GALVANIC CORROSION

Remember - electrochemistry basics in aqueous solution, metal dissolution is ANODIC:

$$M \rightarrow M^{n+} + ne$$
$$\text{(e.g., } Fe \rightarrow Fe^{2+} + 2e\text{)}$$

and there are several possible CATHODIC reactions:

- **hydrogen evolution (acids)**
  $2H^{+} + 2e \rightarrow H_2$
- **oxygen reduction (acids)**
  $O_2 + 4H^{+} + 4e \rightarrow 2H_2O$
- **oxygen reduction (neutral or base)**
  $O_2 + 2H_2O + 4e \rightarrow 4OH^{-}$
- **metal ion reduction**
  $M^{3+} + e \rightarrow M^{2+}$
- **metal deposition**
  $M^{+} + e \rightarrow M$

More than one oxidation and more than one reduction reaction can occur during corrosion.

MULTIPLE CATHODIC REACTIONS ARE IMPORTANT.

Thus, metals tend to dissolve more readily in aerated acids than in pure acids; oxygen reduction AND hydrogen evolution can occur. Also, an "oxidizer" such as ferric ion as an impurity in commercial acids makes them much more corrosive than pure acids - extra cathodic reaction.

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

NOTE: corrosion in sea water or fresh water is usually governed by oxygen reduction; if water is de-aerated, it becomes much less corrosive because the main reaction:

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

can no longer occur.

<u>REMEMBER</u>: the metal dissolution reaction (corrosion) must always be balanced by one or more reduction reactions:

e.g. $2Fe \rightarrow 2Fe^{2+} + 4e$

$\underline{O2 + 2H_2O + 4e \rightarrow 4OH^-}$

add $2Fe + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$ (ppt)

$2Fe(OH)_3 \leftarrow 1/2\ O_2 + H_2O + 2Fe(OH)_2$

"rust" (oxidizes)

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

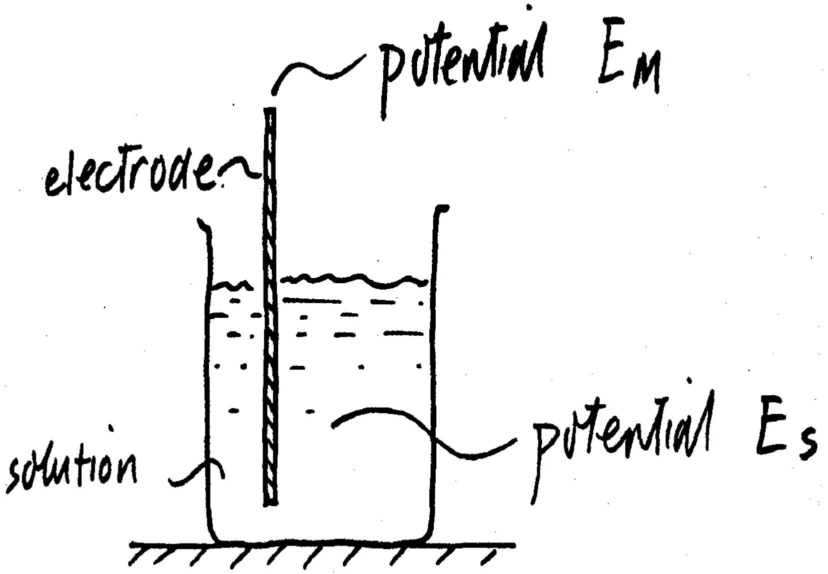
(the "nail in copper sulphate" trick!); clearly, the iron wants to be in solution more than the copper;

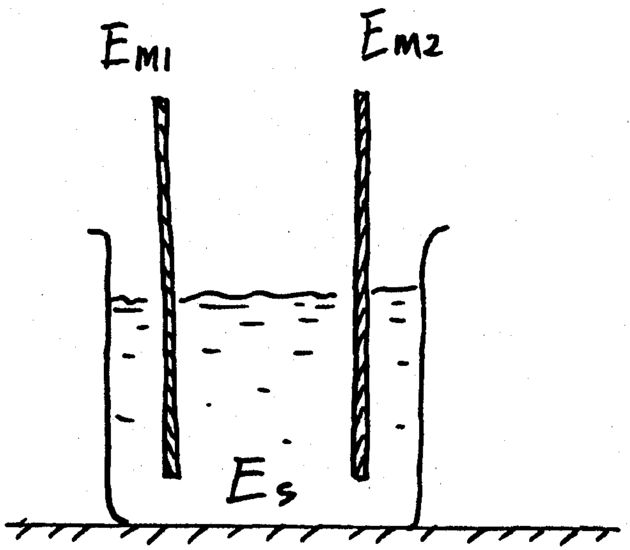
the copper is more NOBLE than the iron;

the iron is more <u>ACTIVE</u> than the copper.

GALVANIC SERIES

A metal in contact with a solution establishes a POTENTIAL with respect to the solution.



