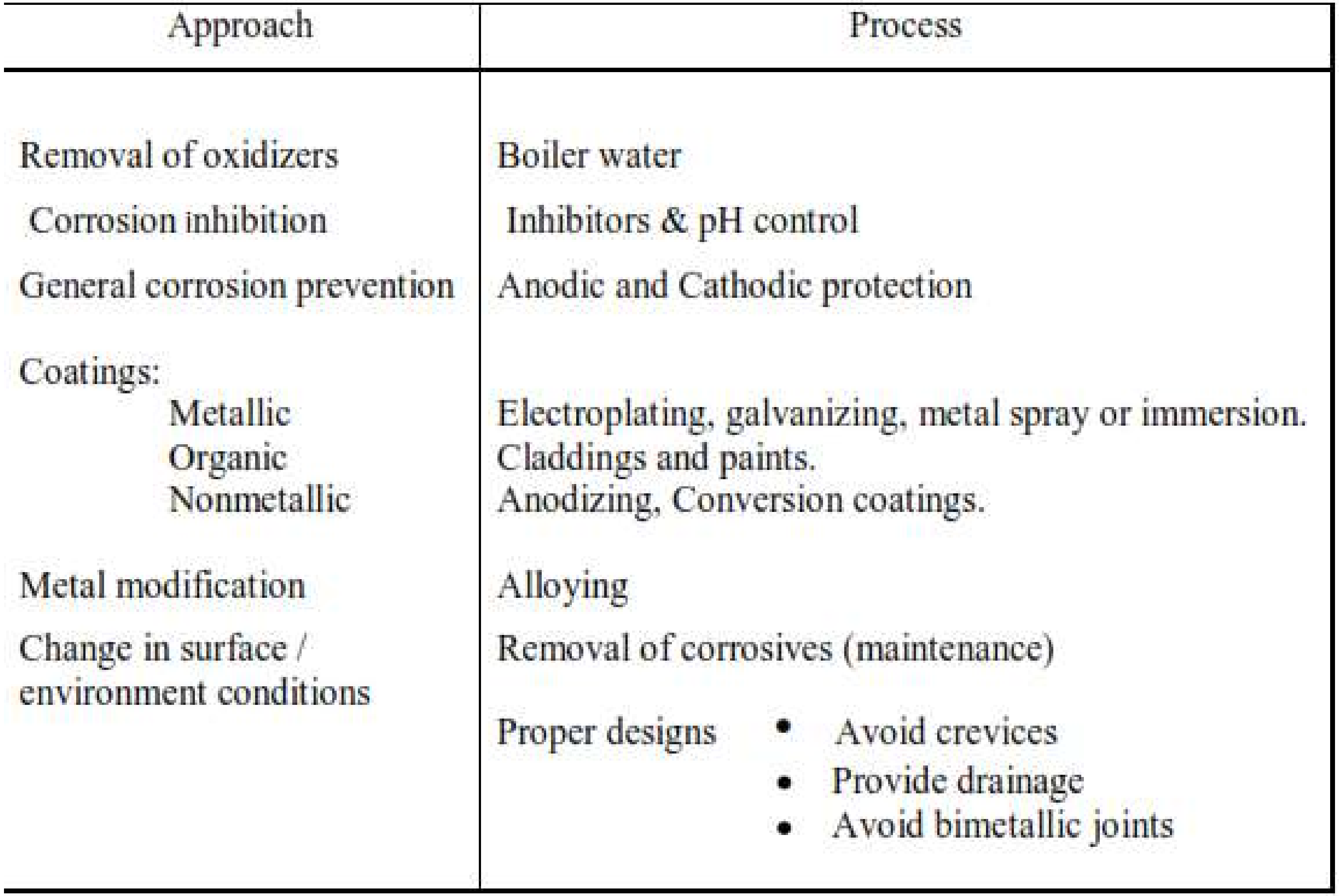
Proper selection of materials and good design reduce costs of corrosion

General choice of metals and alloys for corrosive applications is given in Table 14.1.

Table 14.1 Choice of materials for corrosive environments

Material	Environment
Nickel and alloys	Caustic solutions
Monel	Hydrofluoric acid
Hastelloys	Hot hydrochloric acid
Stainless steels	Nitric acid
Lead	Dil. sulfuric acid
Tin	Water
Titanium	Hot strong oxidizing acids/liquids

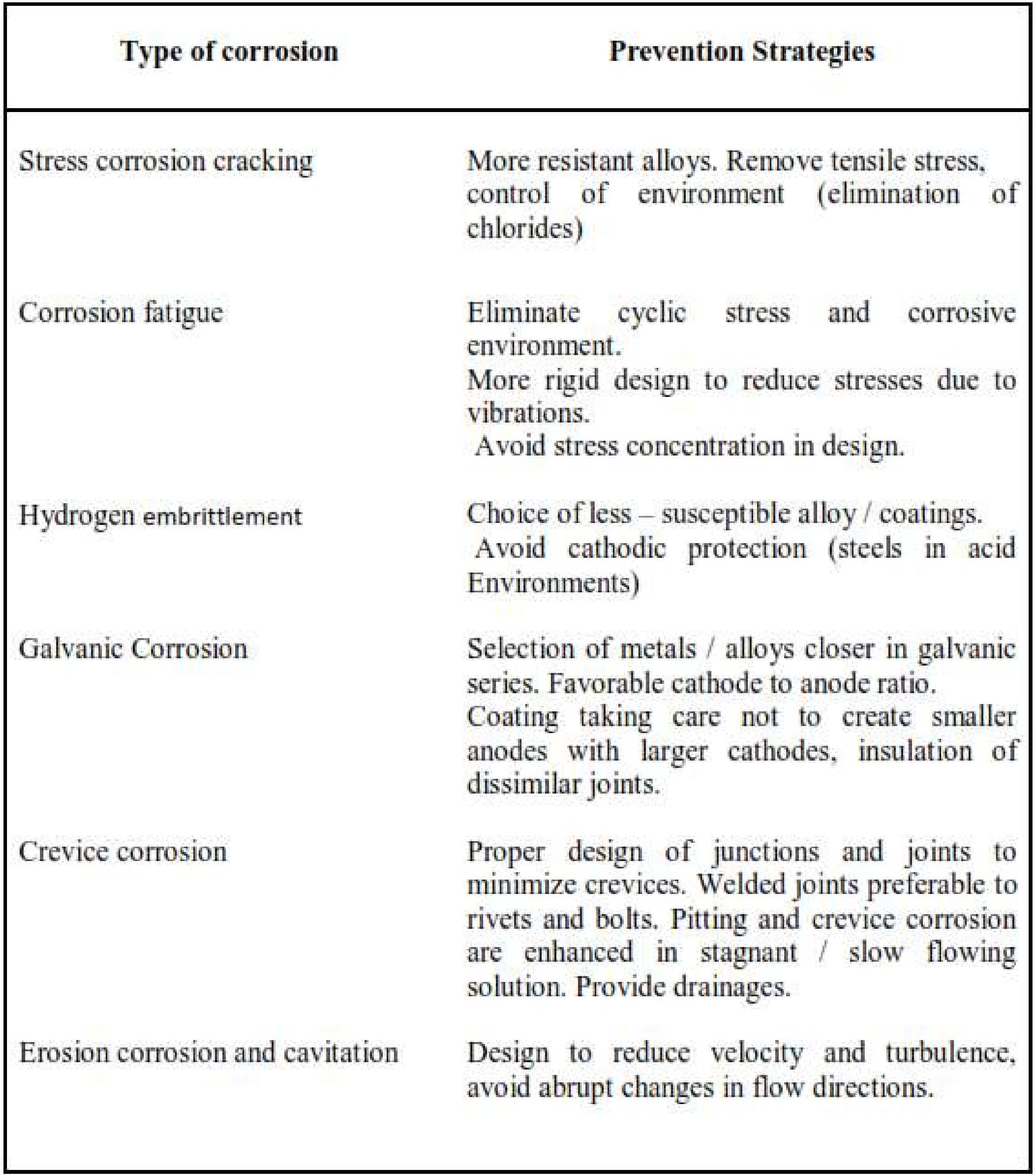
General rules for metallic selection



Approach	Process
Removal of oxidizers	Boiler water
Corrosion inhibition	Inhibitors & pH control
General corrosion prevention	Anodic and Cathodic protection
Coatings:	
Metallic	Electroplating, galvanizing, metal spray or immersion.
Organic	Claddings and paints.
Nonmetallic	Anodizing, Conversion coatings.
Metal modification	Alloying
Change in surface / environment conditions	Removal of corrosives (maintenance)
	Proper designs • Avoid crevices • Provide drainage • Avoid bimetallic joints

1. For reducing or, non-oxidizing conditions such as air-free acids & aqueous solutions, Ni & Cu alloy are often used.
2. For oxidizing conditions, Cr containing alloy are used.
3. For extremely powerful oxidizing conditions, Ti & its alloy are commonly used.

Table 14.3 Corrosion types with prevention strategies



Type of corrosion	Prevention Strategies
Stress corrosion cracking	More resistant alloys. Remove tensile stress, control of environment (elimination of chlorides)
Corrosion fatigue	Eliminate cyclic stress and corrosive environment. More rigid design to reduce stresses due to vibrations. Avoid stress concentration in design.
Hydrogen embrittlement	Choice of less – susceptible alloy / coatings. Avoid cathodic protection (steels in acid Environments)
Galvanic Corrosion	Selection of metals / alloys closer in galvanic series. Favorable cathode to anode ratio. Coating taking care not to create smaller anodes with larger cathodes, insulation of dissimilar joints.
Crevice corrosion	Proper design of junctions and joints to minimize crevices. Welded joints preferable to rivets and bolts. Pitting and crevice corrosion are enhanced in stagnant / slow flowing solution. Provide drainages.
Erosion corrosion and cavitation	Design to reduce velocity and turbulence, avoid abrupt changes in flow directions.

Coatings

- Barrier between corrosive environment and metal.
- Coatings may serve as sacrificial anodes (zinc on steels) or release substances that resist corrosion.
- Metal coatings - Noble coat - Silver, copper, nickel, chromium, tin, lead on steels (ensure pore - free, uniform, adherent coating; favorable anode / cathode ratio to minimise galvanic attacks).

  Sacrificial coatings – Zinc, aluminium, cadmium on steels. (steel is cathodic to plated metal).

Coatings can be applied through hot dipping, hot spraying, electroplating, electro-less plating, vapour deposition and metal cladding.

Aluminium, stainless steel, titanium, platinum etc can be cladded on various metallic substrate for enhanced corrosion protection (physical or chemical).

Other types of surface treatments.

Modification of substrates through ion implantation and laser processing.

Inorganic coatings: glass, cement, ceramic and chemical conversion coatings.

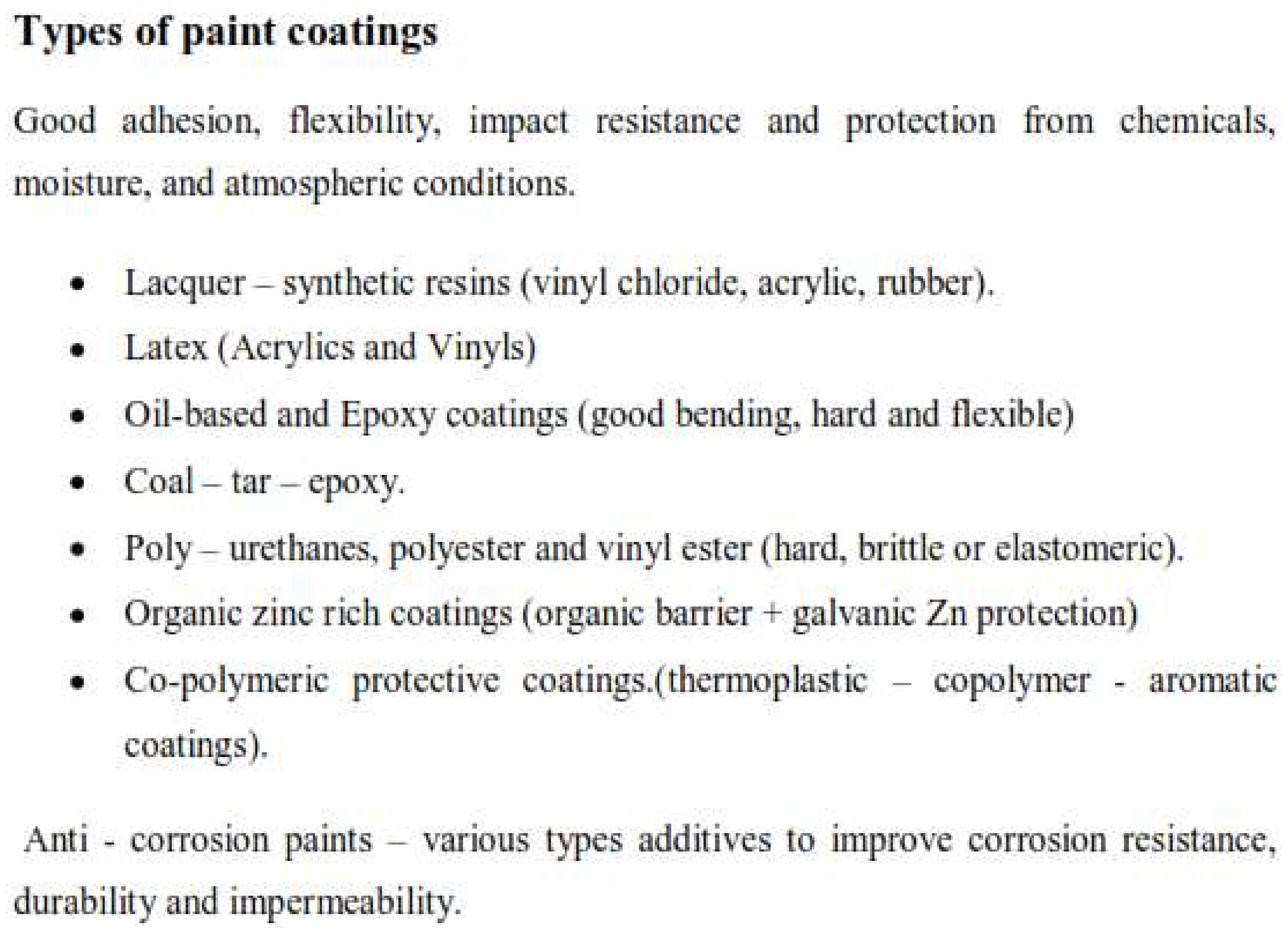
Chemical conversion: Anodizing, oxide, chromate, phosphatizing.

Organic coatings: Paints, lacquers, varnishes (Resin, solvent + pigment in the coating liquid). High performance organic coatings used in petroleum industries.

Development of corrosion – resistant synthetic resins.

❑ Metallic, inorganic, & organic coatings are applied to metals to prevent or reduce corrosion

- Metallic coating eg.; Zinc coating on steel (sacrificial anode)
- Inorganic coating (ceramics & glass) eg.; Glass-lined steel vessels
- Organic coating eg.; paints, varnishes & lacquers



Types of paint coatings

Good adhesion, flexibility, impact resistance and protection from chemicals, moisture, and atmospheric conditions.

- Lacquer – synthetic resins (vinyl chloride, acrylic, rubber).
- Latex (Acrylics and Vinyls)
- Oil-based and Epoxy coatings (good bending, hard and flexible)
- Coal – tar – epoxy.
- Poly – urethanes, polyester and vinyl ester (hard, brittle or elastomeric).
- Organic zinc rich coatings (organic barrier + galvanic Zn protection)
- Co-polymeric protective coatings.(thermoplastic – copolymer - aromatic coatings).

Anti - corrosion paints – various types additives to improve corrosion resistance, durability and impermeability.

A. Metallic coating

The structure is coated with a layer of other metal which may be more noble than the structure or less noble than it e.g. steel structures can be coated with copper which is more noble than steel or zinc which is less noble. In case of coating the structure with a more noble metal care should be taken that the coat is free from pores or cracks to avoid the formation of dissimilar metal corrosion cells which would lead to corrosion of the structure.

Factors that must be considered in selection of a coating metal:

1. The coating should be able to resist direct attack of the environment.
2. The coating should be nonporous and continuous (no cracks) to a void acceleration of corrosion especially in case of a more noble metal (ex: coating of Fe by Cu).
3. The coating should be hard.

In case of coating the structure with a less noble metal the presence of pores and cracks in the coat is not dangerous because in this case the less noble metal will corrode by the formation of dissimilar metal cells while the structure will remain protected.

(1) Electroplating

- Electroplating is the method of coating one metal with another. It is most commonly used for decorative purposes, appearance and protection.
- Electroplated items include chrome bumpers, jewelry, electronics, circuit boards and airplane parts.

Electroplating procedure

1. Preparation of the workpiece. Solutions such as alkaline cleaners, solvent degreasers or acidic pickling mixtures are used to remove dirt, greases, oxidation and contaminants from the piece.
2. The piece to be plated is connected to the negative pole (cathode) of the d. c. power supply while the plating (coating) metal anode is connected to the positive pole (anode). Multi-range ammeter (in series) and voltmeter (in parallel) are connected to the cell to measure the cell current and voltage.
3. The piece is then immersed in the plating solution until coated and rinsed and then buffed or polished, if necessary.

Non-metallic coating (the second method of surface coating)

There are two types of nonmetallic coating:

A. Inorganic coating

Methods of inorganic coating:

i. Oxidation (passivation)

Steel can be coated with an oxide film by a). Heating at high temperature, b). Chemical oxidation by treating steel with hot alkaline nitrate, or persulphate or perchlorate c). Anodic oxidation by making the steel structure an anode in electrolytic cell

ii. Phosphating

Steel is coated with a layer of iron phosphate by dipping in a solution containing phosphoric acid and zinc phosphate. The iron phosphate film is not highly protective because it is porous so it usually covered with paint. The phosphate film improves the bond between the metal and the paint.

i.e. Phosphating is a pre-painting step.

iii. Enamels

Enamels are glassy layer applied to the metal by dipping it in a suspension of powdered glass, and then the metal is heated in a stove (furnace) at high temperature where the glass powder melts and coat the metal.

iv. Cement coating

It is used to coat the inner side of steel pipelines carrying water or wastewater.

B. Organic coating such as the following:

i. Paints:

Paint consists of;

1. a film forming substance such as linseed oil or a polymer (resin),
2. an organic solvent and
3. a pigment (usually an inorganic oxide or metal powder).

Before applying paint to a steel surface, the metal surface should be cleaned of oxides by sand blasting or acid pickling. After cleaning, the metal surface is coated with a thin layer of primer.

What is primer?

A primer is a paint containing a pigment such as lead oxide (Pb_3O_4 red lead) or zinc chromate which oxidizes the steel surface and inhibits its corrosion. Besides, the primer film increases the strength of the bond between steel and final paint film. When the primer film dries a thick film of the required paint is applied over the primer.

Polymers such as alkyd resins, PVC, polyethylene, polyesters, acrylics, polyurethanes, chlorinated rubber, epoxy resins, etc. are used in paint manufacture. For severe conditions such marine and industrial atmosphere, a paint containing epoxy resin (water resistant) is suitable.

ii. Lacquers:

A lacquer consists of a thermoplastic polymer dissolved in an organic solvent. Lacquers can be used to line steel tanks holding corrosive chemicals such as acids.

III. Corrosion Inhibitors

Required: definition, mechanism and types

- Definition of corrosion inhibitors:

Corrosion inhibitors are substances that are added in small amount (e.g 0.1%) to the corrosive medium stop or slow down electrochemical corrosion reactions on a metal surface.

- Mechanism:

Corrosion inhibitors work by one or more of the following mechanisms.

- They adsorb on metal surfaces to form protective films.

