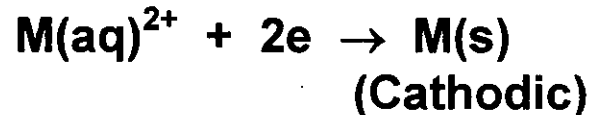


AQUEOUS CORROSION THERMODYNAMICS

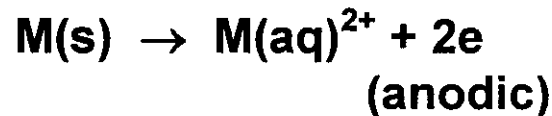
The corrosion of metals in contact with aqueous solutions involves electronic and ionic processes at surfaces . . . i.e., it involves . . .

Electrode Processes

Electronation . . .



De-electronation . . .



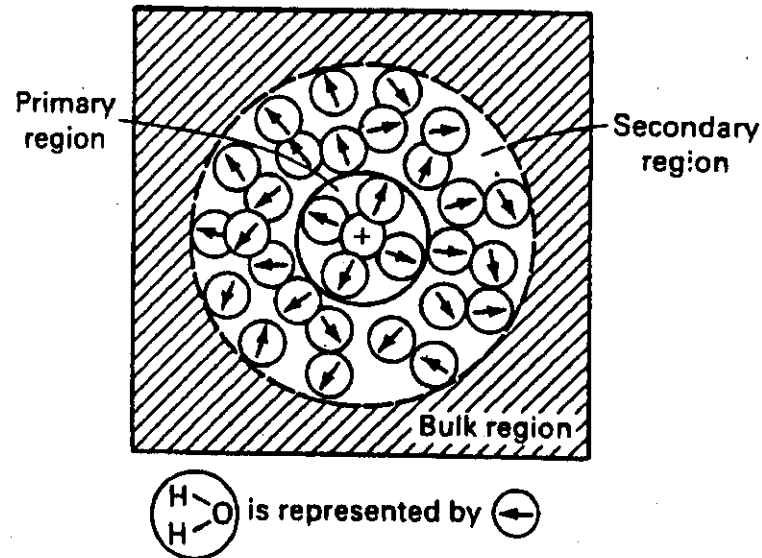
These are coupled processes . . . the oxidized species provide the electrons for the reduced species.

The reactions occur at the metal-solution interface.

Thus . . . an electronation reaction (say, discharge of metal) involves:

- diffusion of hydrated cation to electrode;
- dehydration of cation;
- adsorption of cation onto electrode surface;
- transfer of electron from electrode to cation;
- incorporation of resulting atom in solid matrix.

Note - solvation “shells” of a cation . . .

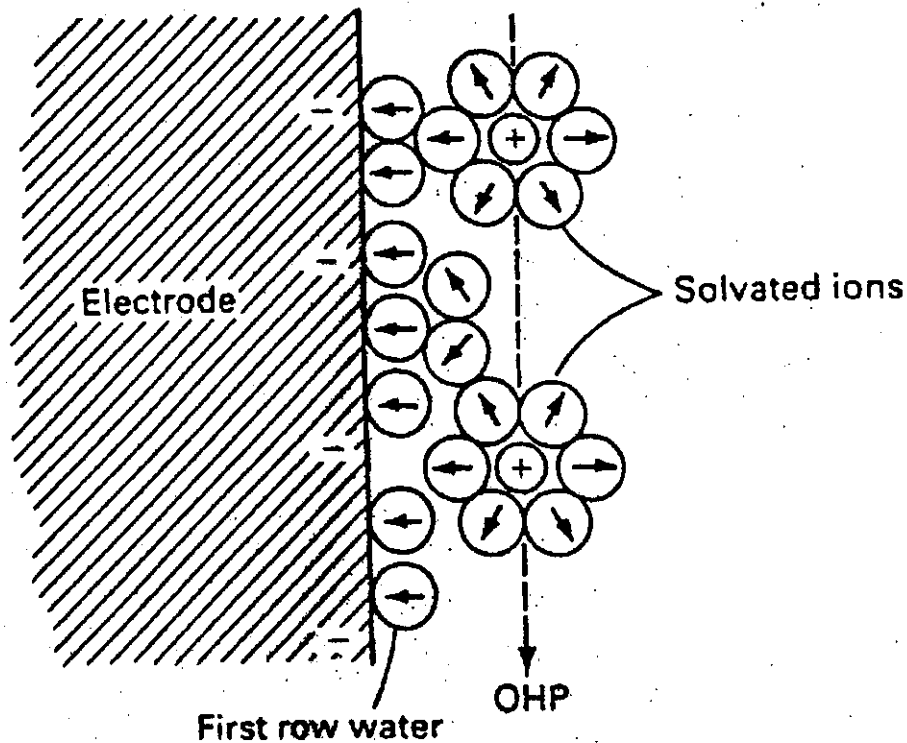


Schematic of the primary and secondary solvent molecules for a cation in water.