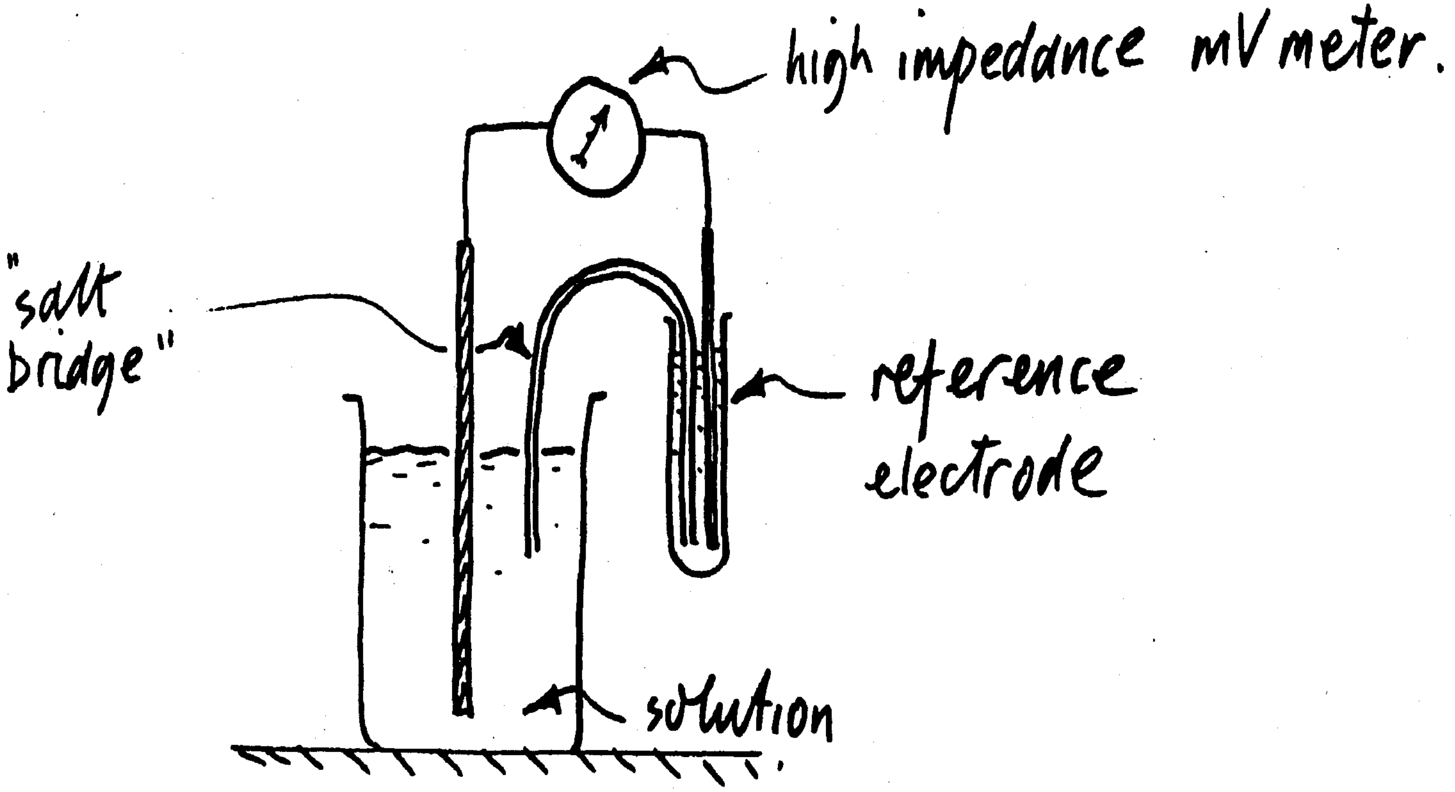


How would we measure the potential difference $E_m - E_s$?

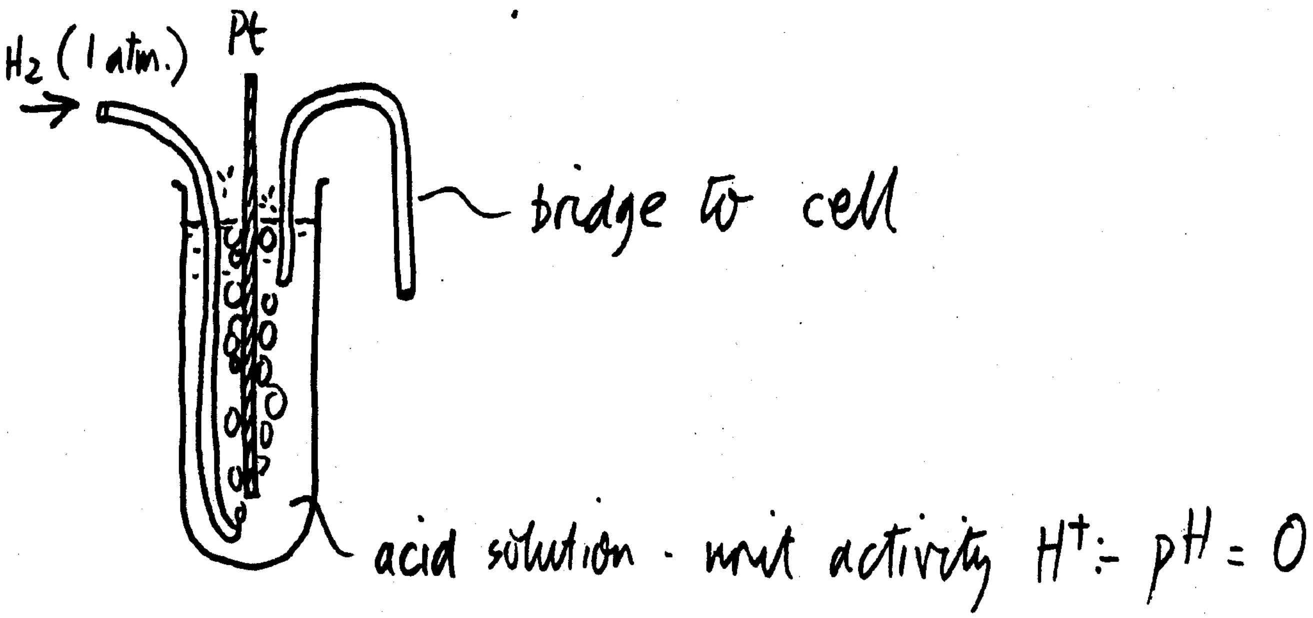
$E_m - E_s$ cannot be measured, we can only measure the difference between it and $E_m - E_s$ for another metal: $(E_{m1} - E_s) - (E_{m2} - E_s) = E_{m1} - E_{m2}$

<u>CHANGES</u> in potential of one electrode can be measured if the other electrode does not change. i.e., if it is a "reference electrode".