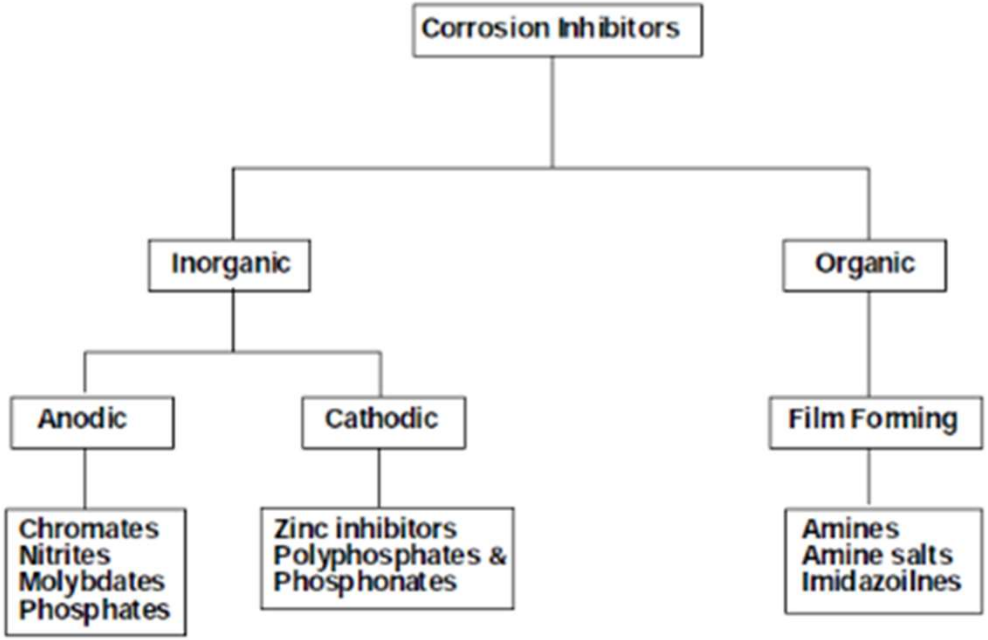
- They combine with corrosion product films to protect metal surfaces.

- They form precipitates, which visibly coat and protect metal surfaces.

Types of inhibitors:

- Inhibitors can be divided into two main categories—inorganic and organic.
- Inorganic inhibitors are used mainly in boilers, cooling towers, and fractionation units.
- Organic inhibitors are used mainly in oil field systems.

As shown in the figure, inorganic inhibitors are further divided into anodic and cathodic classifications. These classifications describe the part of the electrochemical process that is interrupted by the inhibitor. Organic film-forming inhibitors interrupt both the anodic and cathodic processes.



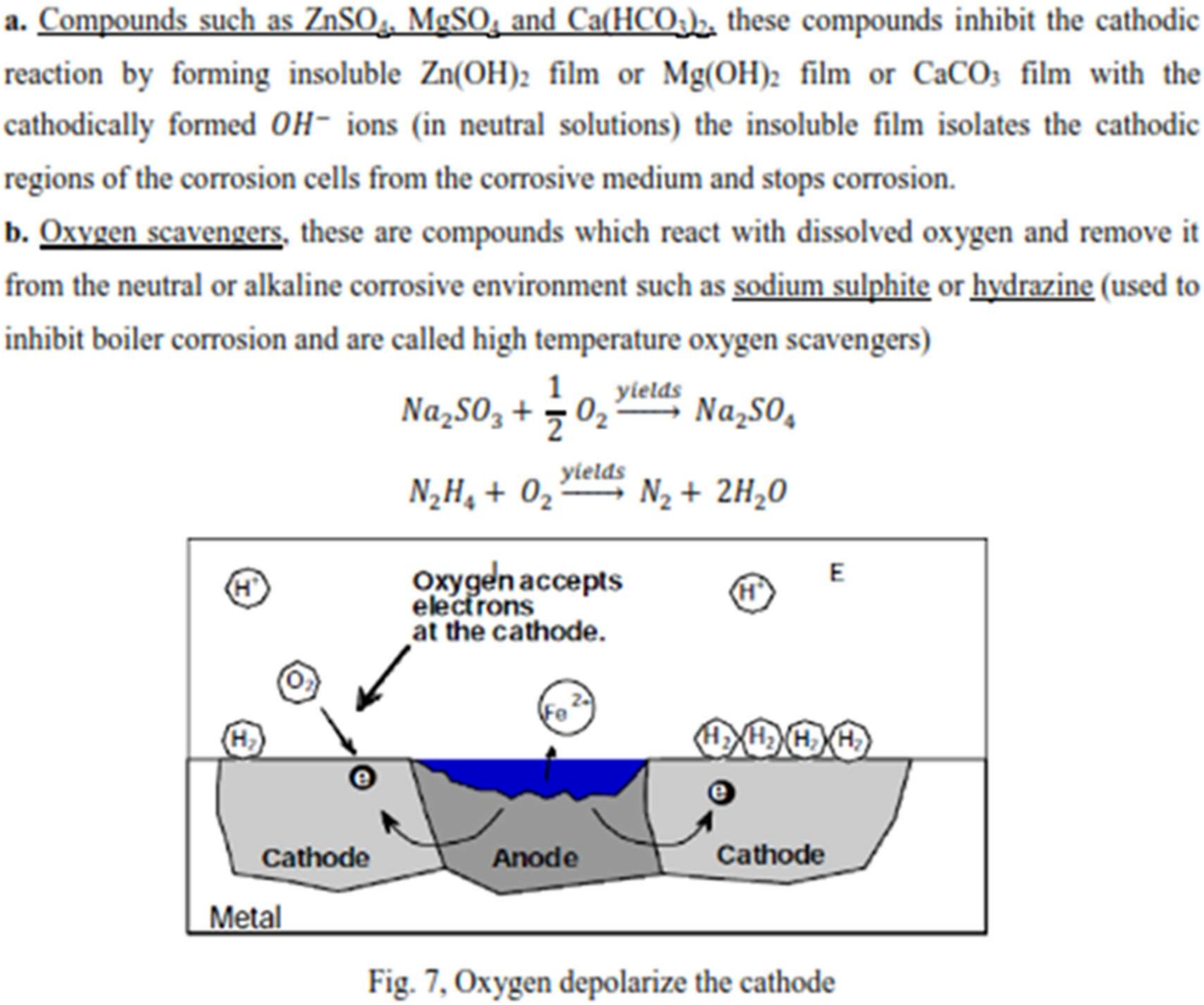
Classification of corrosion inhibitors

Inorganic inhibitors

1. Cathodic inhibitors:

Cathodic inhibitors are chemical compounds which inhibit the cathodic reaction of the corrosion cell.

Examples



a. Compounds such as $ZnSO_4$, $MgSO_4$ and $Ca(HCO_3)_2$, these compounds inhibit the cathodic reaction by forming insoluble $Zn(OH)_2$ film or $Mg(OH)_2$ film or $CaCO_3$ film with the cathodically formed OH^- ions (in neutral solutions) the insoluble film isolates the cathodic regions of the corrosion cells from the corrosive medium and stops corrosion.

b. Oxygen scavengers, these are compounds which react with dissolved oxygen and remove it from the neutral or alkaline corrosive environment such as sodium sulphite or hydrazine (used to inhibit boiler corrosion and are called high temperature oxygen scavengers)

$$Na_2SO_3 + \frac{1}{2}O_2 \xrightarrow{yields} Na_2SO_4$$

$$N_2H_4 + O_2 \xrightarrow{yields} N_2 + 2H_2O$$

Fig. 7, Oxygen depolarize the cathode

c. Compounds such as arsenic (As), mercury (Hg), antimony (Sb) salts which are added to acidic corrosive environments to slowdown the cathodic H_2 evolution reaction.

- These compounds prevent the hydrogen atoms from forming hydrogen gas, and are called cathodic poisons.
- Cathodic poisons are used advantageously as corrosion inhibitors by stifling the cathodic reduction processes that must balance the anodic corrosion reaction. However cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by metal during aqueous corrosion or cathodic charging.

3. Adsorption Inhibitors: (organic inhibitors)

These are organic compounds which contain a polar group such as NH_2 (amino group), these compounds (RNH_2) adsorb on the metallic surface and isolate it from the corrosive solution (usually acids).

Organic corrosion inhibitors are complex mixtures of many different molecular compounds. Organic inhibitors typically affect both anodic and cathodic areas of corrosion cells. They lay down an organic film on the entire metal surface. Their effectiveness depends upon the following conditions:

- the electrical potential of the metal
- the chemical structure of the inhibitor molecule
- the size and shape of the inhibitor molecule

An organic corrosion inhibitor molecule consists of a hydrocarbon chain that is attached to a strongly polar functional group. The hydrocarbon chain of the inhibitor molecule is oil soluble. This chain provides a barrier that keeps water away from the metal surface. The length of the hydrocarbon chain varies (e.g., carbon numbers between 12 and 18). Polar functional groups are based on nitrogen, sulfur, or oxygen.

Most organic inhibitors used in the petroleum industry contain at least one nitrogen functional group. Frequently, these nitrogen-based inhibitors are reacted with organic acids, or they contain oxygen functional groups. The amine (NH2) portion of the molecule is water soluble and has a pair of unshared electrons. These electrons are available to bond with metal surfaces.

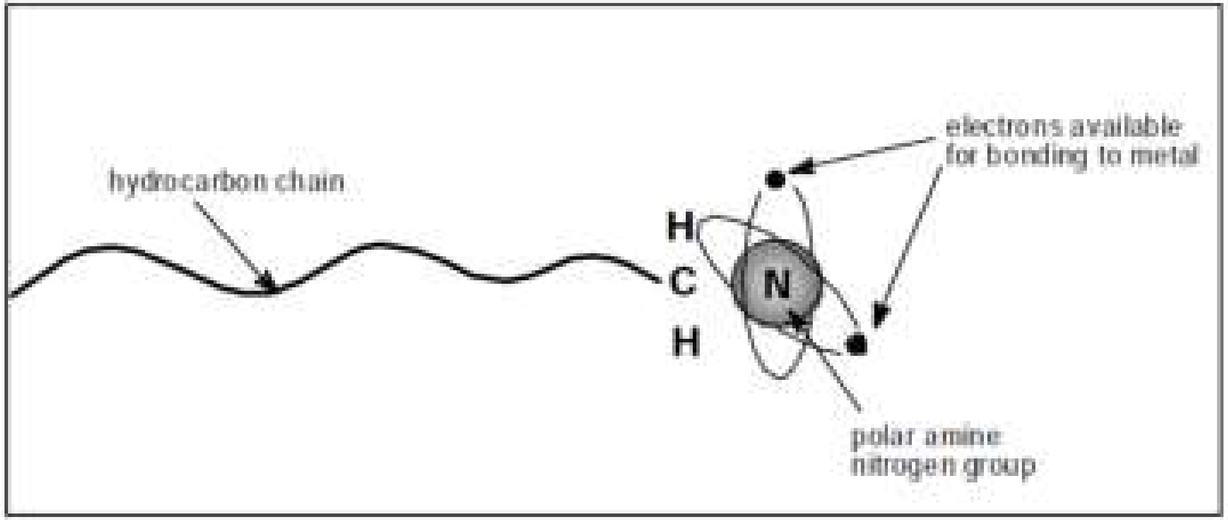


Fig. 8, Organic inhibitor molecule

Prevention of Corrosion

Basic goal → • protect the metal • avoid localized corrosion

- ☐ When possible chose a nobler metal
- ☐ Avoid electrical / physical contact between metals with very different electrode potentials (avoid formation of a galvanic couple)
- ☐ In case of microstructural level galvanic couple, try to use a course microstructure (where possible) to reduce number of galvanic cells formed
- ☐ Modify the base metal by alloying
- ☐ Protect the surface by various means
- ☐ Modify the fluid in contact with the metal
  - Remove a cathodic reactant (e.g. water)
  - Add inhibitors which from a protective layer
- ☐ Cathodic protection
  - Use a sacrificial anode (as a coating or in electrical contact)
  - Use an external DC source in connection with a inert/expendable electrode

Corrosion Control

8 Engineering design rules that are important to the reduction or prevention of corrosion

1	Allow for the penetration action of corrosion along with the mechanical strength requirements when determining the appropriate metal thickness
2	Weld rather than rivet containers to reduce crevice corrosion. If rivets are used, choose a rivet material that is cathodic to the materials being joined.
3	If possible, use galvanically similar metals for the entire structure. Avoid dissimilar metals that can cause galvanic corrosion. If galvanically dissimilar metals are bolted together, separate them with nonmetallic gaskets and washers.
4	Avoid excessive stress and stress concentrations in corrosive environments to prevent stress-corrosion cracking, especially when using susceptible materials such as stainless steels and brasses.

Corrosion Control

5	Avoid sharp bends in piping systems to prevent erosion corrosion.
6	Design tanks and other containers for easy draining and cleaning.
7	Design systems for easy removal and replacement of parts that are expected to fail in service, such as pumps in chemical plants.
8	Design heating systems such that hot spots do not occur.

- Alloying the base metal can improve the oxidation resistance
- E.g. the oxidation resistance of Fe can be improved by alloying with Cr, Al, Ni
- Al, Ti have a protective oxide film and usually do not need any alloying
- An inexpensive Magnesium anode could double the life of a domestic hot water tank.

Corrosion prevention

Treatment of metal
  Surface coating - zinc, tin, plastic
  paint, phosphate
  Alloy - stainless steel

Treatment of environment
  Removal of oxygen
  Control of pH
  Inhibitors

Change of potential
  Cathodic protection
  Anodic protection

- Coatings
    - Barrier films
    - Inhibitive Pigments
    - Sacrificial treatments
    - Paint

- Active Cathodic Protection

Electrochemical Kinetics of Corrosion and Passivity

The basis of a rate expression for an electrochemical process is Faraday's law:

$$Q = n \cdot F \cdot n_i \qquad m = \frac{Ita}{nF}$$

Where m is the mass reacted, I is the measured current in ampere, t is the time, a is the atomic weight, n the number of electrons transferred and F is the Faraday constant (96500 $\mathrm{Cmol^{-1}}$). Dividing Faraday's law by the surface area A and the time t leads to an expression for the corrosion rate r:

$$r = \frac{m}{tA} = \frac{ia}{nF}$$

With the current density i defined as i = I/A.

Exchange current density:

We consider the reaction for the oxidation/reduction of hydrogen:

$$2H^+ + 2e^- \underset{r_r}{\overset{r_f}{\rightleftarrows}} H_2$$

This reaction is in the equilibrium state at the standard half cell potential $e^0(H^+/H_2)$. This means that the forward reaction rate r_f and the reverse reaction rate r_r have the same magnitude. This can be written as:

At an equilibrium hydrogen electrode there is a finite rate of interchange between hydrogen molecules and hydrogen ions in solution

- By plotting electrode potential vs reaction rate, it is possible to establish a point corresponding to the platinum-hydrogen electrode. This point represents the particular exchange reaction rate of the electrode expressed in terms of moles reacting per square centimeter per second.
- Note that there is no net reaction, since both oxidation and reduction rates are equal; the exchange reaction rate can be more conveniently expressed in terms of current density.
- More precisely, the relationship between exchange reaction rate and current density can be directly derived from Faraday’s Law.

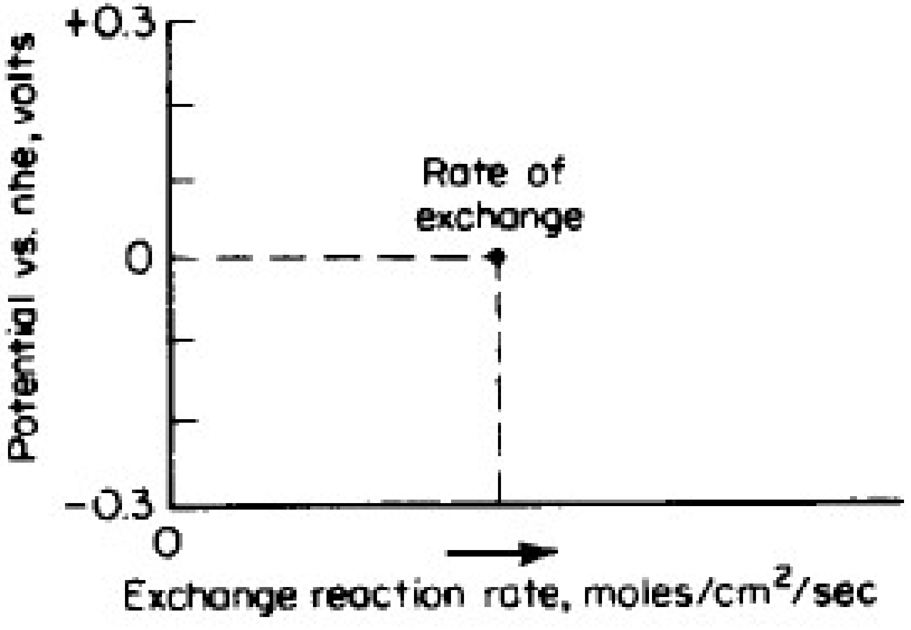
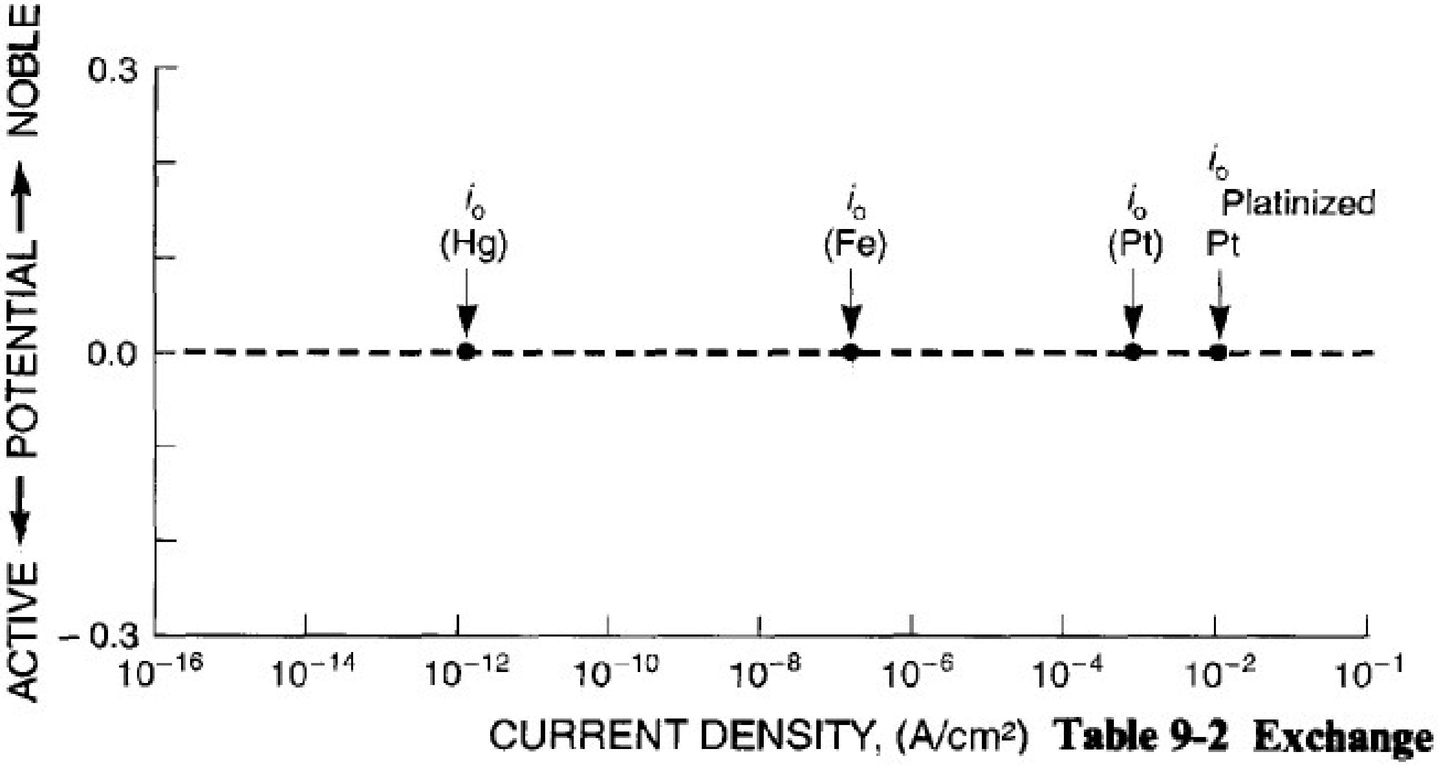


Figure 9-11 Hydrogen-hydrogen-ion exchange on platinum.