Primary shell moves with cation through solution . . . secondary shell is a region of “disturbance”.

Large anions have few, if any primary water molecules.

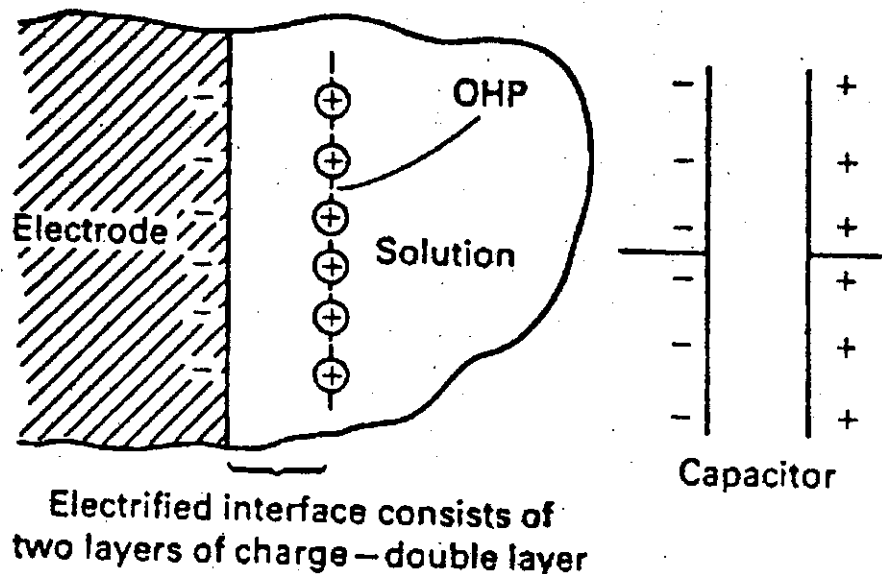
The electrode - solution interface is also hydrated because of the charge effects. (N.B. the potential difference between metal and solution is of the order of $\sim 1V$, - remember, cannot be measured - but over a molecular distance amounts to an electric field of $\sim 10^8 V/cm$).



Schematic of a charged interface and the locations of cations at the electrode surface.

Because of adsorbed H_2O on surface and primary hydration shell, ions can only approach to within a fixed distance from the electrode:

- the OUTER HELMHOLTZ PLANE. The resulting double layer of charge is often treated theoretically as a capacitor



Simplified double layer at a metal aqueous interface.

The electric “double layer” at the surface acts as a barrier to electron transfer, this causes the surface to “Polarize” . . . the potential has to change in order for the electrons to overcome the barrier.

This is called “activation polarization” . . .

(remember, the “standard EMFs” of metals in equilibrium with solutions of unit activity of their own ions change if current is drawn from the electrode systems . . . i.e., “activation polarization”).

For the general chemical reaction . . .



the free energy change, ΔF , is:

$$\Delta F = \Delta F^\circ + RT \ln \frac{(a_L)^{v_L} (a_M)^{v_M}}{(a_A)^{v_A} (a_B)^{v_B}}$$

where:

ΔF° = “standard” free energy change

(= $-RT \ln K$, where K is the equilibrium constant);

a = activity of component;

v = no. mols. of reactant or product.

If the reaction is electrochemical, and takes place in a REVERSIBLE cell of EMF = E

$$\Delta F = - nFE$$

where:

n = no. faradays passed

(≡ no. chemical equivalents);

F = faradays (electrochemical conversion factor
= 96,500 coulomb/g. equivalent).

Therefore:

$$\Delta F^\circ = - nFE^\circ$$

where

E° = standard EMF for cell.