There are several reference electrodes which are constant so long as no current is drawn from them; potentials relative to a reference electrode are therefore measured with meters (e.g., milli-voltmeters) of high impedance.



A metal in contact with a solution <u>of its own ions</u> at unit activity (thermodynamic concentration) establishes fixed potential differences with respect to every other metal in the same condition <u>OF EQUILIBRIUM</u> (potentials are "reversible"); THEREFORE we can set up a series of standard electrode potentials with respect to some reference electrode; the standard hydrogen electrode (SHE) is chosen to have a potential of zero at 25°C.



Standard emf series of metals

	Metal-metal ion equilibrium (unit activity)	Electrode potential vs. normal hydrogen electrode at 25°C, volts
↑	Au-Au^{+3}	+1.498
	Pt-Pt^{+2}	+1.2
Noble or Cathodic	Pd-Pd^{+2}	+0.987
	Ag-Ag^{+}	+0.799
	Hg-Hg_2^{+2}	+0.788
	Cu-Cu^{+2}	+0.337
	H_2-H^{+}	0.000
	Pb-Pb^{+2}	-0.126
	Sn-Sn^{+2}	-0.136
	Ni-Ni^{+2}	-0.250
	Co-Co^{+2}	-2.777
	Cd-Cd^{+2}	-0.403
	Fe-Fe^{+2}	-0.440
	Cr-Cr^{+3}	-0.744
	Zn-Zn^{+2}	-0.763
Active or anodic	Al-Al^{+3}	-1.662
	Mg-Mg^{+2}	-2.363
↓	Na-Na^{+}	-2.714
	K-K^{+}	-2.925

This has the accepted sign convention; however, some workers use opposite sign convention.

Source: A.J. de Bethune and N. A. S. Loud, "Standard Aqueous Electrode Potentials and Temperature Coefficient at 25°C," Clifford A. Hampel, Skokie, Ill., 1964. See also Table 9-1. These potentials are listed in accordance with the Stockholm Convention. See J. O'M. Bockris and A. K. N. Reddy, Modern Electrochemistry, Plenum Press, New York, 1970.

REFERENCE ELECTRODES

Ag/ solid Ag Cl in 0.1N K Cl: + 0.288 V (SHE)

Cu/ satd. Cu SO_4: + 0.316 V (SHE)

Hg/ solid Hg_2Cl_2 in 0.1 N KCL: + 0.334 V (SHE)

By coupling two <u>reversible</u> electrodes together, we get a fixed potential difference:

e.g.

$$Ag / Ag^{+} \quad - \quad Cu^{2+} / Cu$$

$$0.799\ V \quad - \quad 0.337 V$$

$$= 0.462\ V$$

(Discuss the possibility of making a reversible electrode out of an alloy such as brass.)

N.B. **If we drew current from two such electrodes (reversible Ag, Cu) THEY WOULD NO LONGER BE AT EQUILIBRIUM. THE REVERSIBILITY WOULD BE DESTROYED.**

- **silver would be deposited more than silver ions would be formed;**
- **copper ions would be formed more than copper would be deposited;**

(remember, equilibrium or reversibility at an electrode means the rate of the "forward" reaction equals the rate of the "back" reaction).

N.B. **Corroding metals are not at equilibrium.**

NOR are they usually in contact with unit activity of their own ions.

THEREFORE the EMF series is an ideal system, which may be used as an indicator for practical situations.

IN GENERAL, as a rough guide:

any metal in the EMF series will displace from solution any metal above it

e.g., Fe displaces Cu from $CuSO_4$ solution,

Zn displaces H_2 from acid solution.