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

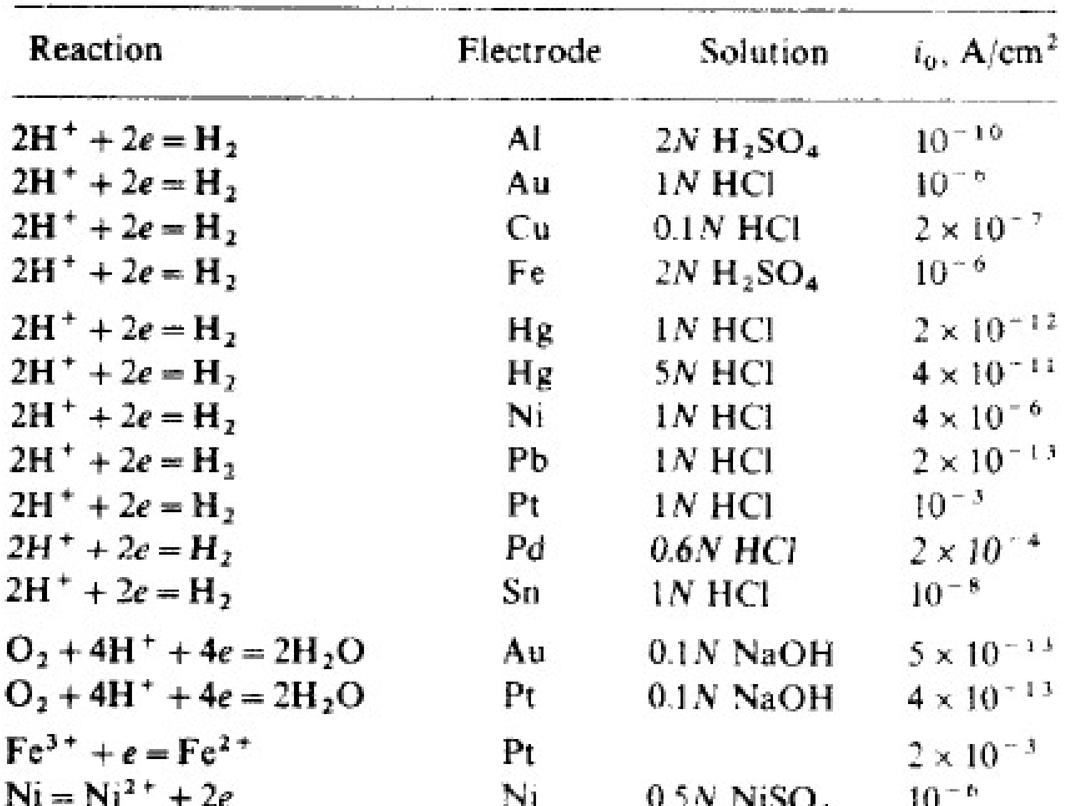
Exchange current density i_0 is the rare of oxidation and reduction reaction at an equilibrium Electrode expressed in terms of current density.

In this case is i_0 the exchange current density equivalent to the reversible rate at equilibrium. In other words, while the standard half cell potential e^0 is the universal thermodynamic parameter, i_0 is the fundamental kinetic parameter of an electrochemical reaction. The exchange current density cannot be calculated. It has to be measured for each system. The following figure shows that the exchange current density for the hydrogen reaction depends strongly on the electrode material, whereas the standard half cell potential remains the same.



The greater the exchange current density of platinized platinum relative to bright platinum is a result of its greater Surface area. Exchange current densities for H+-H2 system are markedly reduced by the presence of trace impurities such as arsenic, Sulphur, and antimony containing ions

Table 9-2 Exchange current densities



Reaction	Electrode	Solution	i_0, A/cm²
$2H^+ + 2e = H_2$	Al	$2N$ H_2SO_4	10^{-10}
$2H^+ + 2e = H_2$	Au	$1N$ HCl	10^{-6}
$2H^+ + 2e = H_2$	Cu	$0.1N$ HCl	2×10^{-7}
$2H^+ + 2e = H_2$	Fe	$2N$ H_2SO_4	10^{-6}
$2H^+ + 2e = H_2$	Hg	$1N$ HCl	2×10^{-12}
$2H^+ + 2e = H_2$	Hg	$5N$ HCl	4×10^{-11}
$2H^+ + 2e = H_2$	Ni	$1N$ HCl	4×10^{-6}
$2H^+ + 2e = H_2$	Pb	$1N$ HCl	2×10^{-13}
$2H^+ + 2e = H_2$	Pt	$1N$ HCl	10^{-3}
$2H^+ + 2e = H_2$	*Pd*	*$0.6N$ HCl*	*2×10^{-4}*
$2H^+ + 2e = H_2$	Sn	$1N$ HCl	10^{-8}
$O_2 + 4H^+ + 4e = 2H_2O$	Au	$0.1N$ NaOH	5×10^{-13}
$O_2 + 4H^+ + 4e = 2H_2O$	Pt	$0.1N$ NaOH	4×10^{-13}
$Fe^{3+} + e = Fe^{2+}$	Pt		2×10^{-3}
$Ni = Ni^{2+} + 2e$	Ni	$0.5N$ NiSO	10^{-6}

Electrochemical Polarization:

- The potentials of oxidation and reduction processes occurring at the electrode interfaces will no longer be at their equilibrium potential. The deviation from equilibrium potential is called Polarization.

- Polarization can be defined as the displacement of electrode potential resulting from a net current. The magnitude of polarization is frequently measured in terms of overvoltage.

- The overvoltage usually abbreviated as η , is a measure of polarization with respect to the equilibrium potential of an electrode.

Polarization η is the change in the standard half cell potential e caused by a net surface reaction rate. Cathodic polarization η_c means that electrons are supplied to the surface and they build up a negative potential in the metal. Therefore η_c is negative by definition. Anodic polarization η_a is the opposite process. There are two different kinds of polarization (sometimes also known as overpotential) namely activation and concentration polarization.

Activation Polarization:

In this case a step in the half cell reaction controls the rate of electron (charge) flow. For example the hydrogen evolution reaction

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

proceeds at a metal surface in three major steps. In the first step H+ reacts with an electron from the metal to form an adsorbed hydrogen atom at the surface.

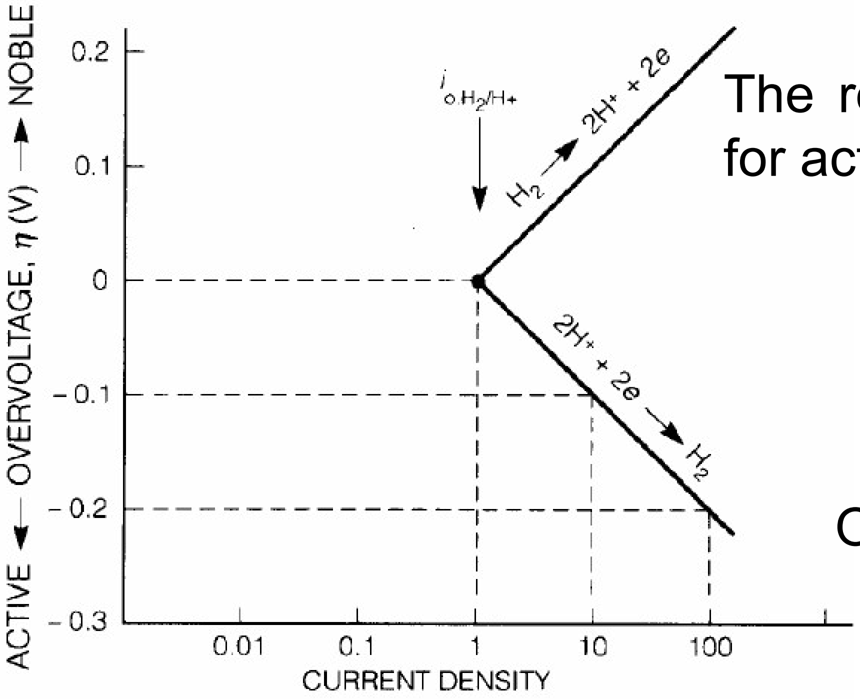
$$H^+ + e^- \rightarrow H_{ads}$$

In the second steps the reaction of two adsorbed hydrogen atoms forms a hydrogen molecule.

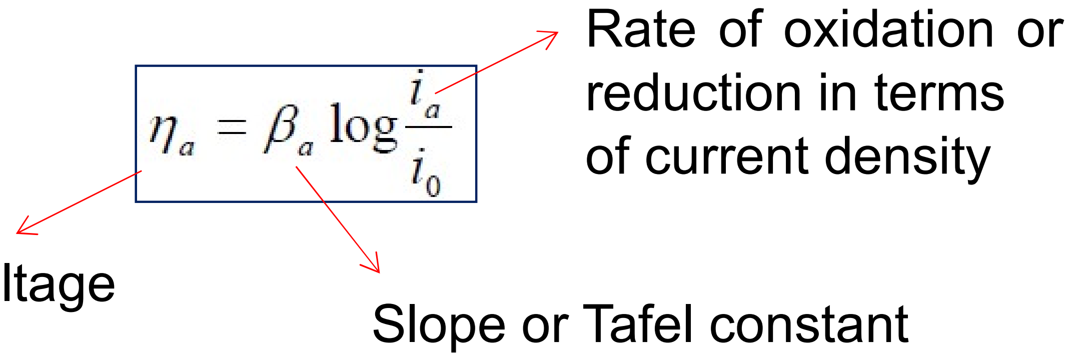
$$H_{ads} + H_{ads} \rightarrow H_{2ads}$$

In the third step enough adsorbed hydrogen molecules combine and nucleate a hydrogen bubble on the surface. Any of these steps can be the rate limiting step and therefore cause the activation polarization. The activation polarization can be calculated using the current densities, which represent the reaction rates. For cathodic η_c and anodic η_a polarization one can write:

$$\eta_c = \beta_c \log\frac{i_c}{i_0} \qquad \eta_a = \beta_a \log\frac{i_a}{i_0}$$



The relationship between reaction rate and overvoltage for activation polarization is called Tafel Equation



$$\eta_a = \beta_a \log \frac{i_a}{i_0}$$

Rate of oxidation or reduction in terms of current density

Overvoltage

Slope or Tafel constant

For zero η both equations reduce to $i = i_0$. For polarization potentials below the equilibrium half cell potential the reduction or forward reaction is favored:

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

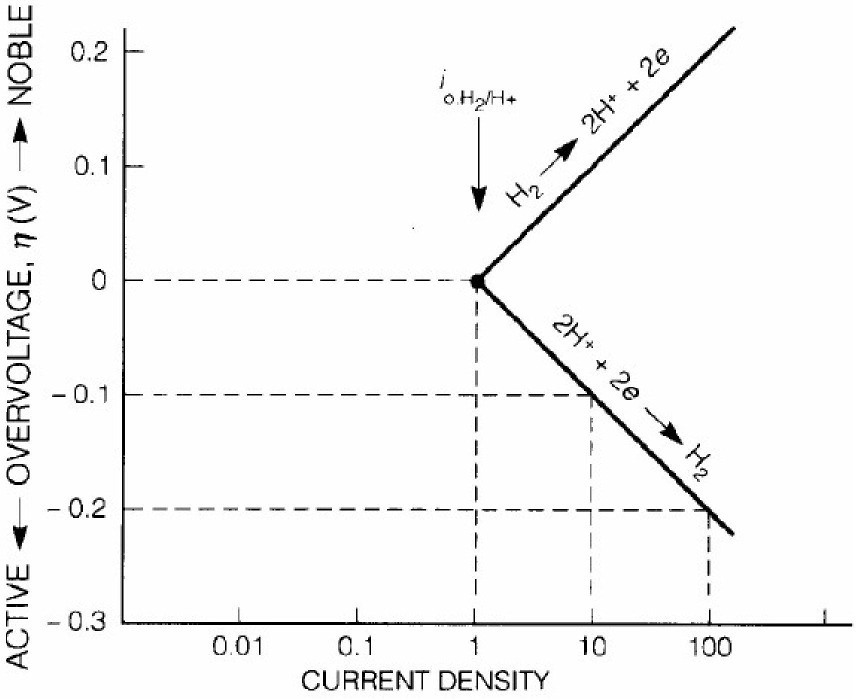
while above the half cell potential the reverse reaction is favored.

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

In the figure the so called Tafel plot is shown. It depicts the change in the polarization potential with the current density.

The activation polarization is related to the activation energy of the rate limiting step. Therefore a thermodynamical derivation of β is possible.

Significance of Tafel Equation



- The value of Tafel constant, beta for electrochemical reactions ranges between 0.05 and 0.15 V. In general, the value of beta is usually 0.1 volt. The significance of this parameter can be seen upon examination this figure. Here the oxidation and reduction reactions corresponding to a hydrogen electrode are plotted with a beta value of 0.1 volt. Note that the reaction rate changes by one order of magnitude for each 100 mV or 0.1 Volt change in overvoltage.
- This illustration shows that the reaction rate of an electrochemical reaction is very sensitive to small changes in electrode potential.
- Further, it can be seen that at all potentials more noble than the reversible potential a net oxidation process occurs, and that at all potentials more active or more negative than the reversible potential a net reduction occurs. At the reversible potential, or at zero overvoltage, there is no net rate of oxidation or reduction since both rates are equal at this intersection point.

9-7 Concentration Polarization

To illustrate the phenomenon of concentration polarization, consider the hydrogen-evolution reaction. As shown schematically in Fig. 9-14, at low reduction rates the distribution of hydrogen ions in the solution adjacent to the electrode surface is relatively uniform. At very high reduction rates the region adjacent to the electrode surface will become depleted of hydrogen ions. If the reduction rate is increased further, a limiting rate will be reached that is determined by the diffusion rate of hydrogen ions to the electrode

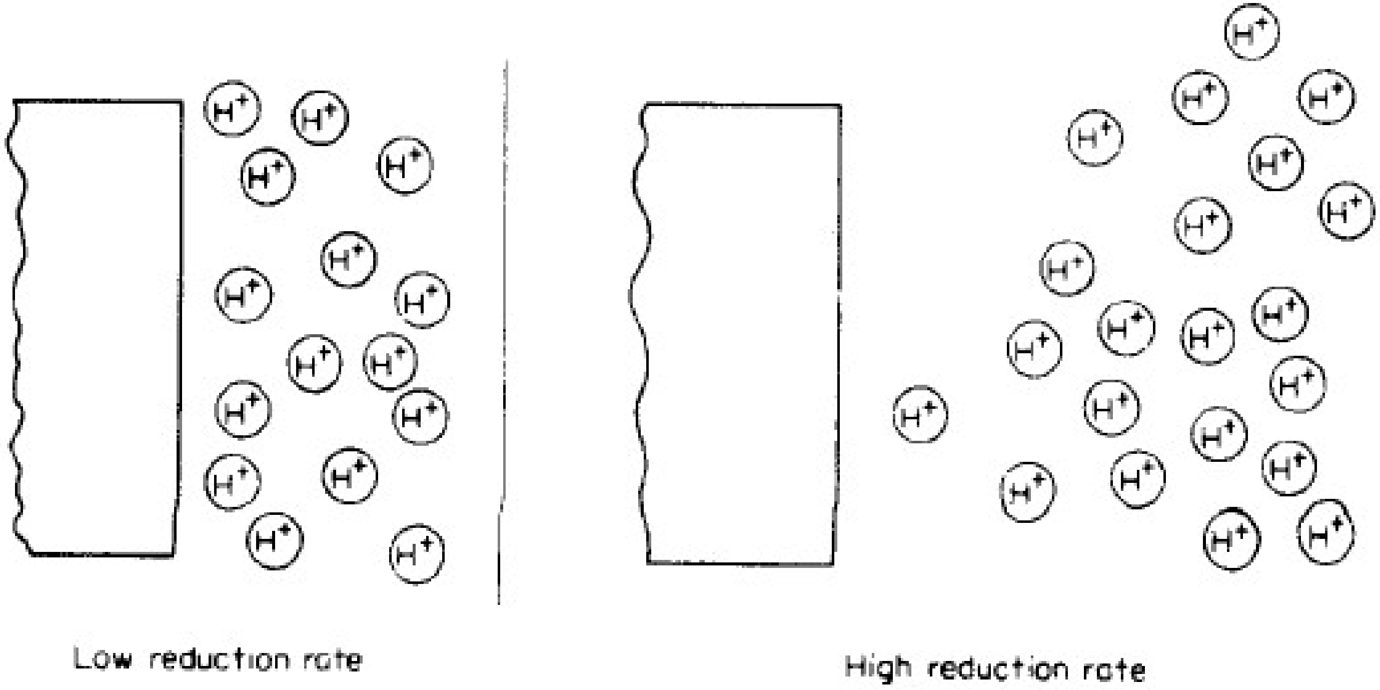
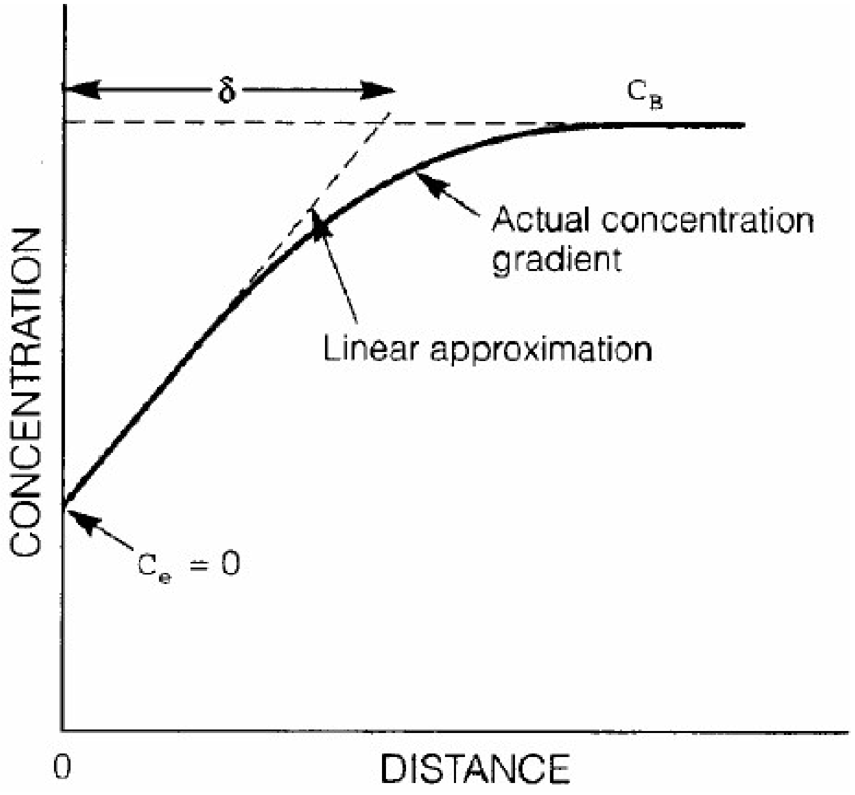


Figure 9-14 Concentration gradients during hydrogen evolution, shown schematically.

Concentration Polarization:

If the reaction on the metal surface is fast it can lead to a depletion of the adjacent solution of the dissolved species that reacts on the surface. This is shown for the H^+ concentration in the next figure. c_B is the H+ concentration in the bulk of the solution.



From the Nernst equation, it is clear that the half cell potential is dependent on H+ concentration, in the form that the potential decreases with decreasing concentration

$$e_{H^+/H_2} = e^0_{H^+/H_2} + \frac{2.3RT}{nF}\log\frac{(H^+)^2}{p_{H_2}}$$

The decrease in the half cell potential is the concentration polarization η_{conc} , which can be written in terms of current density using Nernst equation as:

$$\eta_{conc} = \frac{2.3RT}{nF}\log\left[1 - \frac{i_c}{i_L}\right]$$

Where i_L is diffusion current density

A plot of this equation can be seen in the next figure. One can see that η_{conc} is low until a limiting current density i_L is reached. This current density is the measure of a maximum reaction rate that cannot be exceeded because of a limited diffusion rate of H^+ within the solution. The limiting current density can be calculated as follows:

$$i_L = \frac{D_Z n F C_B}{\delta}$$

- This shows that limiting diffusion current is a function of the diffusion coefficient, the concentration of ions in solution, and the thickness of the diffusion layer. Changes that affect these parameters influence the limiting diffusion current.