This lead to general expression for EMF of any reversible cell...

$$E = E^\circ - \frac{RT}{nF} \ln \frac{(a_L)^{v_L} (a_M)^{v_M}}{(a_A)^{v_A} (a_B)^{v_B}}$$

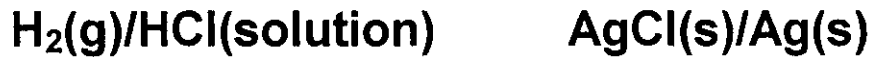
Note: E° is constant for a given cell at a given temperature . . .

$$E^\circ = \frac{RT}{nF} \ln K$$

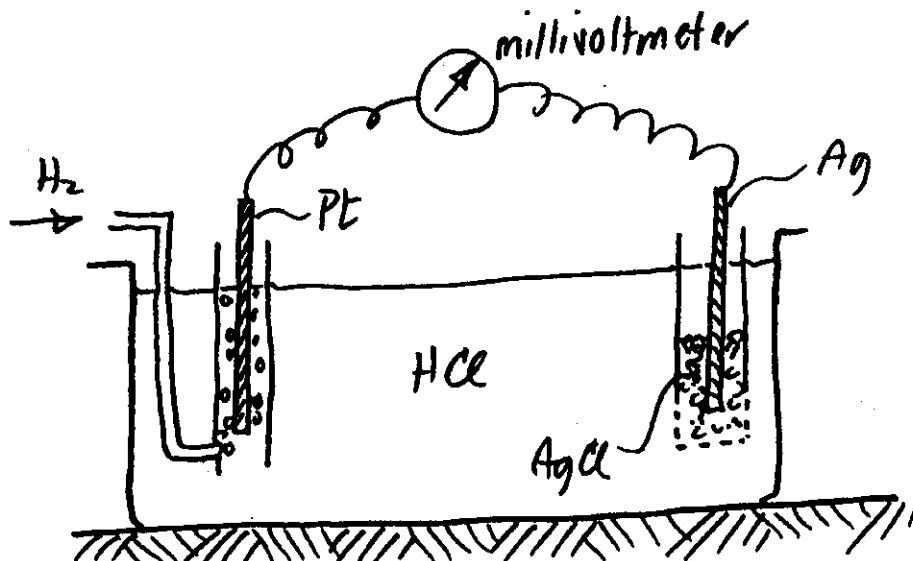
i.e., standard EMF is related to equilibrium constant, K, for cell reaction (from above equation, standard EMF is the cell EMF when all components are at unit activity).

EXAMPLE

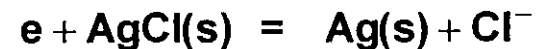
Consider cell . . .



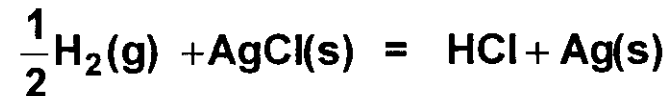
(a hydrogen electrode and a silver electrode [in contact with solid AgCl] in HCl solution)



Electrode reactions . . .



Overall..



Cell EMF given by . . .

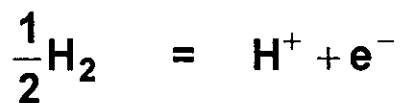
$$E = E^0 - \frac{RT}{F} \ln \frac{(a_{\text{H}^+})(a_{\text{Cl}^-})(a_{\text{Ag}})}{(a_{\text{H}_2})^{\frac{1}{2}}(a_{\text{AgCl}})}$$

If H_2 is at 1 atm (conventional standard state), and since Ag and AgCl are solids, . . .* and a_{H_2} , a_{Ag} and a_{AgCl} are unity, so

$$E = E^0 - \frac{RT}{F} \ln(a_{\text{H}^+})(a_{\text{Cl}^-})$$

$$E = E^0 - \frac{2RT}{F} \ln(a_{\text{HCl}}).$$

The cell can be considered as two “half-cells” . . . each with an electrode . .



The total cell potential . . .

$$E = \left(E_{\text{H}}^0 - \frac{RT}{F} \ln \frac{(a_{\text{H}^+})}{(a_{\text{H}_2})^{1/2}} \right) - \left(E_{\text{AgCl}}^0 - \frac{RT}{F} \ln \frac{(a_{\text{AgCl}})}{(a_{\text{Ag}})(a_{\text{Cl}^-})} \right)$$

“single-electrode” potentials...

$$E_{\text{H}} = E_{\text{H}}^0 - \frac{RT}{F} \ln(a_{\text{H}^+}) \quad \dots \text{ for H}_2 \text{ at 1 atm}$$

$$E_{\text{AgCl}} = E_{\text{AgCl}}^0 - \frac{RT}{F} \ln(a_{\text{Cl}^-}) \quad \dots \text{ for solid Ag \& AgCl}$$

N.B. E_{H}^0 and E_{AgCl}^0 are “STANDARD ELECTRODE POTENTIALS”.