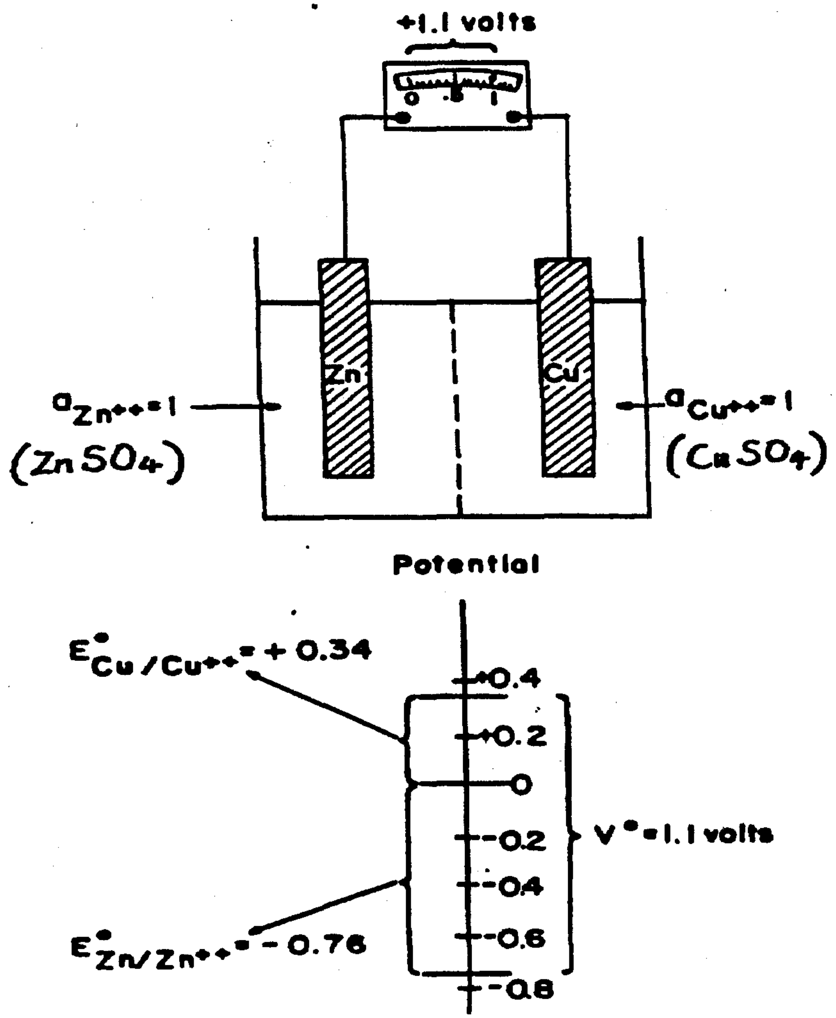
BUT "passivation" of some metals alters behavior; passivation is the formation of a very protective oxide layer that makes the metal noble.

E.g., Cr is a reactive element, but Cr metal is usually passivated and cathodic to most common metals (hence Cr plating).

Galvanic corrosion MAY arise when dissimilar metals are in contact in aqueous solution.

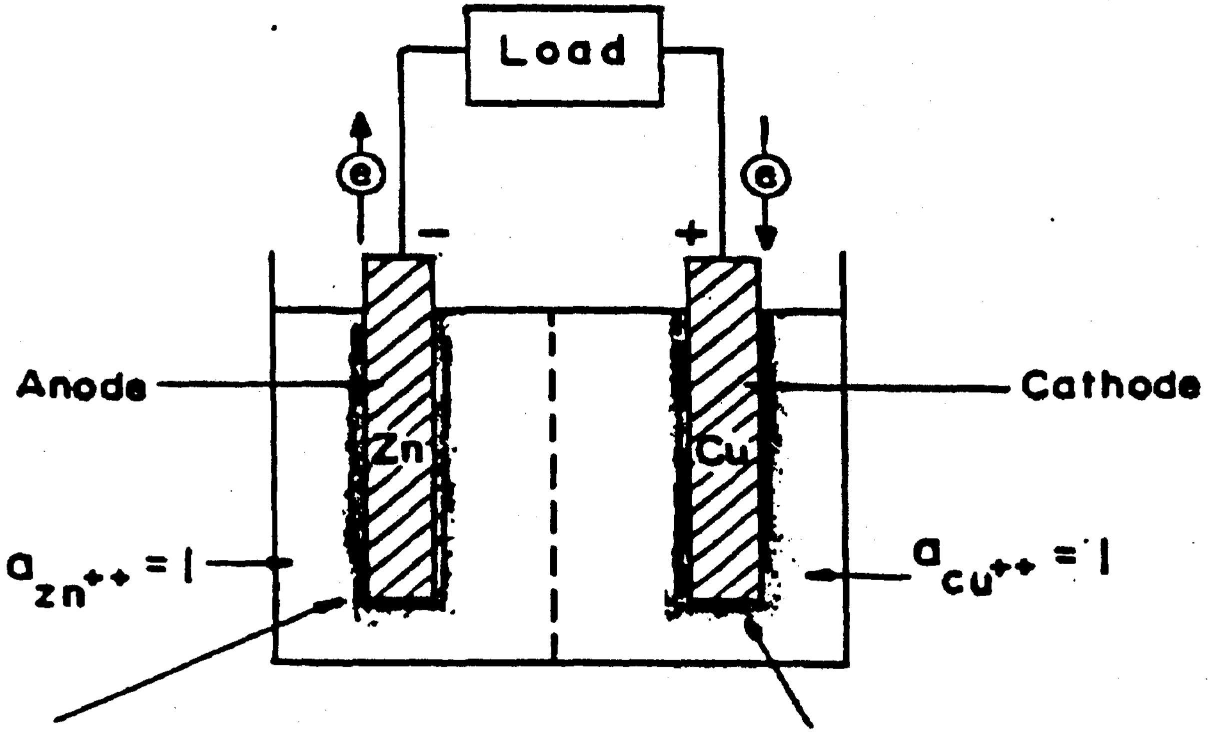
The potential difference between them will initiate attack, the corrosion rate depends on the surface reactions of (usually) both metals (i.e., we usually consider galvanic COUPLES of just two metals).

Galvanic potentials are made use of in batteries, e.g., the Daniel cell.



In the Daniel cell, the zinc electrode is 1.1V negative with respect to the copper electrode.

Which is the anode, the cathode? Which way does the electrical current flow?



Zn/Zn⁺⁺ Interface is site for de-electronation. (oxidation): $Zn \rightarrow Zn^{++} + 2e$

Cu/Cu⁺⁺ Interface is site for electronation (reduction): $Cu^{++} + 2e \rightarrow Cu$

The sign of the voltage on the Daniel cell indicates that, upon placing a load on the cell, a spontaneous de-electronation will occur on the zinc electrode; and electronation, on the copper electrode.