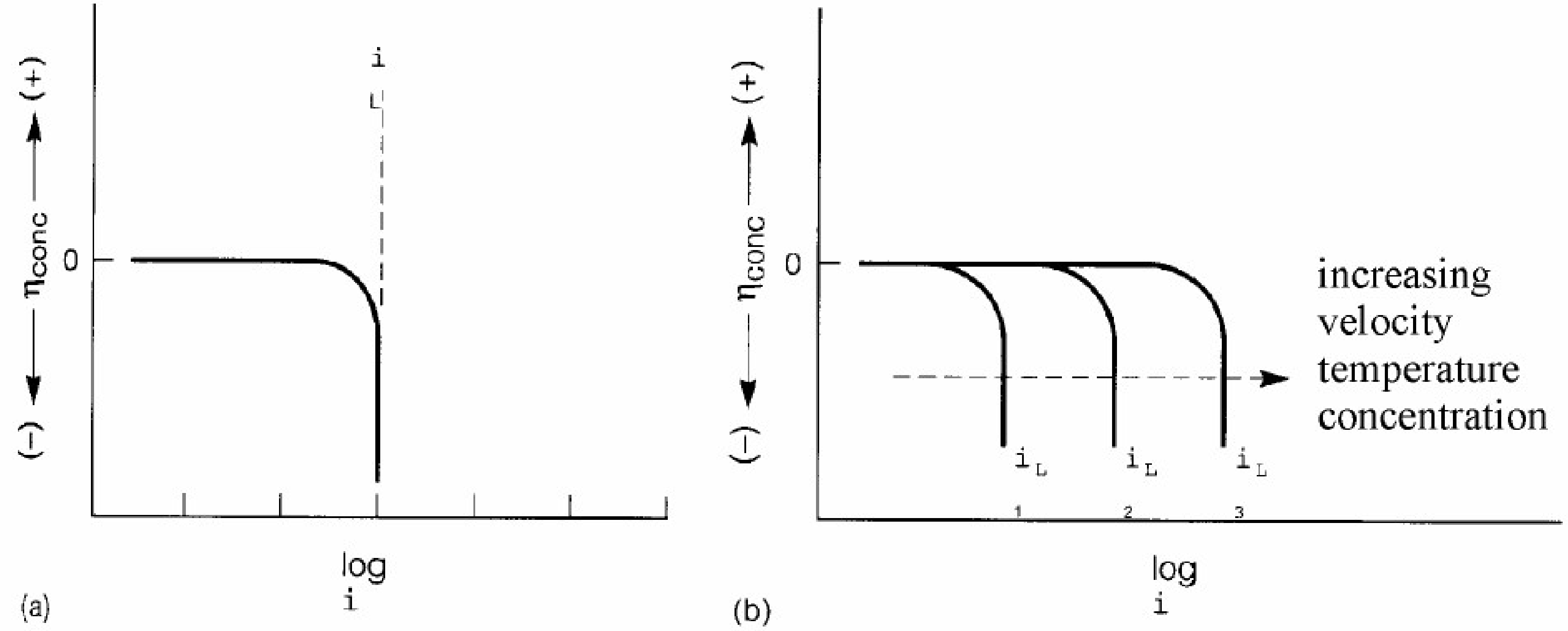
- It is generally observed that there is a linear relationship between the concentration of reactive ions in solution and the limiting diffusion current density.

- The diffusion layer thickness is influenced by the shape of the particular electrode, the geometry of the system, and by the agitation.

- Agitation tends to decrease the diffusion layer thickness because of convection currents and consequently increases the limiting diffusion current density.

- Limiting diffusion current density is usually only significant during reduction processes and is usually negligible during metal dissolution reactions. Hence, limiting diffusion current density can be ignored during most metal dissolution reactions.

D_Z is the diffusivity of the reacting species Z, C_B is the concentration in the bulk of the solution and δ is the thickness of the depleted zone. i_L is increased with increasing concentration, with increasing diffusivity (temperature) and higher solution agitation, which decreases δ.

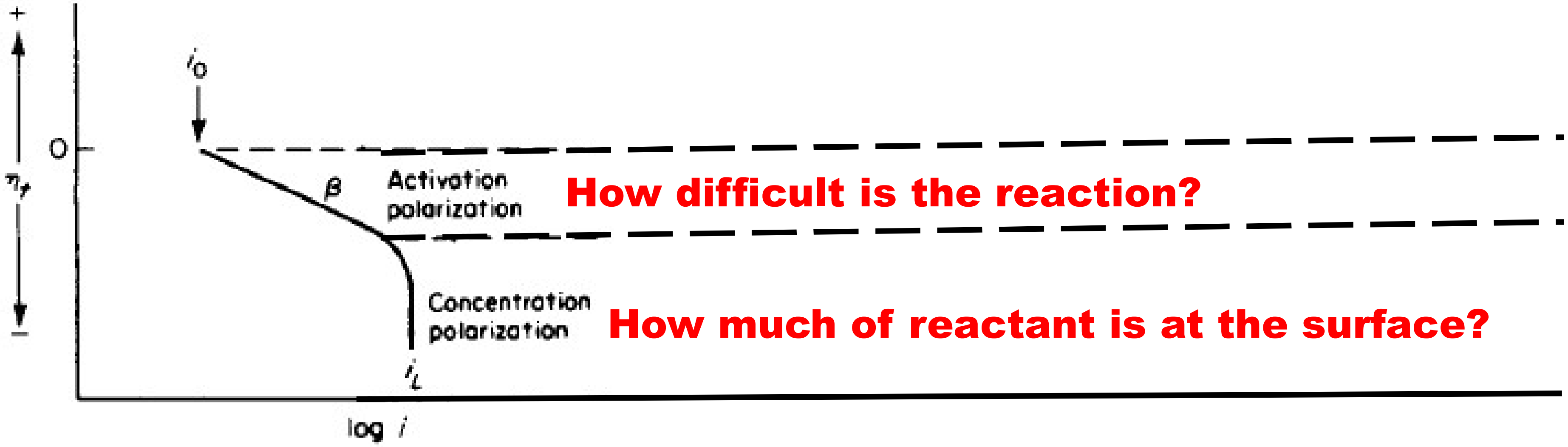


Concentration polarization is only significant for cathodic reduction processes, as for anodic oxidation one usually has an unlimited supply of metal atoms at the interface. Only at very high corrosion rates or during intentional anodic dissolution by an impressed current one can find concentration polarization due to limited rates of transport of soluble oxidation products away from the surface.

9-6 Combined Polarization

Both activation and concentration polarization usually occur at an electrode. At low reaction rates, activation polarization usually controls, whereas at higher reaction rates concentration polarization becomes controlling. The total polarization of an electrode is the sum of the contributions of activation polarization and concentration polarization:

$$\eta_T = \eta_a + \eta_c \tag{9.14}$$



where η_T is total overvoltage. During anodic dissolution, concentration polarization is not a factor as mentioned above, and the equation for the kinetics of anodic dissolution is given by:

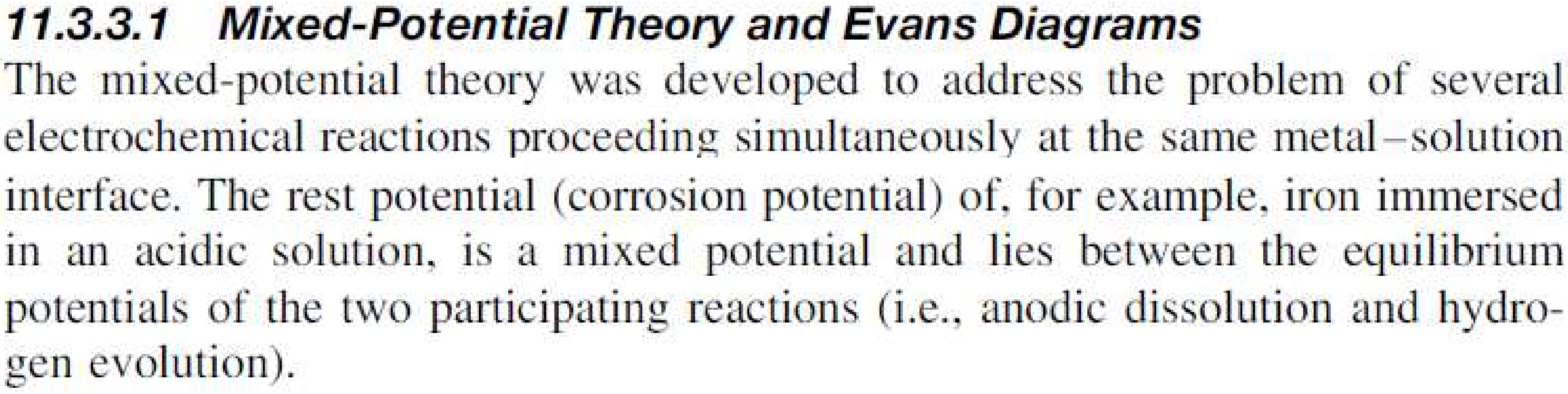
$$\eta_{\text{diss}} = \beta \log \frac{i}{i_o} \tag{9.15}$$

See Eq. (9.11). During reduction processes such as hydrogen evolution or oxygen reduction, concentration polarization becomes important as the reduction rate approaches the limiting diffusion current density. The overall reaction for a reduction process is given by combining Eqs. (9.11) and (9.13) with appropriate signs:

$$\eta_{\text{red}} = -\beta \log \frac{i}{i_o} + 2.3\,\frac{RT}{nF} \log\left(1 - \frac{i}{i_L}\right) \tag{9.16}$$

Equation (9.16) is graphically illustrated in Fig. 9-17.

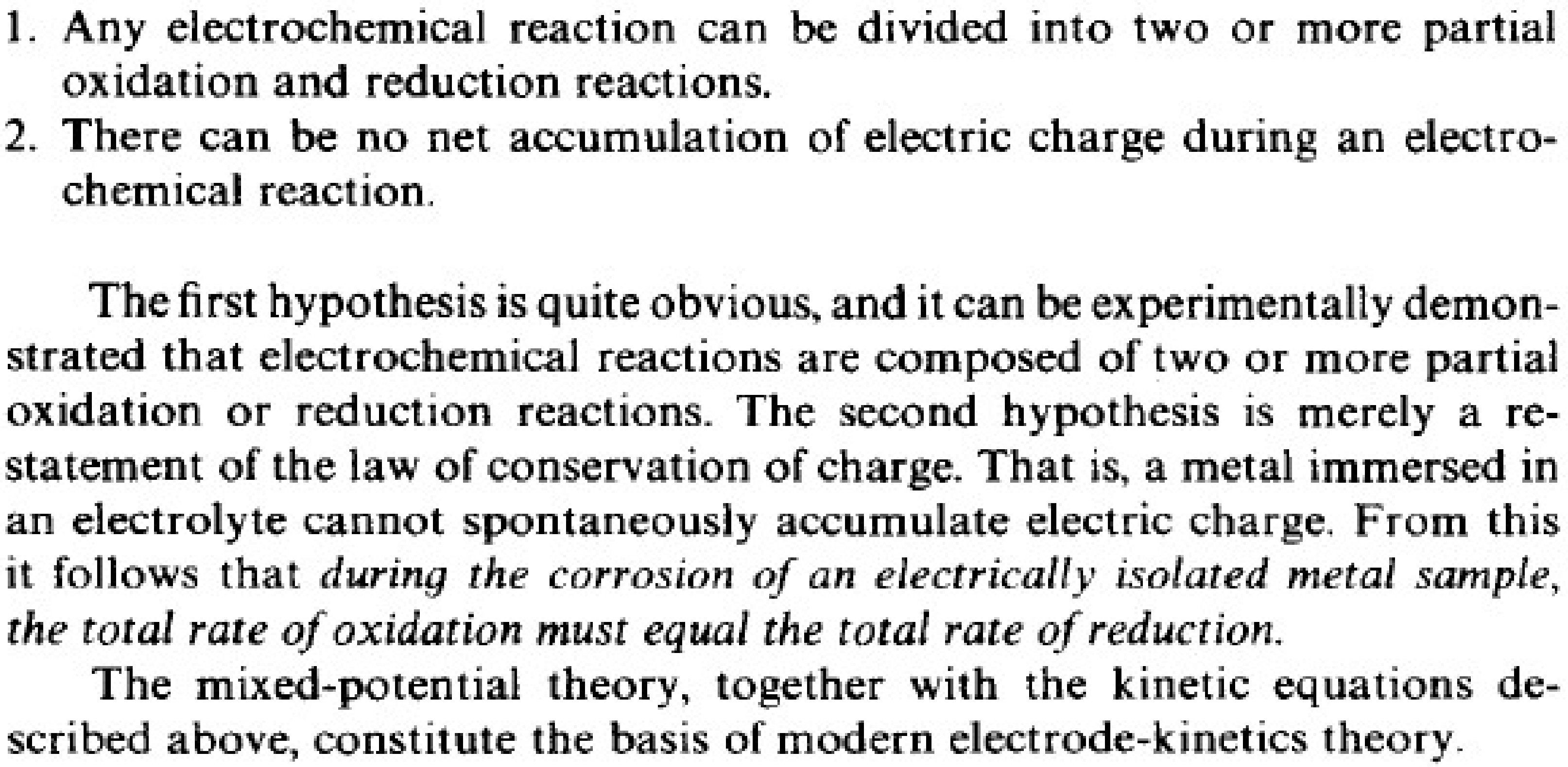
The importance of Eqs. (9.15) and (9.16) cannot be overemphasized since they are the basic equations of all electrochemical reactions. Equation (9.16) applies to any reduction reaction, and Eq. (9.15) applies to almost all anodic dissolution reactions. Exceptions to Eq. (9.15) are metals which demonstrate active-passive behavior; these discussed in detail below. Using only three basic parameters, namely, β, i_0 and i_L, the kinetics of virtually every corrosion reaction can be precisely described. Equations (9.15) and (9.16) represent an outstanding simplification of the complex phenomena observed during corrosion reactions. The use and application of these two equations are described below and also in greater detail in Chap. 10.



11.3.3.1 Mixed-Potential Theory and Evans Diagrams

The mixed-potential theory was developed to address the problem of several electrochemical reactions proceeding simultaneously at the same metal–solution interface. The rest potential (corrosion potential) of, for example, iron immersed in an acidic solution, is a mixed potential and lies between the equilibrium potentials of the two participating reactions (i.e., anodic dissolution and hydrogen evolution).

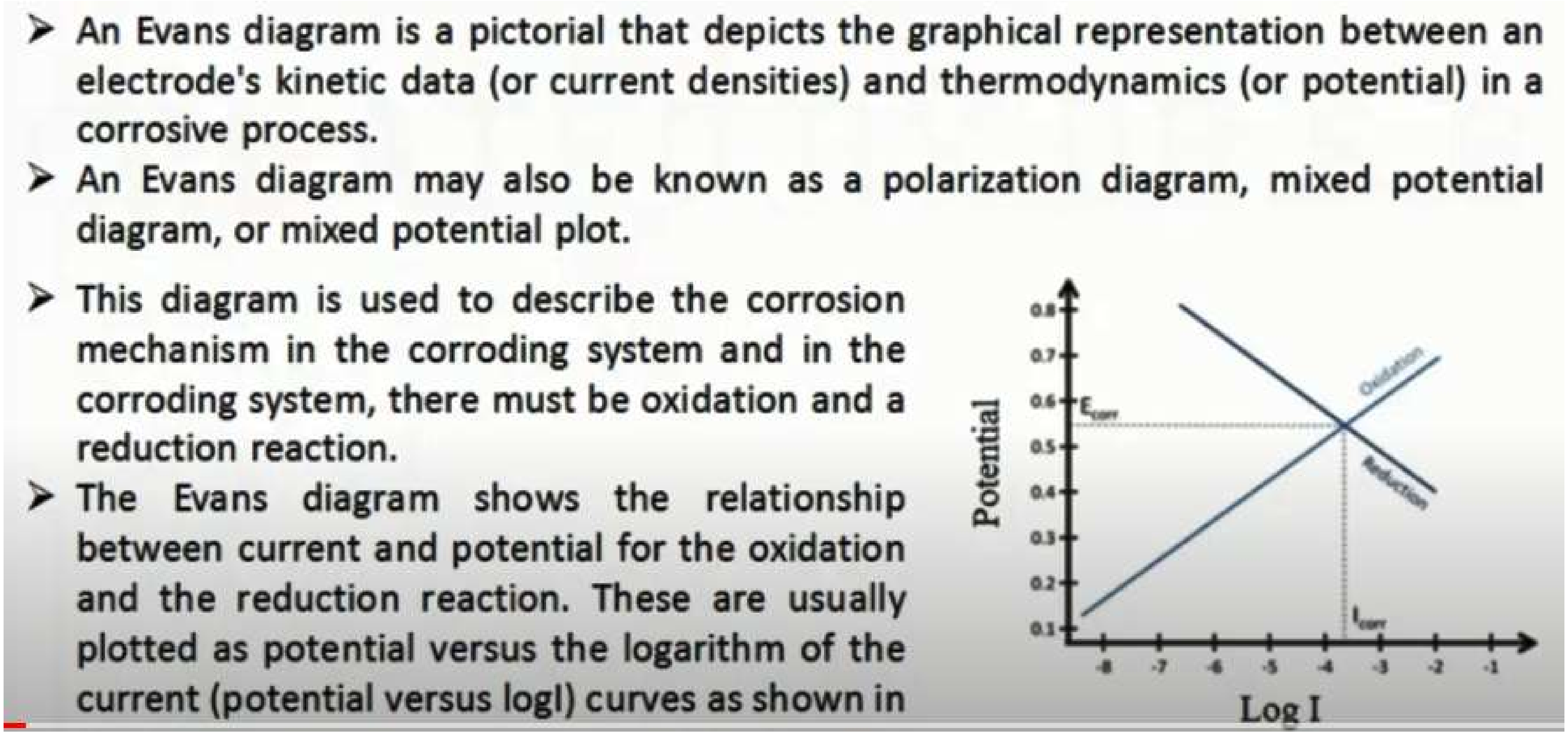
Mixed Potential theory consists of two simple hypothesis:



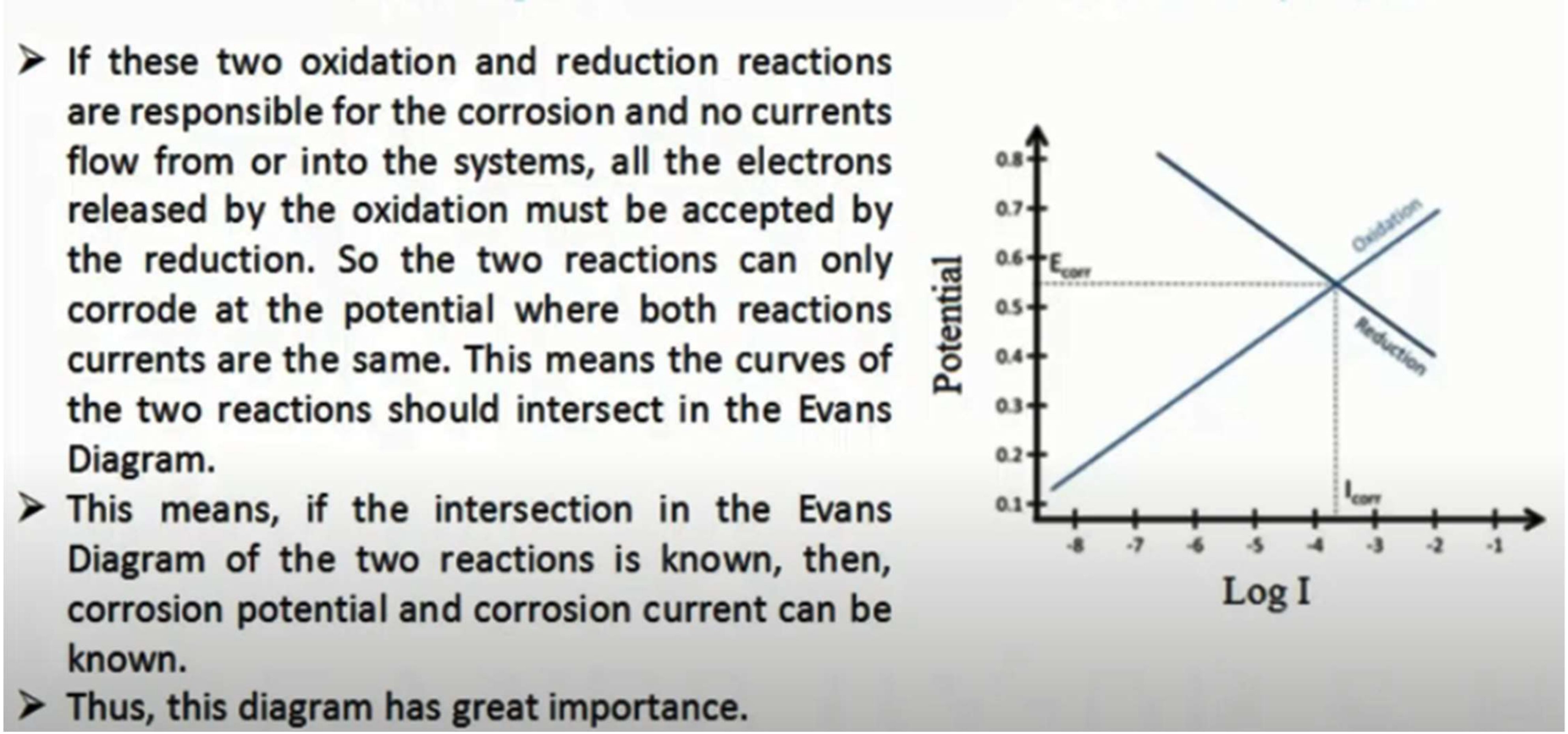
1. Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions.
2. There can be no net accumulation of electric charge during an electrochemical reaction.