We can now relate the potential of a system to the standard potential . . . i.e., to the potential with unit activity of the reactants and products.

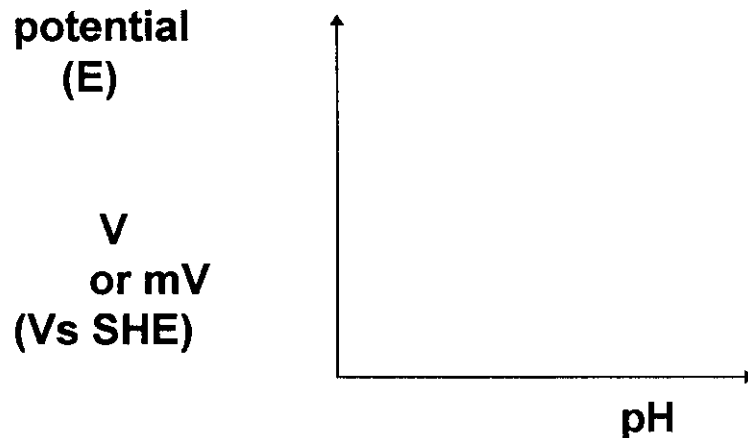
The NERNST EQUATION . . .
$$E = E_0 + \frac{RT}{nF} \ln \frac{(a_{\text{oxide}})}{(a_{\text{red}})}$$

a_{oxid} = activity ($\equiv \text{conc}^{n\cdot}$) of oxidized species;

a_{red} = activity ($\equiv \text{conc}^{n\cdot}$) of reduced species.

Potential-pH Diagrams (“Pourbaix Diagrams”)

Graphical representations of the domains of stability of metal ions, oxides, hydroxides, etc. in aqueous solution.

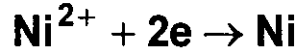


The Nernst Equation allows us to compute lines on the diagram for equilibrium reactions of interest . . .

- electrochemical reactions of pure charge transfer (horizontal lines - since no H^+ or OH^- dependence - corresponding to potentials of equilibria at given concentrations);
- pure acid-base reactions (vertical lines - since no electron transfer and no dependence on potential - corresponding to equilibrium concentrations of H^+ (OH^-) for given concentrations of species);
- electrochemical reactions involving charge transfer and H^+ (OH^-) (sloping lines).

Pure Charge Transfer Reactions

Consider ...



so the Nernst Equation becomes:

$$E = E^{\circ} + \frac{RT}{2F} \ln(\text{Ni}^{2+})$$

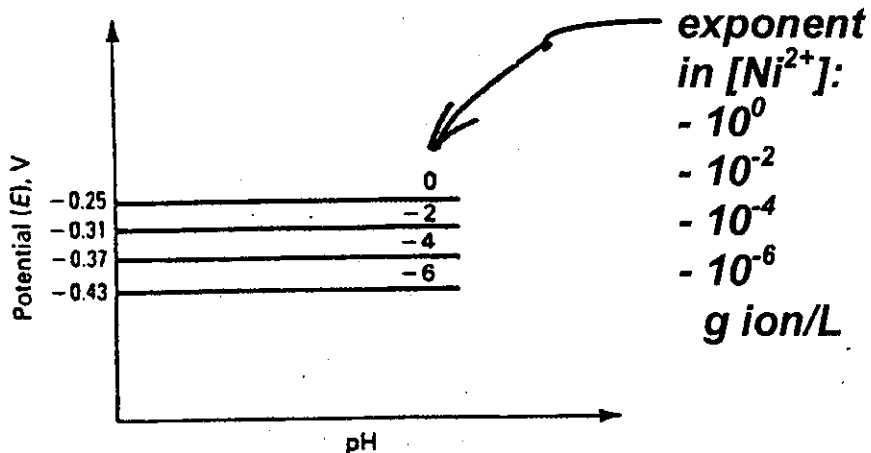
since, by definition, activity solid Ni = 1.0

$$E^{\circ} = -0.25 \text{ V}$$

so...

$$E^{\circ} = -0.25 + 0.03 \log(\text{Ni}^{2+})$$

We usually compute for 4 conc^{ns} ... 10^0 (i.e., 1.0), 10^{-2} , 10^{-4} , 10^{-6} g-ion/L.

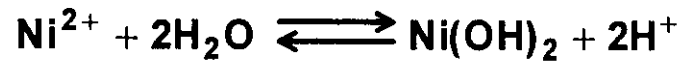


The region above a particular line is the region of stability for Ni^+ ... so, if we are on the equilibrium line at -0.43 V for a Ni^+ concentration of 10^{-6} mol. and we raise the potential to -0.31 V (say), the Ni metal in contact with the solution will dissolve to try and make the concentration 10^{-2} mol.