A Dry Cell. Dry cells are electrochemical energy storers in which the electrolyte is immobilized in the form of a paste. A typical dry cell is the Leclanche cell. A schematic diagram of this cell is shown below. The reactions occurring in the cell during discharge are:

at anode, $Zn \rightarrow Zn^{2+} + 2e$

at cathode, $2MnO_2 + 2H_3O^+ + 2e \rightarrow Mn_2O_3 + 3H_20$

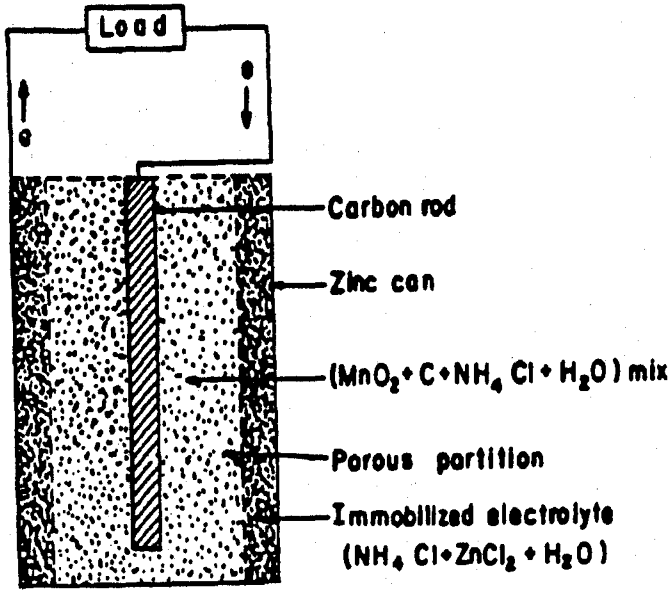
Since hydroxide ions are produced during working (because H_30^+ is consumed), the following irreversible side reactions occur:

$$OH^- + NH_4 + \rightarrow H_20 + NH_3$$

$$Zn^{2+} + 2NH_3 + 2Cl^- \rightarrow Zn(NH_3)_2Cl_2$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_20$$

$$ZnO + Mn_2O_3 \rightarrow Mn_2O_3\, ZnO$$



Owing to the above reactions, the cell is only partially rechargeable and this to such a small extent that it is never done in practice.

NOTE WELL:

The analogy between aqueous corrosion processes (e.g., galvanic couples) and cells / batteries is illuminating but limited. The cathodic reaction in galvanic corrosion is usually oxygen reduction or hydrogen evolution, not metal deposition.

To predict galvanic corrosion of couples in seawater, use the table of "Galvanic Series of some commercial metals and alloys in seawater" that follows.

↑
Noble or
cathodic

Platinum
Gold
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 Mn)
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)
Cadmium
Commercially pure aluminum (1100)
Zinc
Magnesium and magnesium alloys

Active or
anodic
↓

metals in a bracket can be coupled

note differences between active and passive

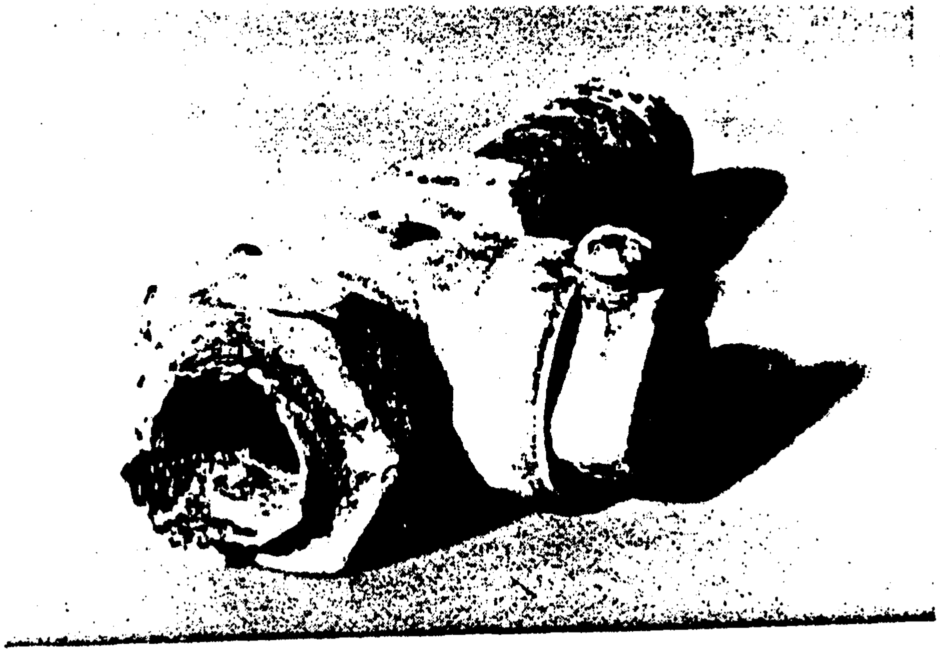
(also gives a rough guide for other environments)

EXAMPLES (from Fontana):

A yacht with a Monel hull and steel rivets became unseaworthy because of rapid corrosion of the rivets. Severe attack occurred on aluminum tubing connected to brass return bends. Domestic hot-water tanks made of steel fail where copper tubing is connected to the tank. Pump shafts and valve stems made of steel or more corrosion-resistant materials fail because of contact with graphite packing.