The first hypothesis is quite obvious, and it can be experimentally demonstrated that electrochemical reactions are composed of two or more partial oxidation or reduction reactions. The second hypothesis is merely a restatement of the law of conservation of charge. That is, a metal immersed in an electrolyte cannot spontaneously accumulate electric charge. From this it follows that *during the corrosion of an electrically isolated metal sample, the total rate of oxidation must equal the total rate of reduction.*

The mixed-potential theory, together with the kinetic equations described above, constitute the basis of modern electrode-kinetics theory.

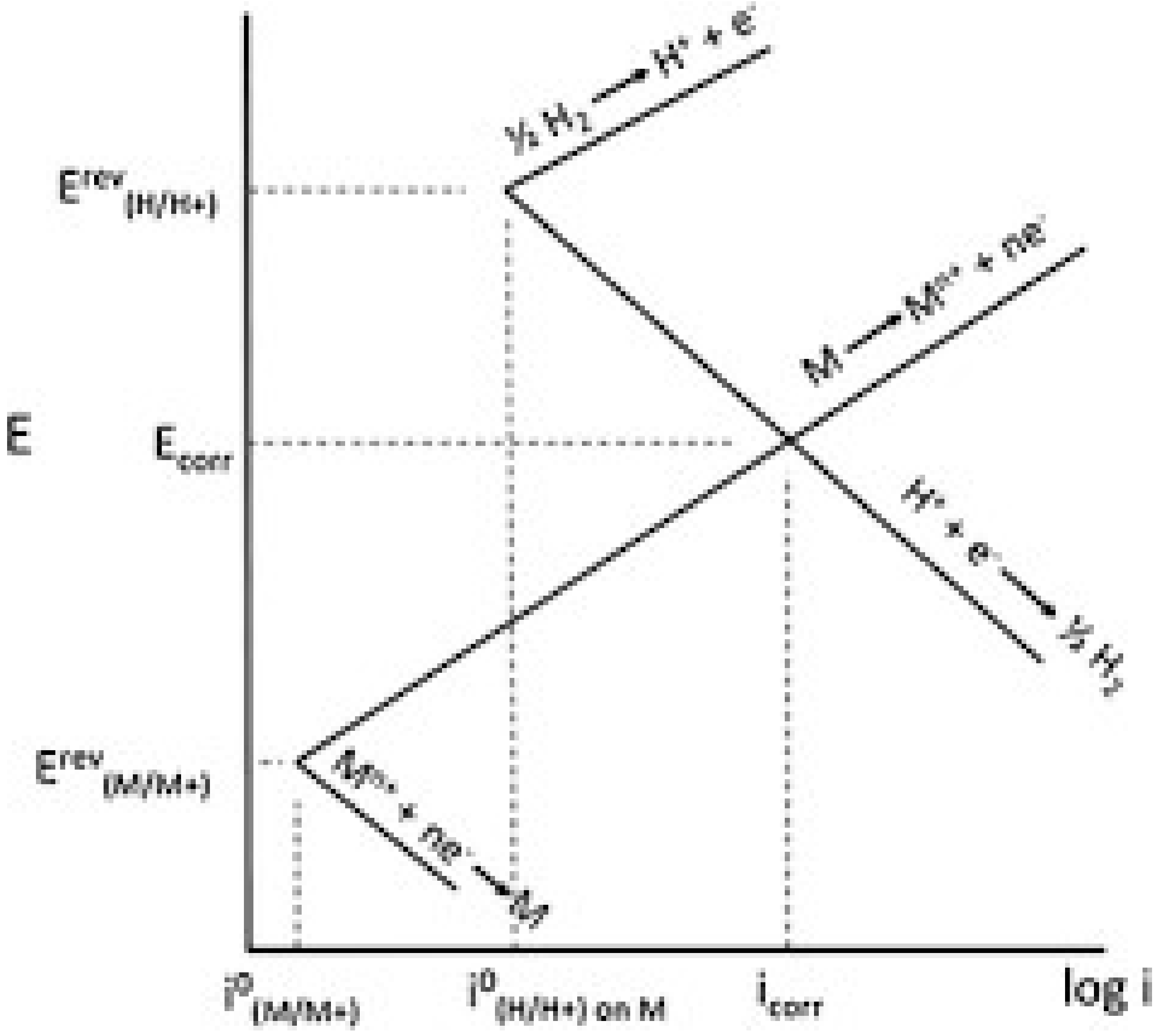


- An Evans diagram is a pictorial that depicts the graphical representation between an electrode's kinetic data (or current densities) and thermodynamics (or potential) in a corrosive process.
- An Evans diagram may also be known as a polarization diagram, mixed potential diagram, or mixed potential plot.
- This diagram is used to describe the corrosion mechanism in the corroding system and in the corroding system, there must be oxidation and a reduction reaction.
- The Evans diagram shows the relationship between current and potential for the oxidation and the reduction reaction. These are usually plotted as potential versus the logarithm of the current (potential versus logI) curves as shown in



- If these two oxidation and reduction reactions are responsible for the corrosion and no currents flow from or into the systems, all the electrons released by the oxidation must be accepted by the reduction. So the two reactions can only corrode at the potential where both reactions currents are the same. This means the curves of the two reactions should intersect in the Evans Diagram.
- This means, if the intersection in the Evans Diagram of the two reactions is known, then, corrosion potential and corrosion current can be known.
- Thus, this diagram has great importance.

The point of intersection of anodic and cathodic polarization curves in an Evans diagram gives the Mixed potential E_{corr} (corrosion potential) also called as compromise potential or mixed potential of free corrosion potential and the corrosion current (i_{corr})



$E^{rev}_{(H/H+)}$
$\frac{1}{2} H_2 \longrightarrow H^+ + e^-$
$M \longrightarrow M^{n+} + ne^-$
E
E_{corr}
$H^+ + e^- \longrightarrow \frac{1}{2} H_2$
$E^{rev}_{(M/M+)}$
$M^{n+} + ne^- \longrightarrow M$
$i^0_{(M/M+)}$
$i^0_{(H/H+)\ on\ M}$
i_{corr}
log i

Mixed Potential Theory:

Charge conservation is required to apply the equations derived for polarization potentials. This means that the sum of anodic oxidation currents must equal the sum of cathodic reduction currents. For anodic oxidation there is one reaction of the general form:

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

There are basically three different kinds of cathodic reactions:

1. Evolution of Hydrogen from acid or neutral solutions:

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(acid solutions)}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{(neutral and alkaline solutions)}$$

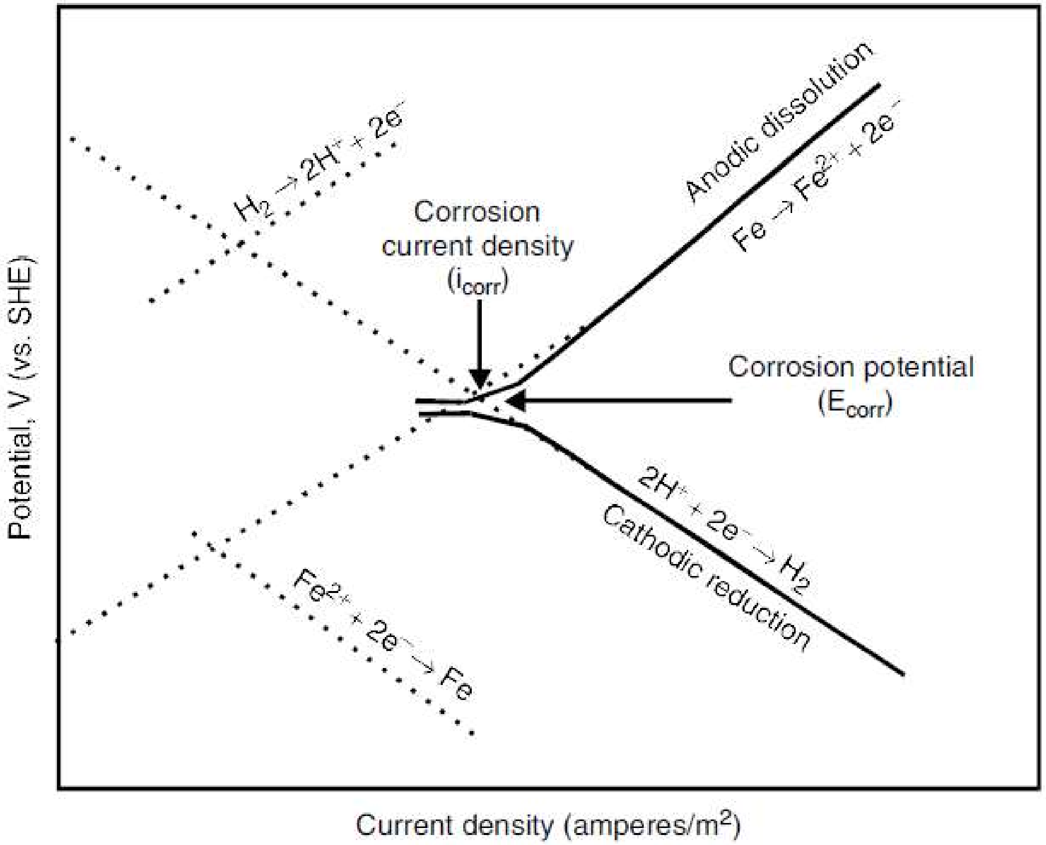
2. Reduction of dissolved oxygen in acid or neutral solutions:

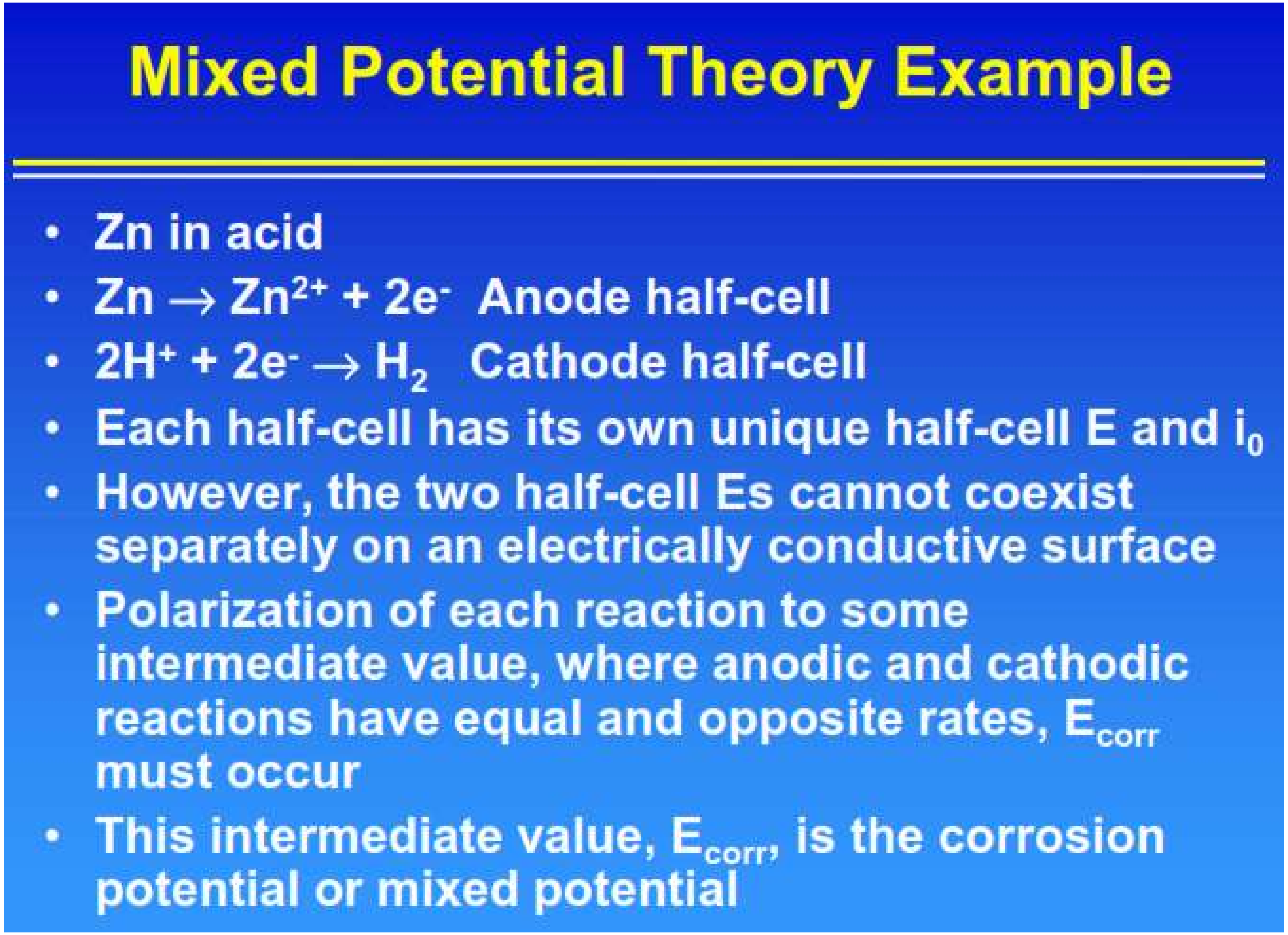
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(acid solutions)}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(neutral and alkaline solutions)}$$

3. Reduction of a dissolved oxidizer in a redox reaction (e.g.):

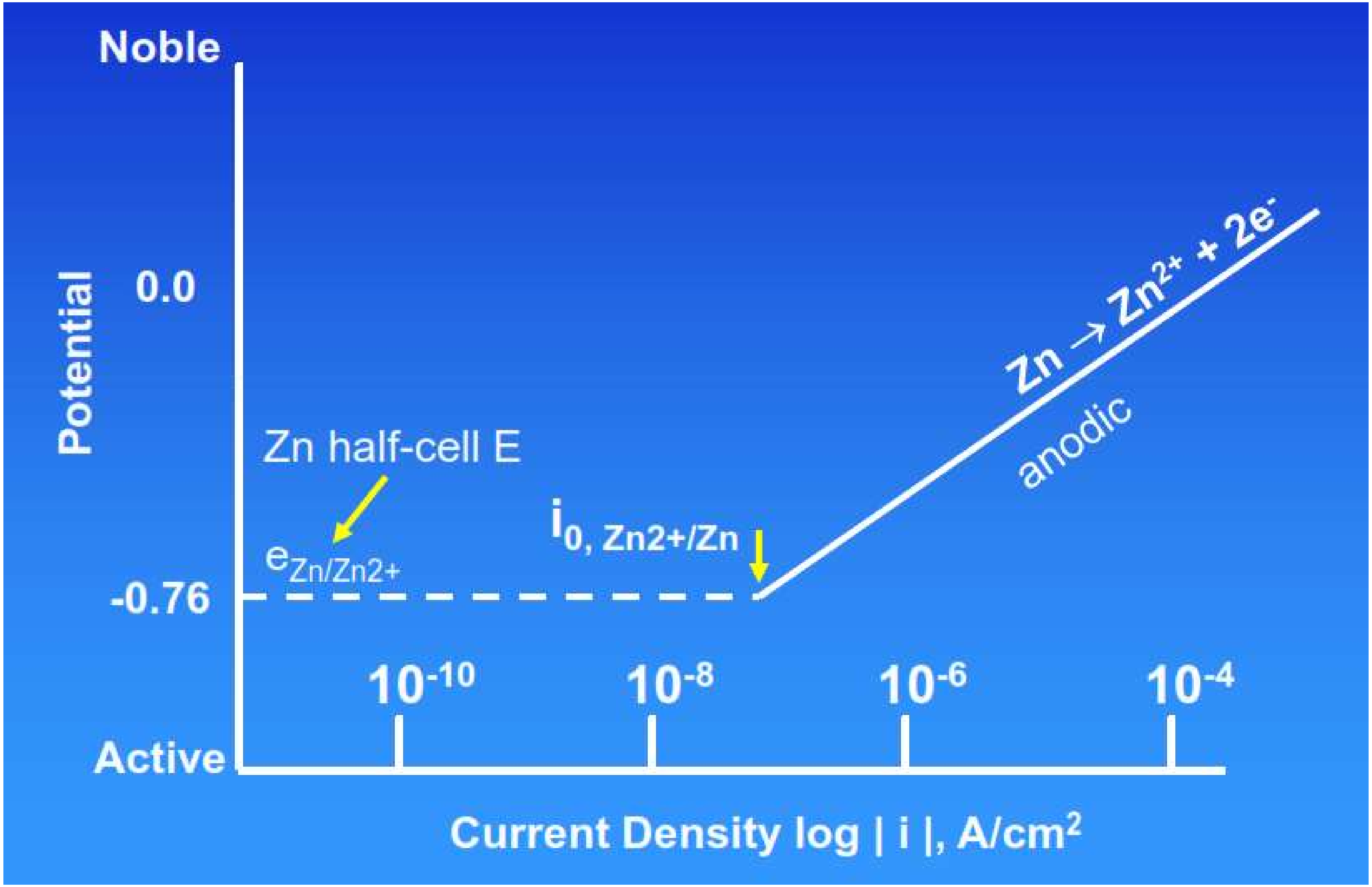
The Evans diagram is a kinetic diagram representing electrode potential in volts versus corrosion current in amperes per unit area. Figure 11.3 presents an Evans diagram for iron immersed in an acidic solution. Theoretically, four reactions are possible for this system, that is, iron dissolution to from ferrous ions (Fe^{2+}), the reverse of this process, that is, ferrous ions attaining electrons to form Fe, hydrogen ions in solution forming hydrogen gas or the reverse of this process. Hence four E vs. i lines are presented in Fig. 11.3. For clarity the two thermodynamically feasible reactions are given as solid lines. An extrapolation of the portions of the two solid lines gives rise to an intersection at the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) for the given system. Evans diagrams provide kinetic information, that is, the rate of a corrosion reaction, as a function of the applied potential.