Partial E-pH diagram for the
 $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$ reaction.

Pure Acid-Base Reaction

Consider...



There is no charge transfer, so the E-pH diagram is a vertical line for a given Ni²⁺ concentration.

We evaluate the equilibrium constant, K, from the standard free energy change for the reaction ...

$$\Delta G^0 = -RT \ln K$$

$$\text{or } \log K = -\frac{\Delta G^0}{2.303RT}$$

ΔG^0 is calculated from the standard chemical potentials (μ^0) of the reactants and products....

$$\Delta G^0 = \sum v_P \mu_P^0 - \sum v_R \mu_R^0$$

so

$$\log K = \frac{\mu_{\text{Ni}^{2+}}^0 + 2\mu_{\text{H}_2\text{O}}^0 - \mu_{\text{Ni}(\text{OH})_2}^0 - 2\mu_{\text{H}^+}^0}{2.303RT}$$

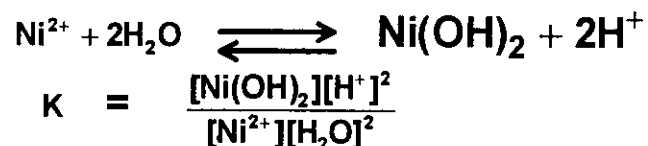
$$\mu^0 \text{ values are tabulated } \dots \quad \mu_{\text{Ni}^{2+}}^0 = -11,100 \text{ cal/mol}$$

$$\mu_{\text{H}_2\text{O}}^0 = -56,690 \text{ cal/mol}$$

$$\mu_{\text{Ni}(\text{OH})_2}^0 = -108,300 \text{ cal/mol}$$

$$\text{and } \mu_{\text{H}^+}^0 = 0 \text{ (convention), so, at } 25^\circ\text{C} \quad \log K = -12.$$

Remember . . . reaction . . .



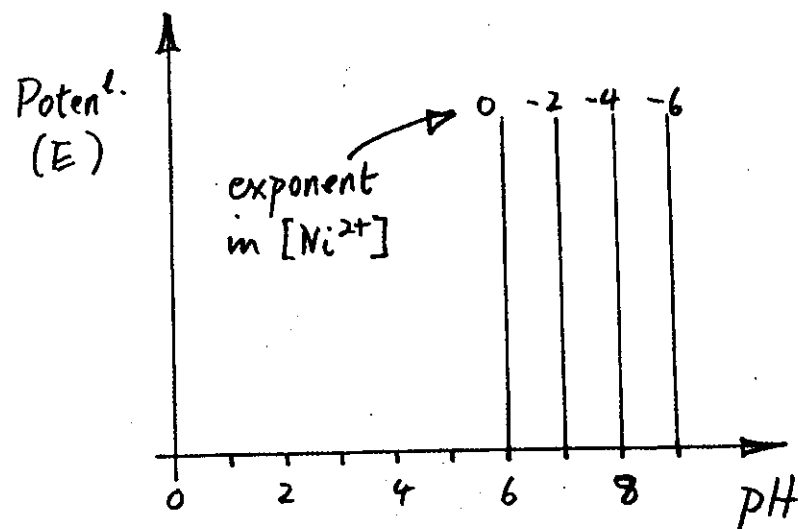
Since the continuous phases H_2O and (solid) $\text{Ni}(\text{OH})_2$ have activities of 1

$$\log \frac{[\text{H}^+]^2}{[\text{Ni}^{2+}]} = -12$$

$$\log[\text{H}^+]^2 = -12 + \log[\text{Ni}^{2+}]$$

or $\text{pH} = 6 - 0.5 \log[\text{Ni}^{2+}]$

Again, we compute for $[\text{Ni}^{2+}] = 10^0, 10^{-2}, 10^{-4}$ and 10^{-6} mol.



The region to the left of a particular line (i.e., more acid) is the region of stability for Ni^{2+} . . . so, if we are on the equilibrium line at pH 9 for a Ni^{2+} concentration of 10^{-6} mol., and we drop the pH to 7 (say), the $\text{Ni}(\text{OH})_2$ solid in contact with the solution will dissolve to try and make the concentration to 10^{-2} mol.