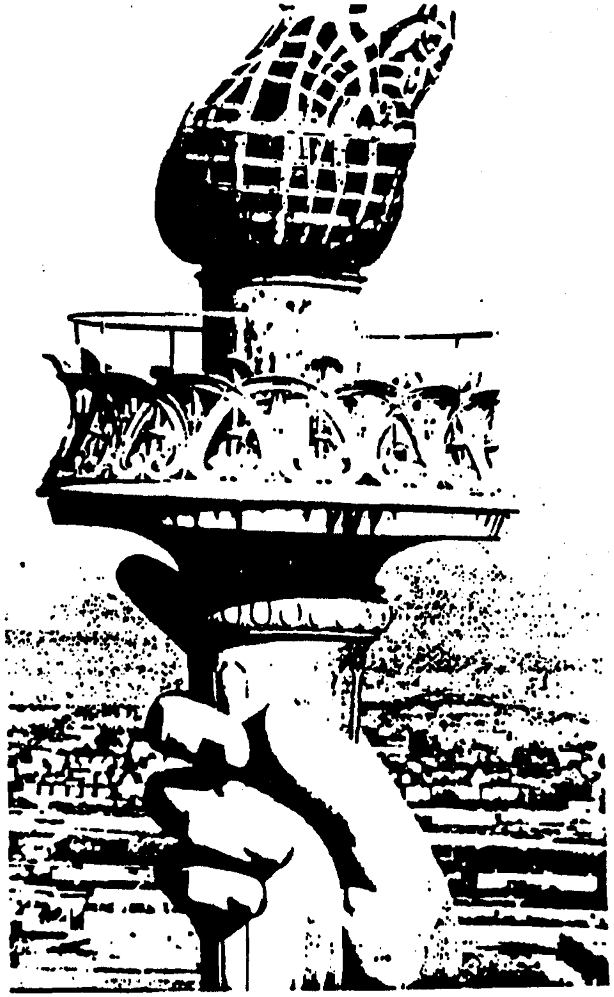
Other examples:

Galvanic corrosion of steel pipe at brass fitting in humid marine atmosphere.



Galvanic corrosion of painted steel auto body panel in contact with stainless steel wheel opening molding.

Moisture that collected on the inside of the Statue of Liberty caused galvanic corrosion of armature in contact with the copper skin. The copper skin on the nose was ruptured due to me forces of the resulting corrosion products. Courtesy of R. Baboian, Texas Instruments, Inc.



Rust staining of the Statue of Liberty torch due to galvanic corrosion of the iron armature in contact with the copper skin. Courtesy of R. Baboian, Texas Instruments, Inc.

Statue of Liberty

Surface oxides (e.g., "rust") are very important in galvanic corrosion:

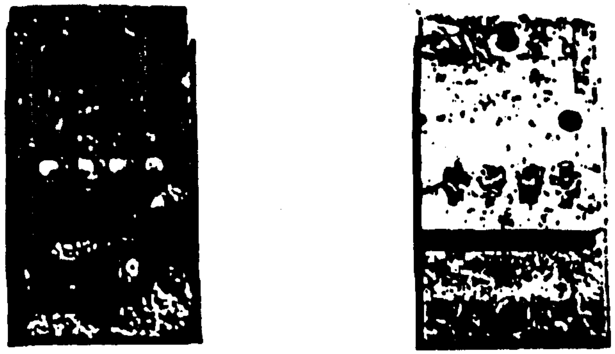
- bare metal is a better cathode than oxide-covered metal
  oxide interferes with hydrogen evolution and impedes oxygen diffusion.
  oxide puts an additional electrical resistance in the electrochemical circuit.

Oxide film effects:

- In standard EMF series, Al is more active than Zn (-1.662 v versus -0.763 v); we might expect that in a Zn-Al couple the Al would be anodic to the Zn. NOT SO!
  The Al_2O_3 film makes the Al more noble, so that Zn is anodic to it and actually protects it when coupled to it in solution (see "Galvanic Series in Seawater").
- The oxide film on stainless steel is electrically insulating and impedes the charge flow between galvanic couples.
- The oxide film on copper is easily reduced. The resulting exposed metal is an efficient cathode. Oxygen is readily reduced there. Galvanic couples with copper can be very corrosive.

NOTE: diffusion & reduction of O_2 often control galvanic corrosion, a large cathode area relative to the anode can be disastrous; such effects common at joints, where structures/components may be joined together with a different metal.

Effects of area relationship on corrosion of rivets (steel-copper couple) in seawater for 15 months.



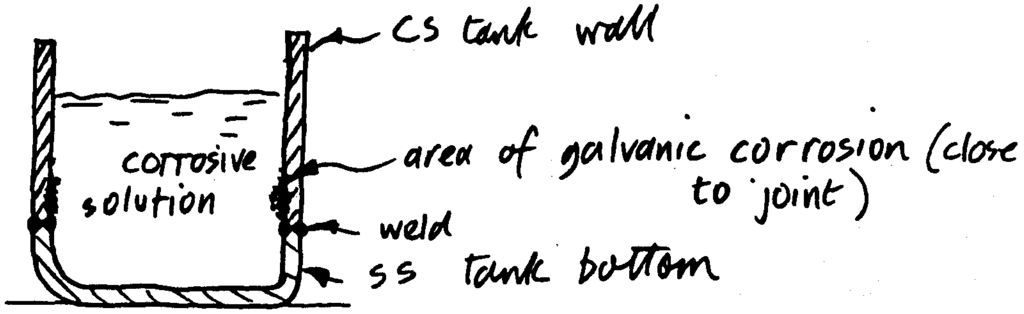
Copper rivets
in steel plate
Large anode
Small cathode