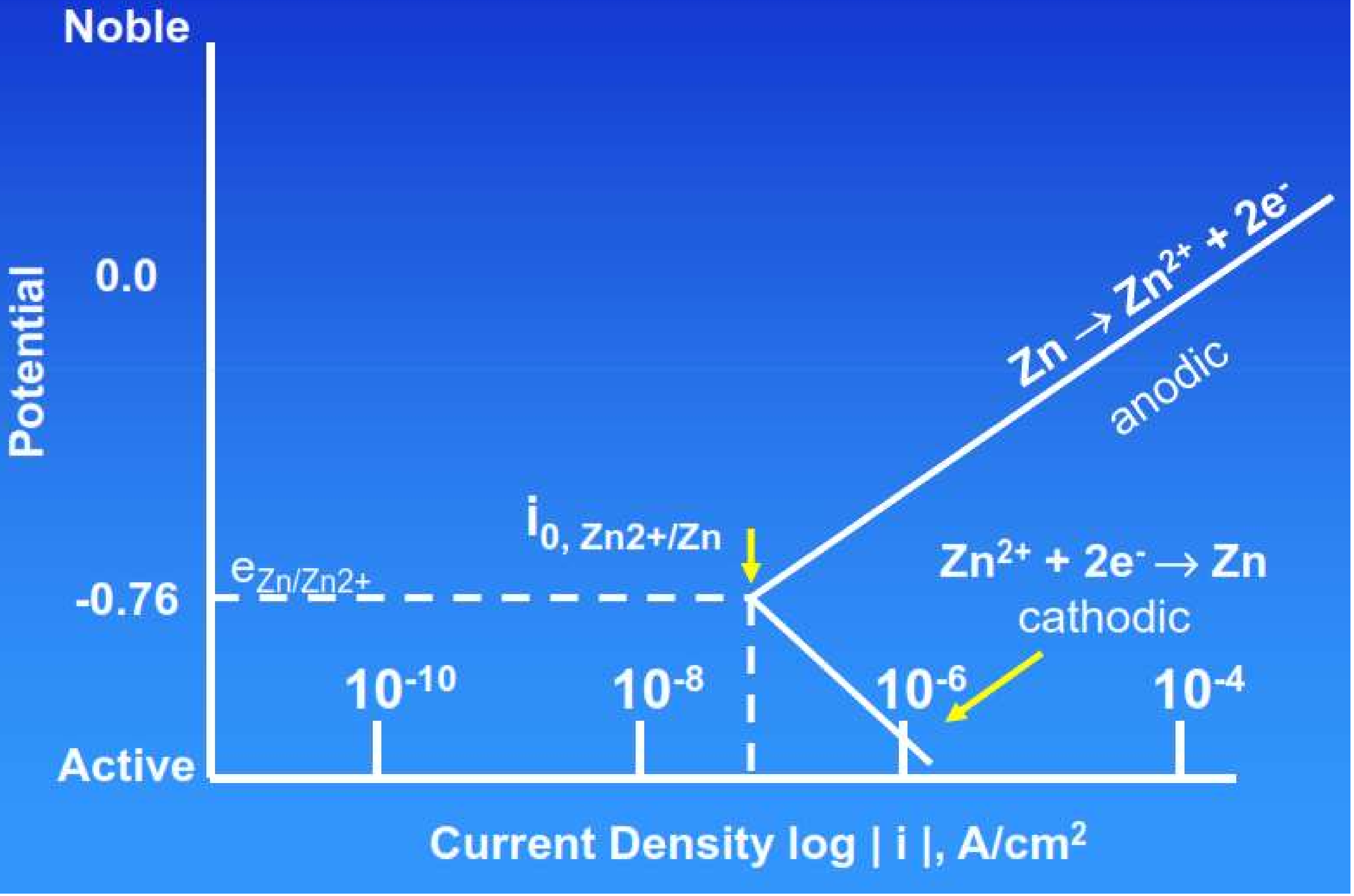


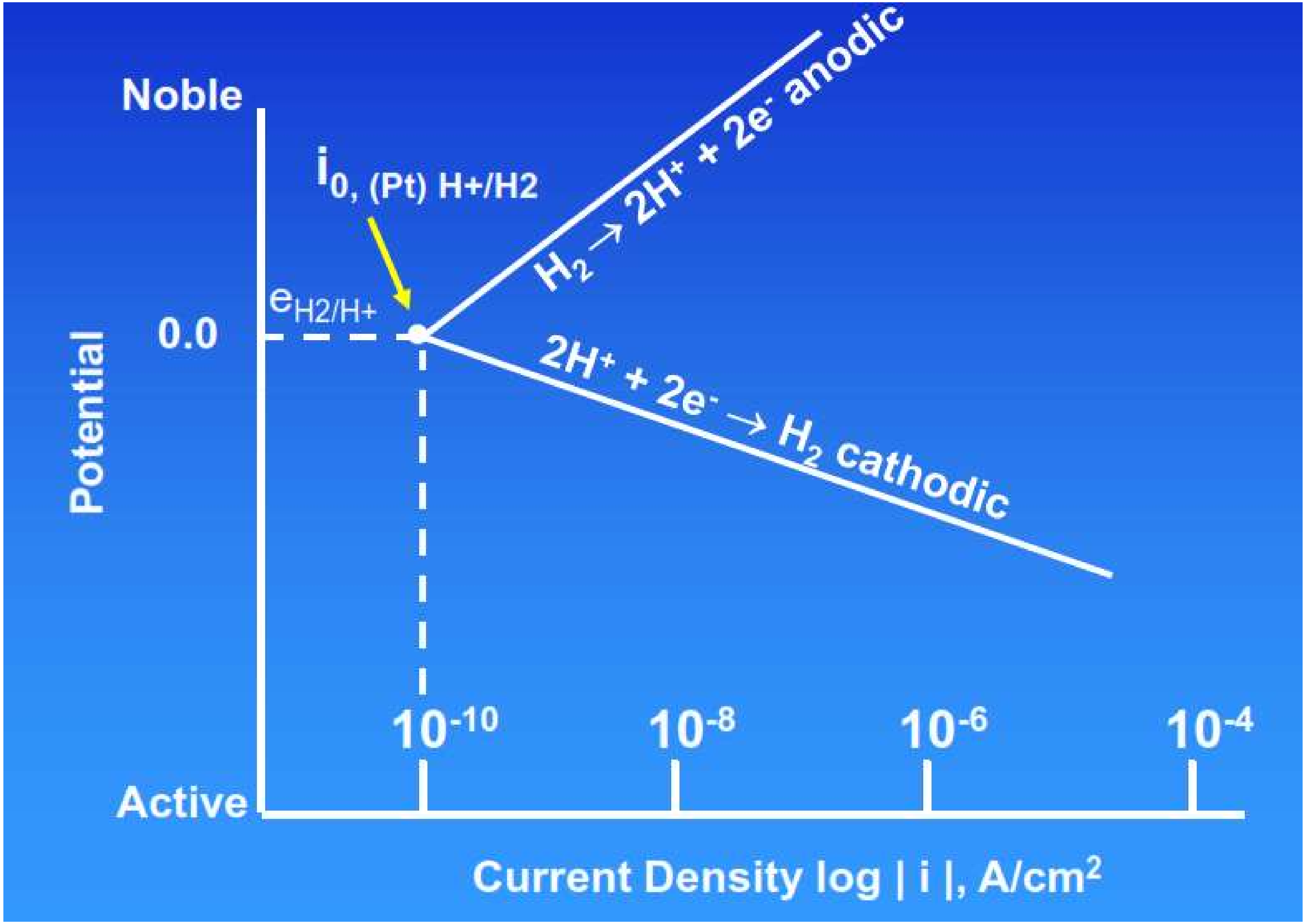


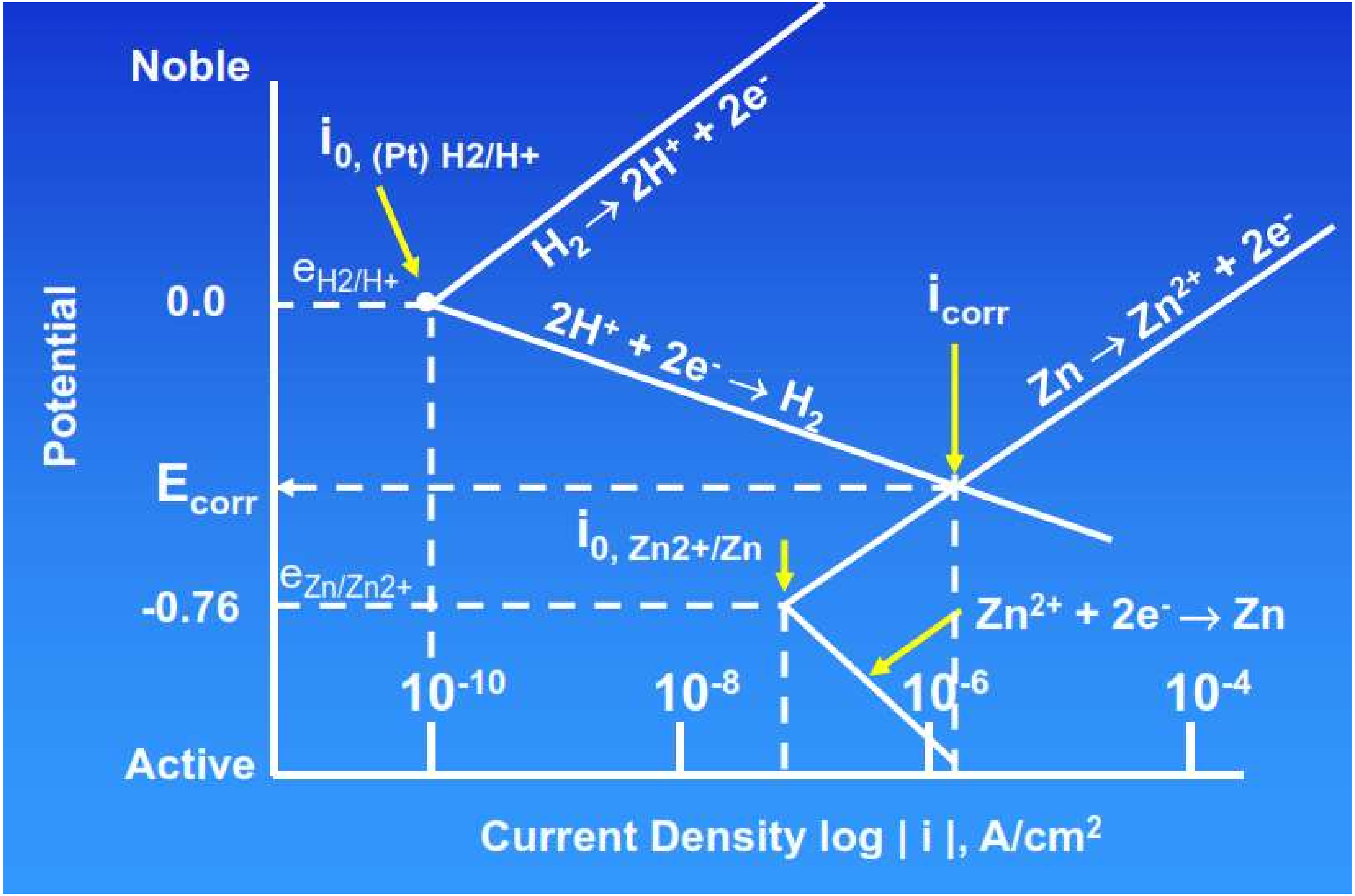
Mixed Potential Theory Example

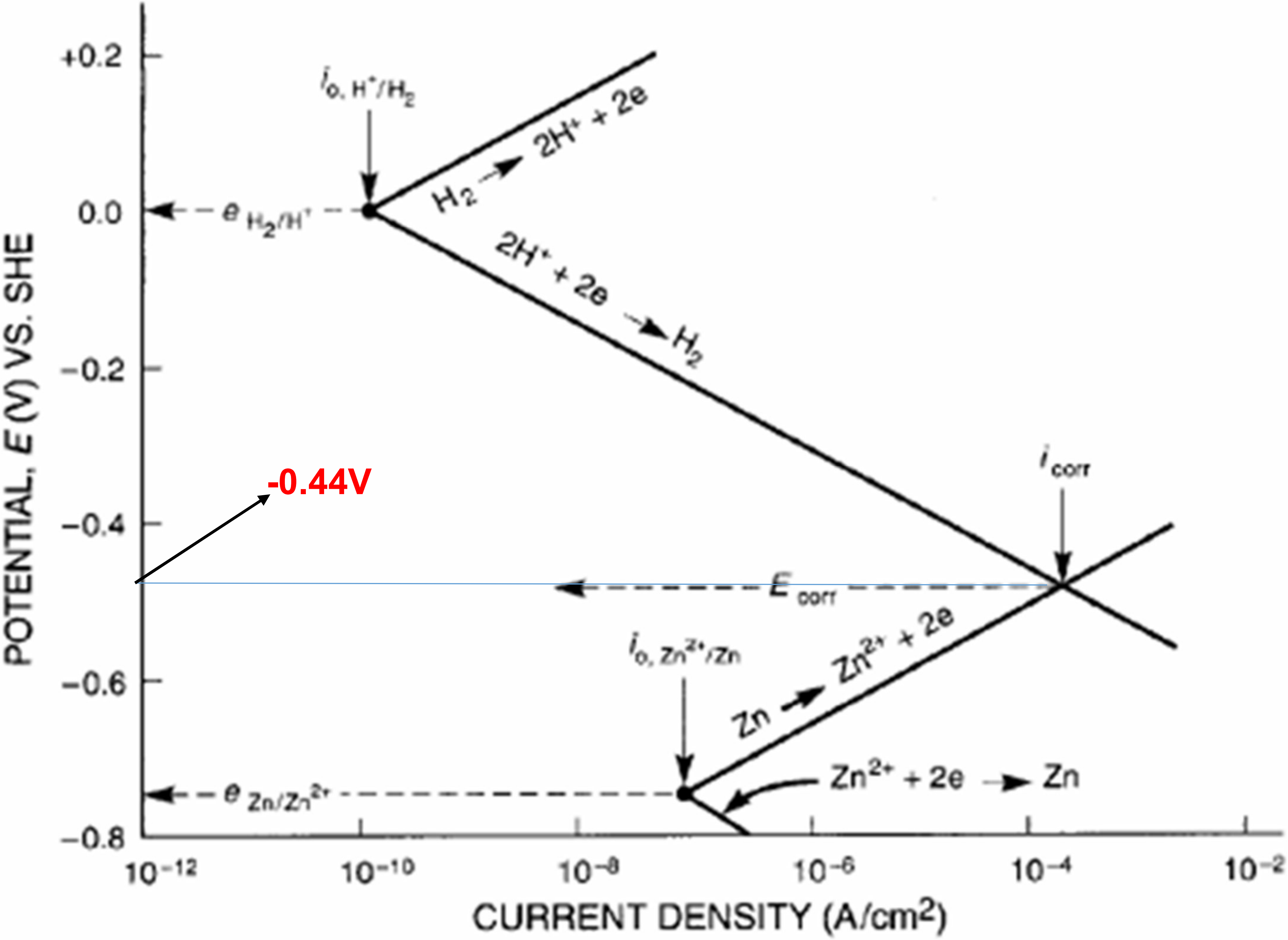
- Zn in acid
- $Zn \rightarrow Zn^{2+} + 2e^-$ Anode half-cell
- $2H^+ + 2e^- \rightarrow H_2$ Cathode half-cell
- Each half-cell has its own unique half-cell E and i_0
- However, the two half-cell Es cannot coexist separately on an electrically conductive surface
- Polarization of each reaction to some 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


Noble
Potential
0.0
-0.76
Active
Zn half-cell E
$e_{Zn/Zn2+}$
$i_{0,\ Zn2+/Zn}$
$Zn \rightarrow Zn^{2+} + 2e^-$
anodic
10^{-10}
10^{-8}
10^{-6}
10^{-4}
Current Density log | i |, A/cm^2


Noble
Potential
0.0
-0.76
Active
$e_{Zn/Zn2+}$
$i_{0,\ Zn2+/Zn}$
$Zn \rightarrow Zn^{2+} + 2e^-$
anodic
$Zn^{2+} + 2e^- \rightarrow Zn$
cathodic
10^{-10}
10^{-8}
10^{-6}
10^{-4}
Current Density log | i |, A/cm^2


Noble
$i_{0,\ (Pt)\ H+/H2}$
$e_{H2/H+}$
0.0
Potential
Active
$H_2 \rightarrow 2H^+ + 2e^-$ anodic
$2H^+ + 2e^- \rightarrow H_2$ cathodic
10^{-10}
10^{-8}
10^{-6}
10^{-4}
Current Density log | i |, A/cm^2


Noble
Potential
Active
$i_{0, (Pt)\ H2/H+}$
$e_{H2/H+}$
0.0
E_{corr}
-0.76
$e_{Zn/Zn2+}$
$H_2 \rightarrow 2H^+ + 2e^-$
$2H^+ + 2e^- \rightarrow H_2$
i_{corr}
$Zn \rightarrow Zn^{2+} + 2e^-$
$i_{0,\ Zn2+/Zn}$
$Zn^{2+} + 2e^- \rightarrow Zn$
10^{-10}
10^{-8}
10^{-6}
10^{-4}
Current Density log | i |, A/cm^2



POTENTIAL, E (V) VS. SHE
+0.2
0.0
−0.2
−0.4
−0.6
−0.8
$i_{o,\,H^+/H_2}$
e_{H_2/H^+}
$H_2 \rightarrow 2H^+ + 2e$
$2H^+ + 2e \rightarrow H_2$
-0.44V
i_{corr}
E_{corr}
$Zn \rightarrow Zn^{2+} + 2e$
$i_{o,\,Zn^{2+}/Zn}$
$Zn^{2+} + 2e \rightarrow Zn$
$e_{Zn/Zn^{2+}}$
10^{-12}
10^{-10}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
CURRENT DENSITY (A/cm^2)

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

Corrosion Potential E_{corr}:

When two half cell reactions occur simultaneously on a metal surface, both of them will change the potential to an intermediate value called the corrosion potential. At the corrosion potential all the rates (current densities) are equal: $i_c = i_a = i_{corr}$. This is schematically shown in the figure.