Steel rivets
in copper plate
Large cathode
Small anode

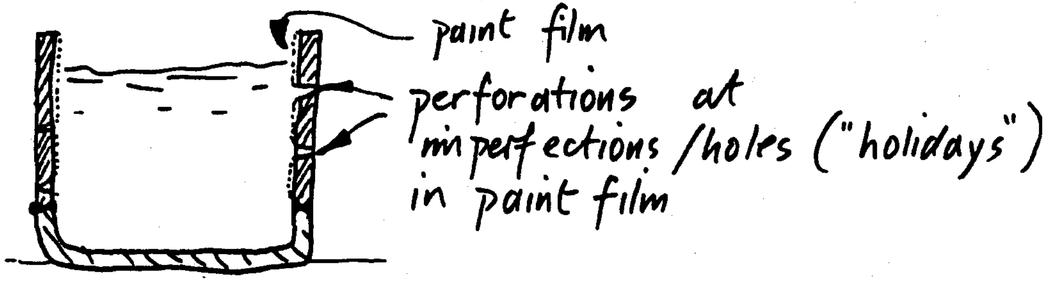
Discuss:

- **Two different metals of approximately the same area are joined to form a galvanic couple in a corrosive solution; we are to reduce the corrosion by coating (e.g., painting) one component of the couple. Do we coat the anode or the cathode?**

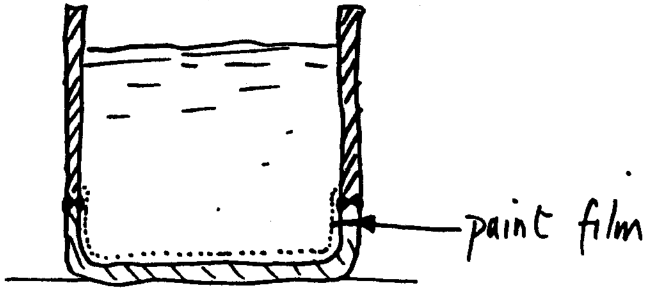
Example Before



After painting anode . . .



After painting cathode . . .



Generally..

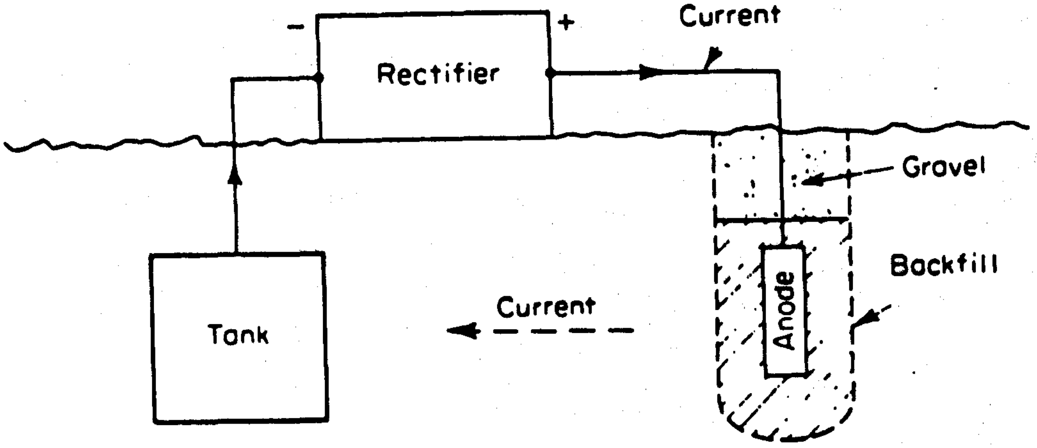
Galvanic corrosion is under cathodic control.... if we reduce the area of the Cathode (by coating, etc.) we reduce the corrosion; if we reduce the area of the Anode, corrosion will continue at the same rate but over a smaller area, so perforation etc. will occur sooner.

TO REDUCE GALVANIC CORROSION BY COATING, THE MORE CORROSION-RESISTANT (i.e., THE MORE NOBLE OR CATHODIC) COMPONENT OF THE COUPLE IS COATED.

CATHODIC PROTECTION

To reduce metallic corrosion, the component can made the CATHODE of a galvanic cell

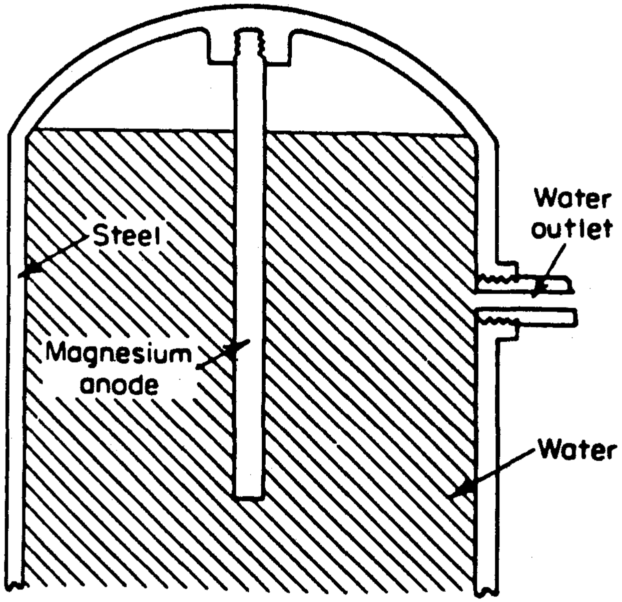
(a) by impressing an electric current from an external power source.