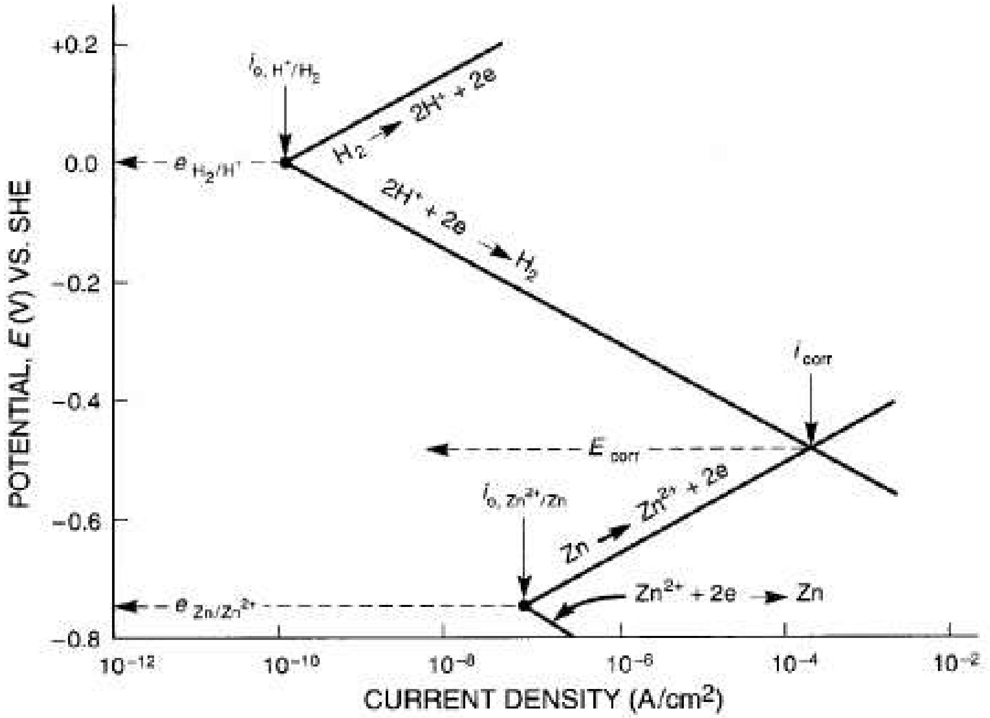


FIGURE 3.7 Polarization of anodic and cathodic half-cell reactions for zinc in acid solution to give a mixed potential, E_{corr}, and a corrosion rate (current density), i_{corr}. *(From M. G. Fontana,* Corrosion Engineering, *3rd ed., McGraw-Hill, New York, p. 457, 1986. Reprinted by permission, McGraw-Hill Book Company.)*

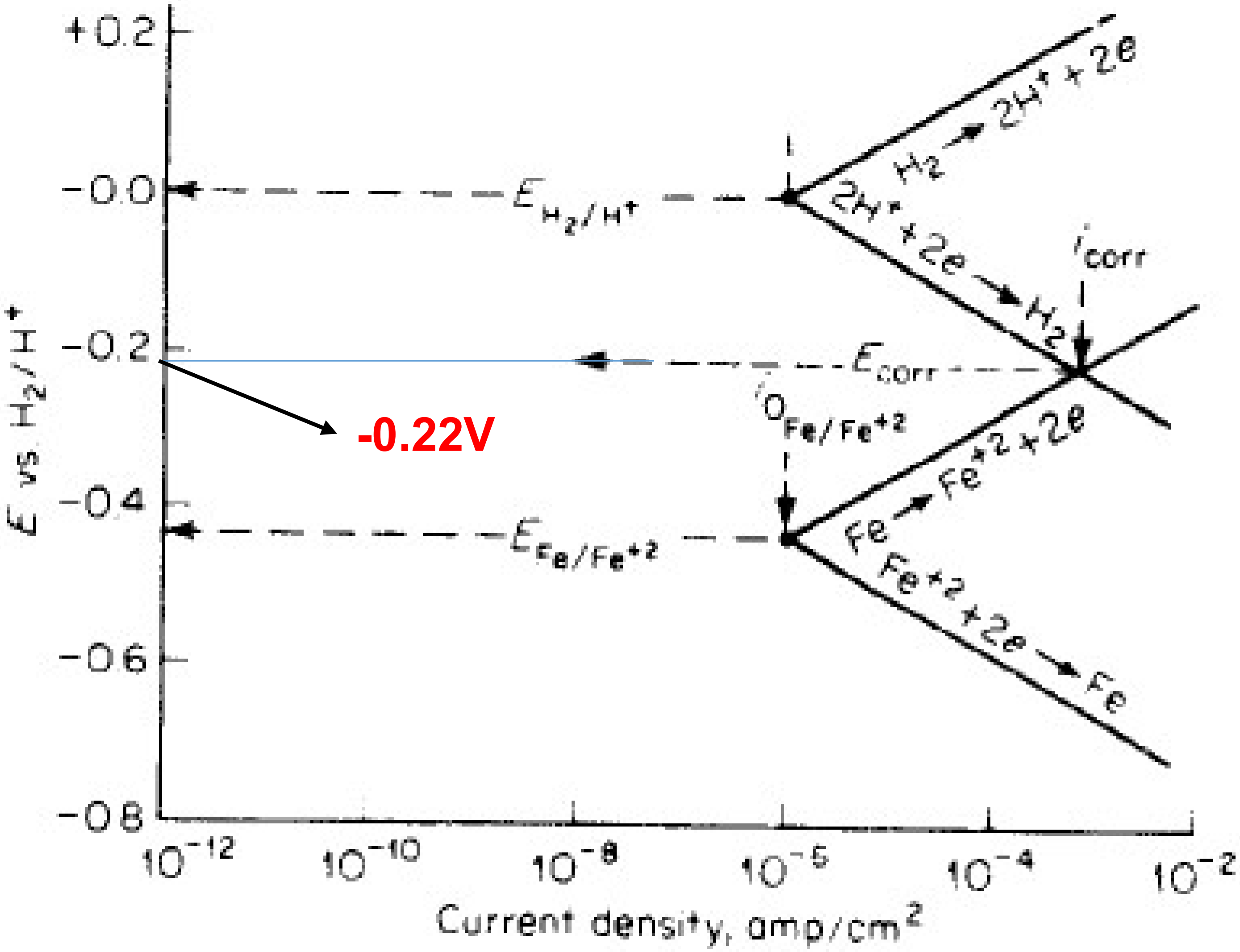
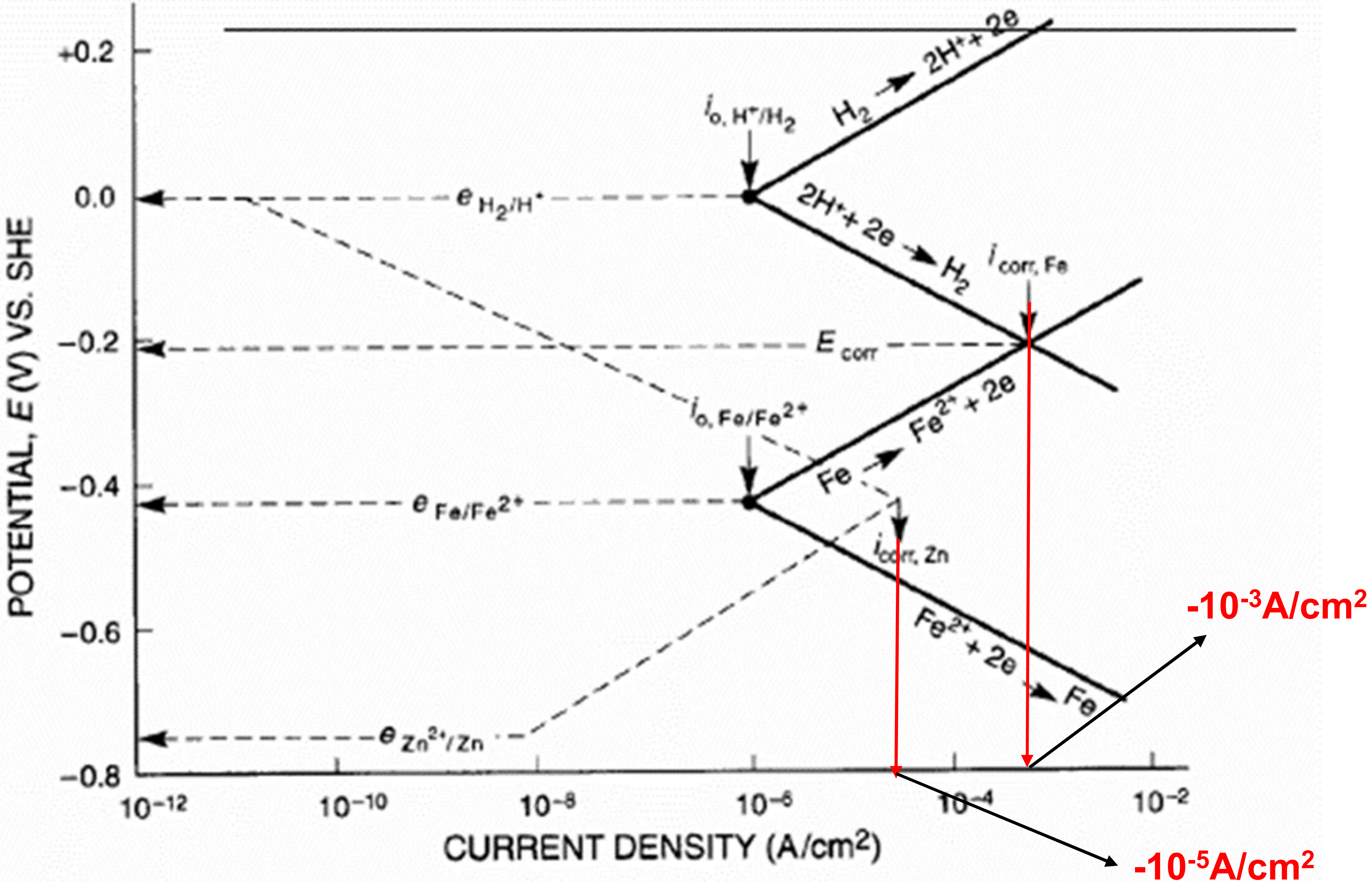


Figure 9-19 Schematic representation of electrode kinetic behavior of pure iron in acid solution.

Effect of Exchange Current Density:

The exchange current density often outweighs the thermodynamic driving force in determining the rate of reaction. This is shown for the example of Fe and Zn. The half cell potential for the anodic oxidation of Fe is about –0.44V, while for Zn it is about –0.76V. Therefore Zn should corrode before Fe. Figure 3.8. shows the polarization diagrams for Zn (dashed lines) and Fe (solid lines). One can see that the current density at the corrosion potential for Fe is larger than the current density for Zn at the respective potential. Therefore Zn corrodes slower than Fe, although it has the more negative E_{corr}. Both i_{corr} and E_{corr} are used in corrosion protection of iron with a Zn coating, as the Zn starts to corrode first (E_{corr}), and the corrosion is much slower than that of Fe (i_{corr}).

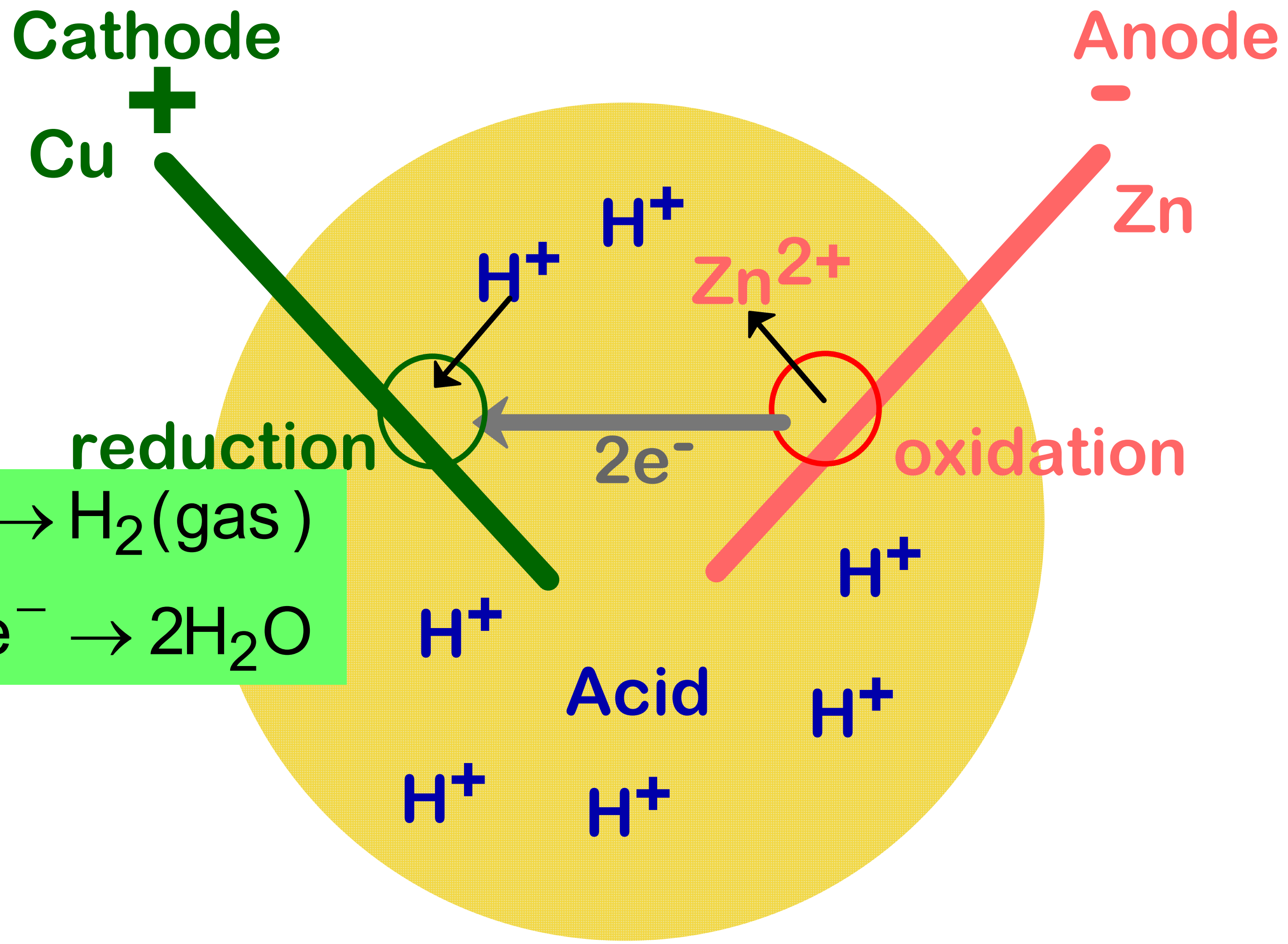


-10^{-3}A/cm^2

-10^{-5}A/cm^2

FIGURE 3.8 Comparison of electrochemical parameters for iron and zinc in acid solution, demonstrating the importance of i_o on determination of corrosion rates. Dashed lines represent lines from Figure 3.7 superimposed for comparison.

CORROSION IN A GRAPE FRUIT?

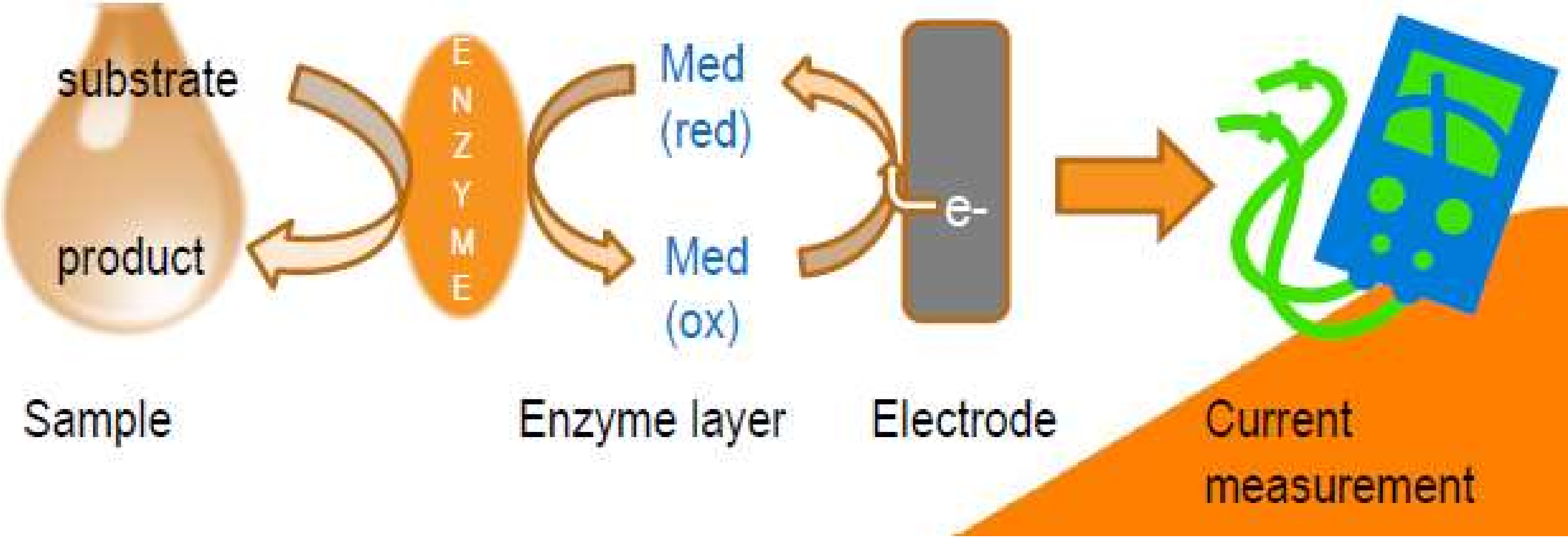


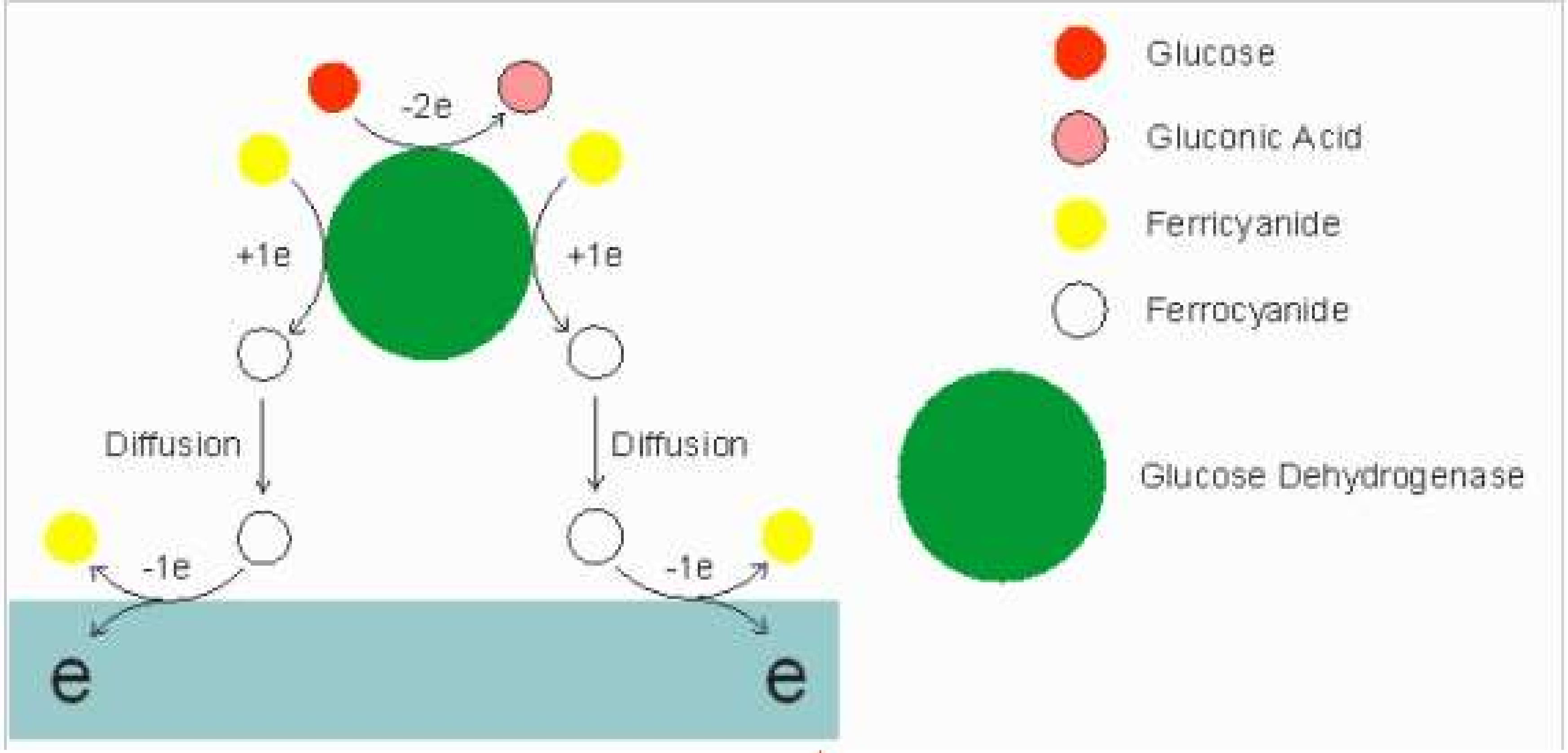
$$2H^+ + 2e^- \rightarrow H_2(gas)$$

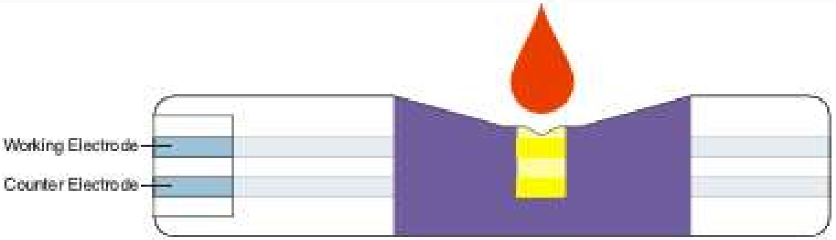
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Grape fruits juice contain different organic compounds (e.g. alkaloids, tannins, pigments, organic and amino acids) and most are known to have inhibitive action

- Electrochemical biosensors are analytical devices which can regognize their target molecule from sample. The recognition is tranduced to electrical signal in proportion to the target molecule.
- Electrochemical transduction is based on the **movement of electrons in the redox reactions** detected when a potential is applied between electrodes.



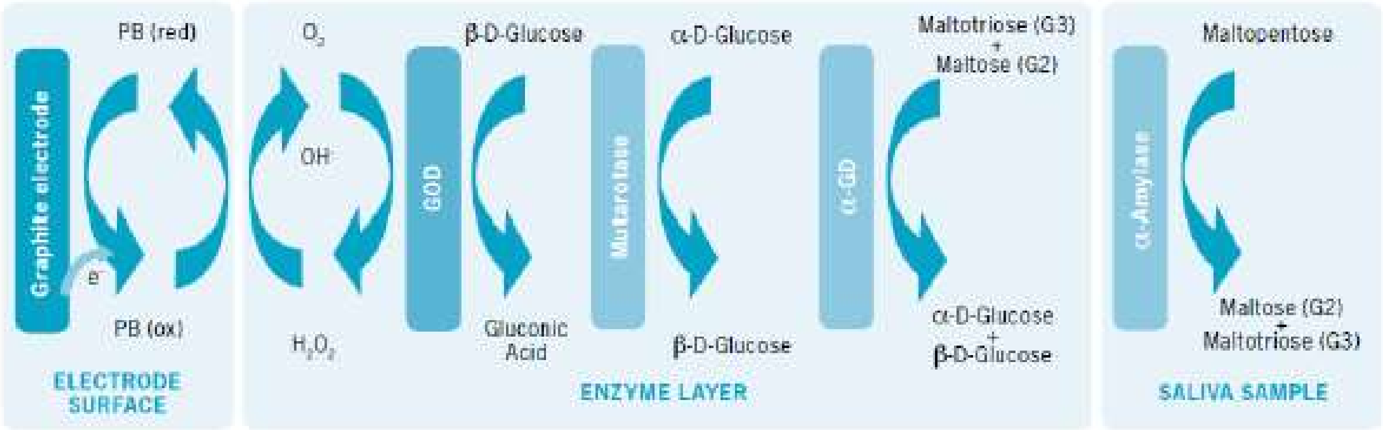




1. Glucose first reacts with the enzyme glucose dehyrogenase. Glucose is oxidized to gluconic acid and the enzyme is temporarily reduced by two electrons transferred from glucose to the enzyme.
2. The reduced enzyme next reacts with the mediator (Mox), transferring a single electron to each of two mediator ions. The enzyme is returned to its original state, and the two Mox are reduced to Mred.
3. At the electrode surface, Mred is oxidized back to Mox and the measured current is used to determine the concentration of glucose in the sample.

Saliva alfa amylase sensor for stress monitoring

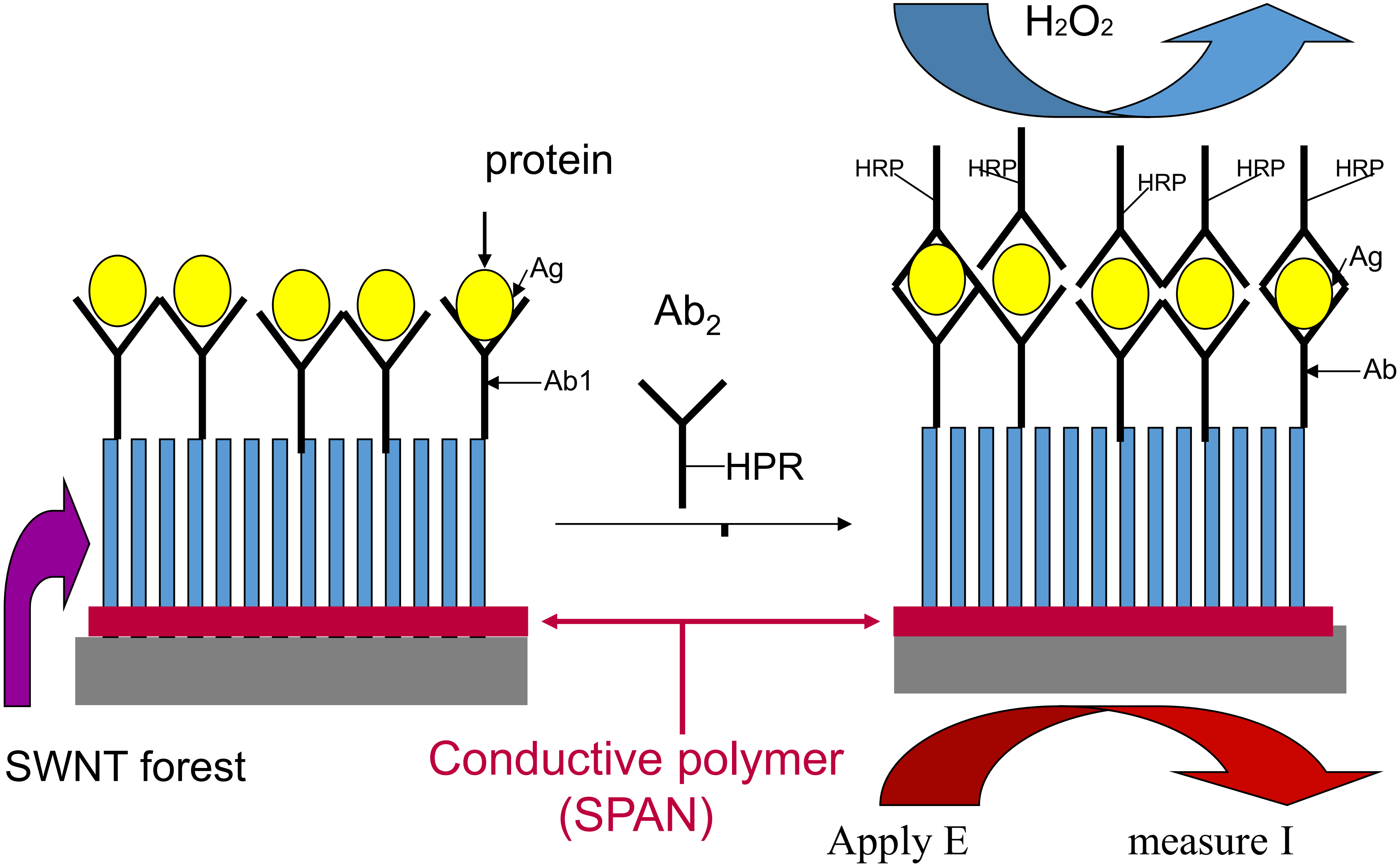
- Human saliva α-amylase is mainly involved in the digestion of starch in the oral cavity. Several studies have shown that increased levels of salivary α-amylase (sAA) levels are related to physical and psychological stress.
- Potential marker to stress palette with other markers (e.g.cortisol, glucocorticoids)
- Detection based on three enzymatic sensor, published by Dr. Sesay and coworkers.



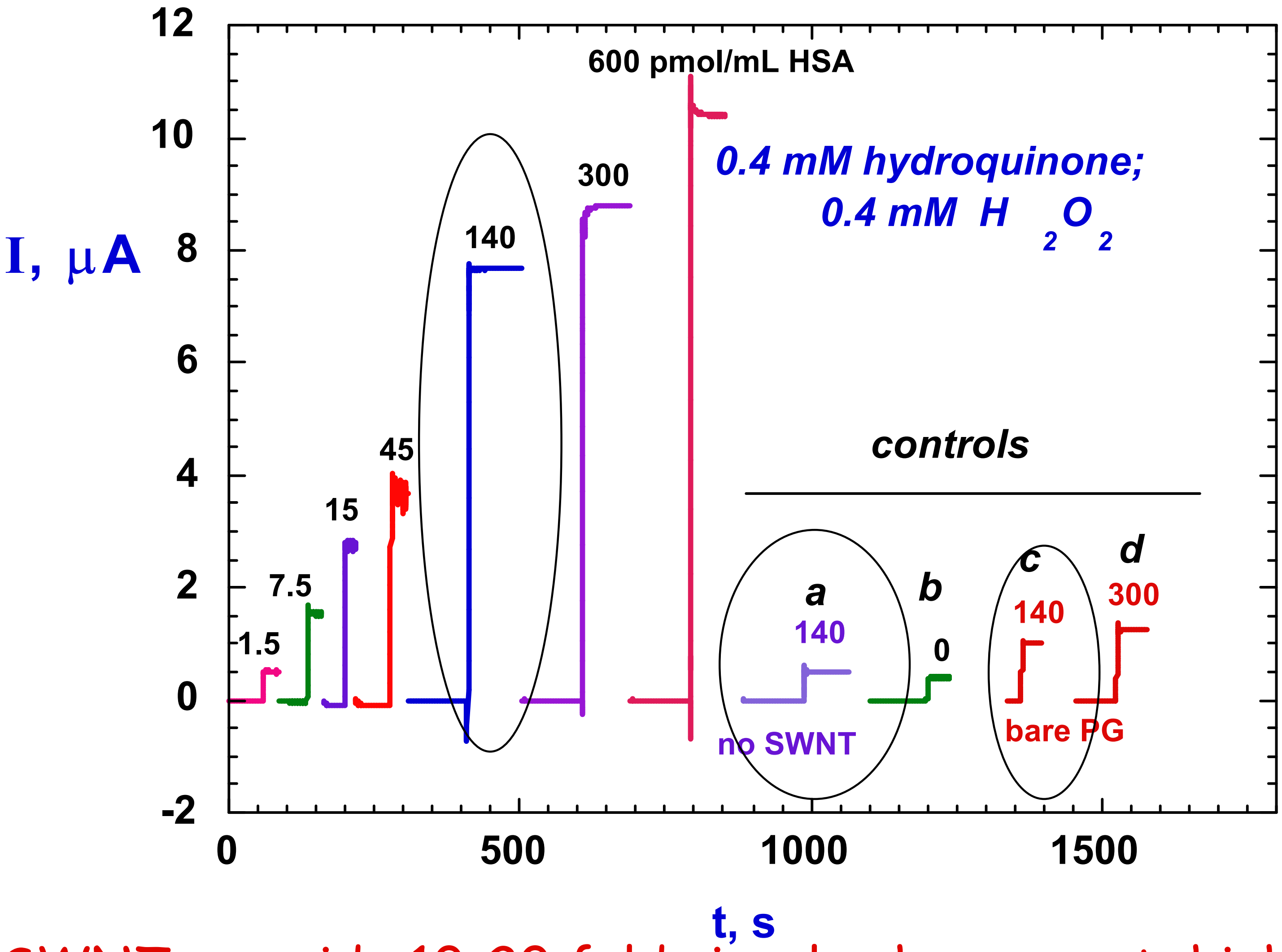
Detection pathway for saliva α-amylase.

Mahosenaho, Caprio, Micheli, Sesay, Palleschi and Virtanen (2010). A disposable biosensor for the determination of alpha-amylase in human saliva. Microchimica Acta. Volume 170, Issue 3-4, pp 243-249.

Sandwich Electrochemical Immunosensor Proteins



Amperometry Detection of Human Serum albumin



- SWNTs provide 10-20 fold signal enhancement; high surf. area
- Nanotubes aged in DMF □ fewer defects □ denser forests

. Xin Yu, Sang Nyon Kim, Fotios Papadimitrakopoulos and James F. Rusling, "Protein Immunosensor Using Single-Wall Carbon Nanotube Forests with Electrochemical Detection of Enzyme Labels", *Molecular Biosystems,* **2005** , *1*, 70 -78.

Corrosion Measurement Techniques

- Polarization curves
- Open Circuit Potential Decay
- Linear Polarization Resistance
- AC Impedance Measurement
- Electrochemical Noise Measurement
- Weight Loss Measurement

Summary and Conclusions

- ❑Corrosion of materials leading to degradation of material of properties and is a great concern to society

- ❑Corrosion plays an important role in technology areas which include energy production (power plants, oil & gas etc), bio-medical engineering (implants), water distribution & sewerage, electronics and nanotechnology

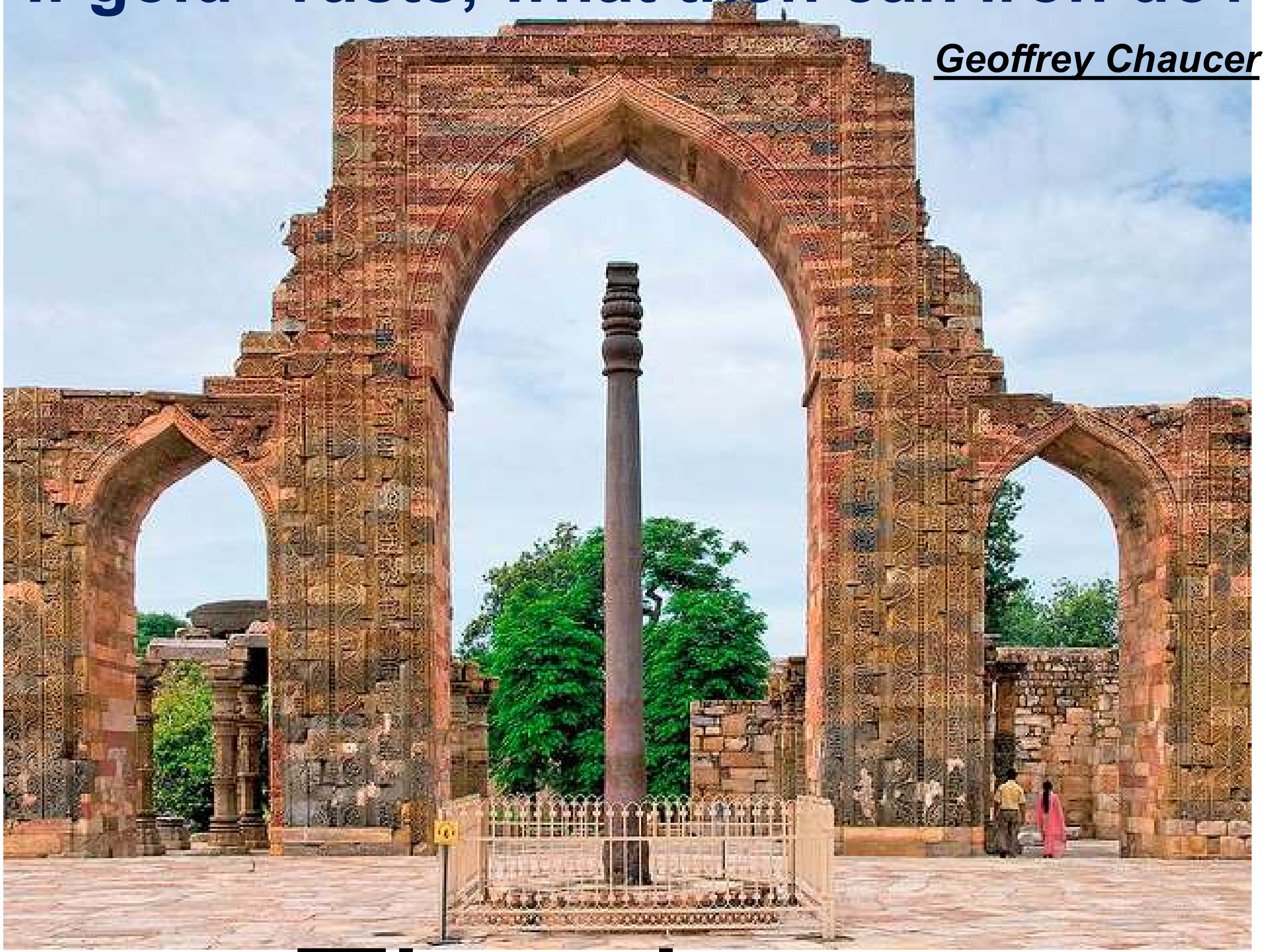
- ❑ Advances in corrosion control are integral to the development of better technologies that make current, legacy, and future engineered products, systems, an infrastructures more sustainable and less vulnerable.

- ❑ Implement best design practices for better corrosion management

- ❑ Country needs corrosion knowledge engineers and an active corrosion research community

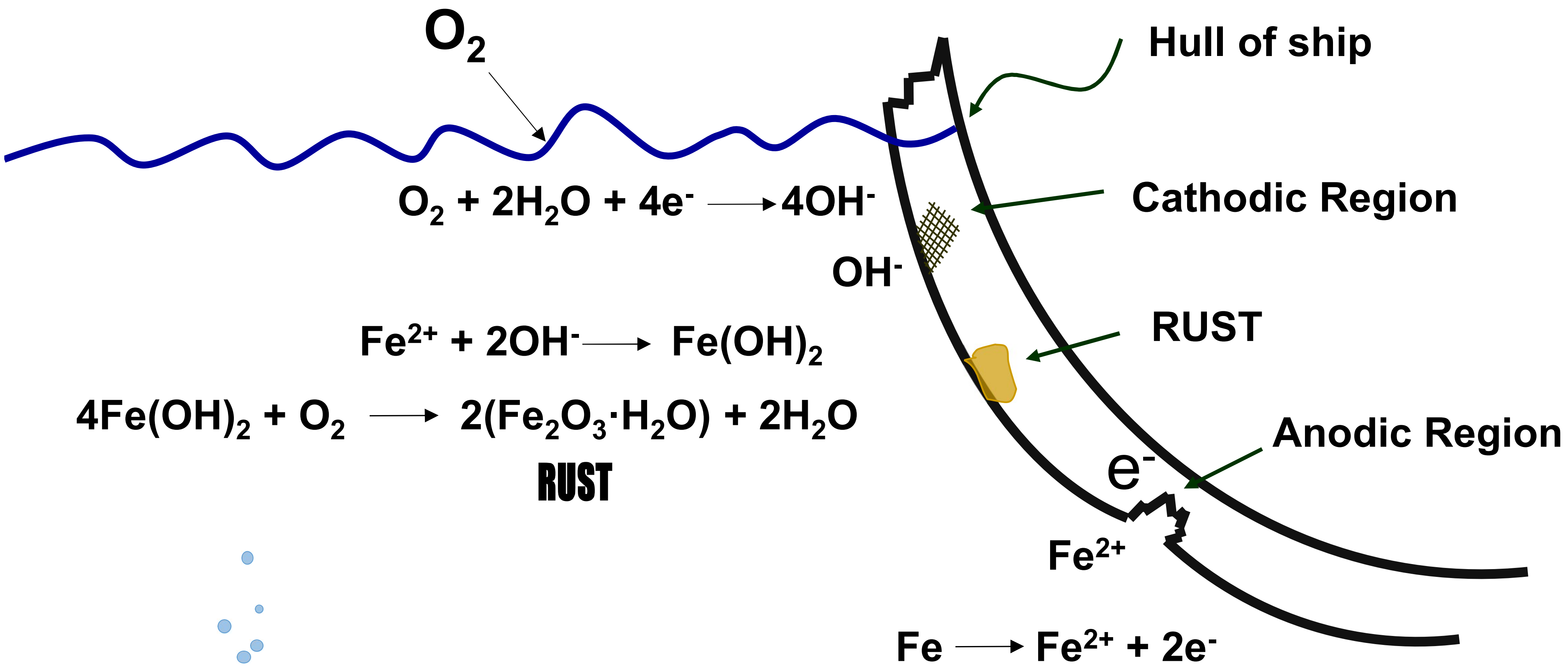
“If gold rusts, what then can iron do?”

Geoffrey Chaucer



Thank you

Corrosion of a Ship's Hull Anodic and Cathodic Regions



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

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

$$4Fe(OH)_2 + O_2 \longrightarrow 2(Fe_2O_3 \cdot H_2O) + 2H_2O$$

RUST

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

Electrons Migrate from Anodic to Cathodic Region