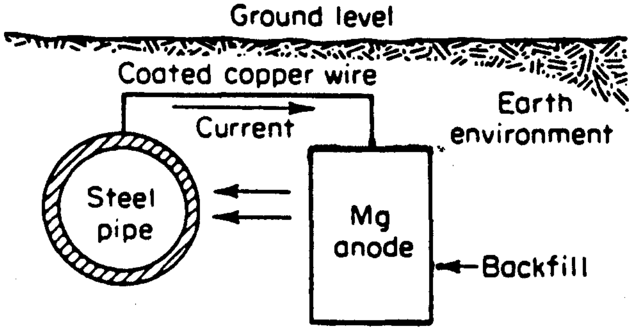
Cathodic protection of an underground tank using impressed currents.

b)

by connecting the component to a SACRIFICIAL ANODE . . .



Cathodic protection of a domestic hot-water tank using a sacrificial anode.

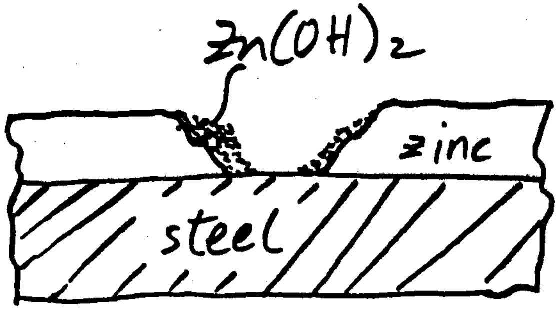


Protection of an underground line with a magnesium anode.

ZINC PLATING (" GALVANIZING")

Steel sheeting is coated with zinc by hot-dipping in the molten metal. by heating with zinc dust ("Sherardizing"), etc.

The Zn coating acts as a sacrificial anode... at the inevitable imperfections, cruds, etc., zinc dissolves preferentially, deposits loose, flocculant $Zn(OH)_2$ from aqueous solution.



Protection continues as long as enough Zn is left...if large enough areas of steel are exposed steel corrosion will occur usually at the middle of the exposed area.

If the temperature >60°C, the Zn $(OH)_2$ changes from a loose to a hard, compact form.

This MAY change the polarity of the steel/Zn couple by making the Zn more noble than the steel; this CAN lead to rapid failure of the steel.

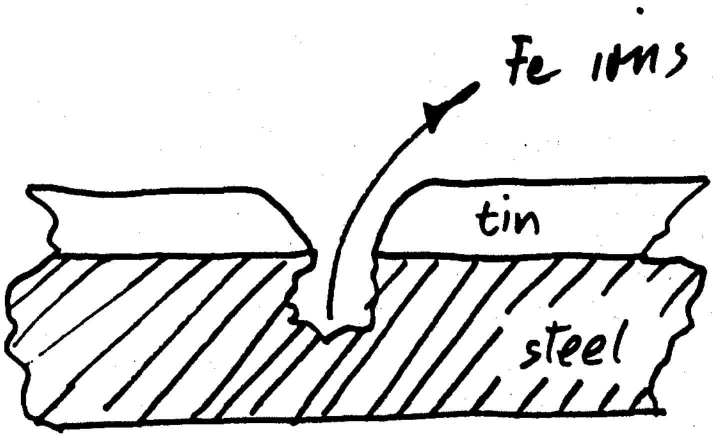
NOTE:

Galvanized steel should only be used in pH range 6 - 12.5.. ready dissolution of Zn in acids and alkalis quickly removes protection outside the range.

CADMIUM PLATING . . . similar action on steels to zinc plating

- **galvanic ΔE less than for Zn;**
- **more protective than Zn in marine environments (chloride less soluble than Zn Cl_2- gives more protective coat);**
- **better than zinc in humid conditions indoors;**
- **used less and less because Cd is toxic**

TIN PLATING . . . different action from Zn or Cd; Sn is CATHODIC to steel; "pinhole" corrosion can occur at imperfections in tin plate.



Tin plate commonly used on steel cans for foodstuffs. Organic acids in foods, fruit juices etc., complex Sn^{2+} very readily.. lower potential, make tin anodic to steel.

Also, efficiency of Sn (and Fe) for H_2 evolution poor in O_2 - starved environment inside a food can, only possible cathodic reaction is H_2 evolution; if evolution rate slow, corrosion rate slow (tins don't explode very often).

NOTE: Galvanic corrosion can occur without components of different metals actually being in electrical contact;

e.g., if soft water containing CO_2 (i.e., slightly acid from carbonic acid) flows through copper pipes into a galvanized tank, copper ions will deposit on the zinc as metal

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

The Cu is an efficient cathode and will rapidly destroy Zn coating.

MINIMIZE GALVANIC CORROSION

1. **Select metals as close together as possible in galvanic series;**
2. **Avoid small-anode/large-cathode combinations . . . choose fasteners of more noble materials;**
3. **Insulate dissimilar metals (e.g., sleeve bolts in flange joints, as well as use insulating washers);**
4. **Apply coatings carefully, keep in good condition (esp. those on anodes);**
5. **Add inhibitors, if possible, to environment;**
6. **Avoid threaded joints where possible;**
7. **Design for anodic member (make thicker, easily replaceable, etc.);**
8. **Install a third metal that is anodic to BOTH in the couple.**