Reactions Involving Electrons and H⁺

Consider . . .



so the Nernst Equation is . . .

$$E = E^\circ + \frac{RT}{2F} \ln \frac{[\text{NiO}][\text{H}^+]^2}{[\text{Ni}][\text{H}_2\text{O}]}$$

$$= E^\circ + 0.03 \log [\text{H}^+]^2$$

since, by definition, $[\text{NiO}] = [\text{Ni}] = [\text{H}_2\text{O}] = 1$

$$E^\circ = \frac{\Delta G^\circ}{nF} = \frac{\mu_{\text{NiO}}^\circ - \mu_{\text{Ni}}^\circ - \mu_{\text{H}_2\text{O}}^\circ}{2F}$$

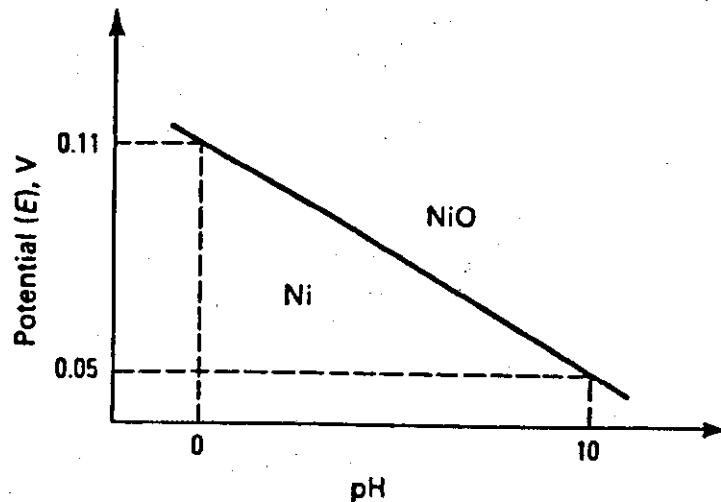
$$= \frac{-51,610 - 0 + 56,690}{2F}$$

(since, by definition, μ° element = 0),

$$E^\circ = 0.11 \text{ V}$$

$$E = 0.11 - 0.06 \text{ pH..}$$

Above the line, solid NiO is stable.
Below the line, Ni metal is stable.



Partial E-pH diagram for the
 $\text{Ni} + \text{H}_2\text{O} \rightarrow \text{NiO} + 2\text{H}^+ + 2\text{e}^-$ reaction.

NOTE : We can also depict the Ni - H₂O reaction as . . .



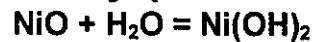
so that

$$\begin{aligned} E &= E^\circ + \frac{RT}{2F} \ln \frac{[\text{Ni}(\text{OH})_2][\text{H}^+]^2}{[\text{Ni}][\text{H}_2\text{O}]^2} \\ &= E^\circ + 0.03 \log [\text{H}^+]^2 \dots \quad (\text{as for NiO}). \end{aligned}$$

$$\begin{aligned} E^\circ &= E^\circ = \frac{\Delta G^\circ}{nF} = \frac{\mu_{\text{Ni}(\text{OH})_2}^\circ - \mu_{\text{Ni}}^\circ - 2\mu_{\text{H}_2\text{O}}^\circ}{2F} \\ &= 0.11 \text{ V} \end{aligned}$$

$$E = 0.11 - 0.06 \text{ pH}$$

This is identical with the line for the Ni → NiO equilibrium . . . i.e., Ni(OH)₂ is as likely (thermodynamically) as NiO. Alternatively...



for which

$$K = \frac{[\text{Ni}(\text{OH})_2]}{[\text{NiO}][\text{H}_2\text{O}]}$$

$$\Delta G^\circ = -RT \ln K$$

or

$$\begin{aligned} \log K &= \frac{\sum \nu_R \mu_R^\circ - \sum \nu_P \mu_P^\circ}{2.303RT} \\ &= \frac{\mu_{\text{H}_2\text{O}}^\circ + \mu_{\text{NiO}}^\circ - \mu_{\text{Ni}(\text{OH})_2}^\circ}{2.303RT} \end{aligned}$$

now, $\mu_{\text{H}_2\text{O}}^0 = -59,690 \text{ cal/mol}$

$$\mu_{\text{NiO}}^0 = -51,610 \text{ cal/mol}$$

$$\mu_{\text{Ni(OH)}_2}^0 = -108,300 \text{ cal/mol}$$

so that $\Delta G^0 = 0$

and $\log K = 0$

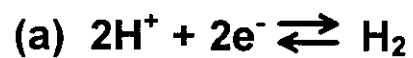
so $K = 1$

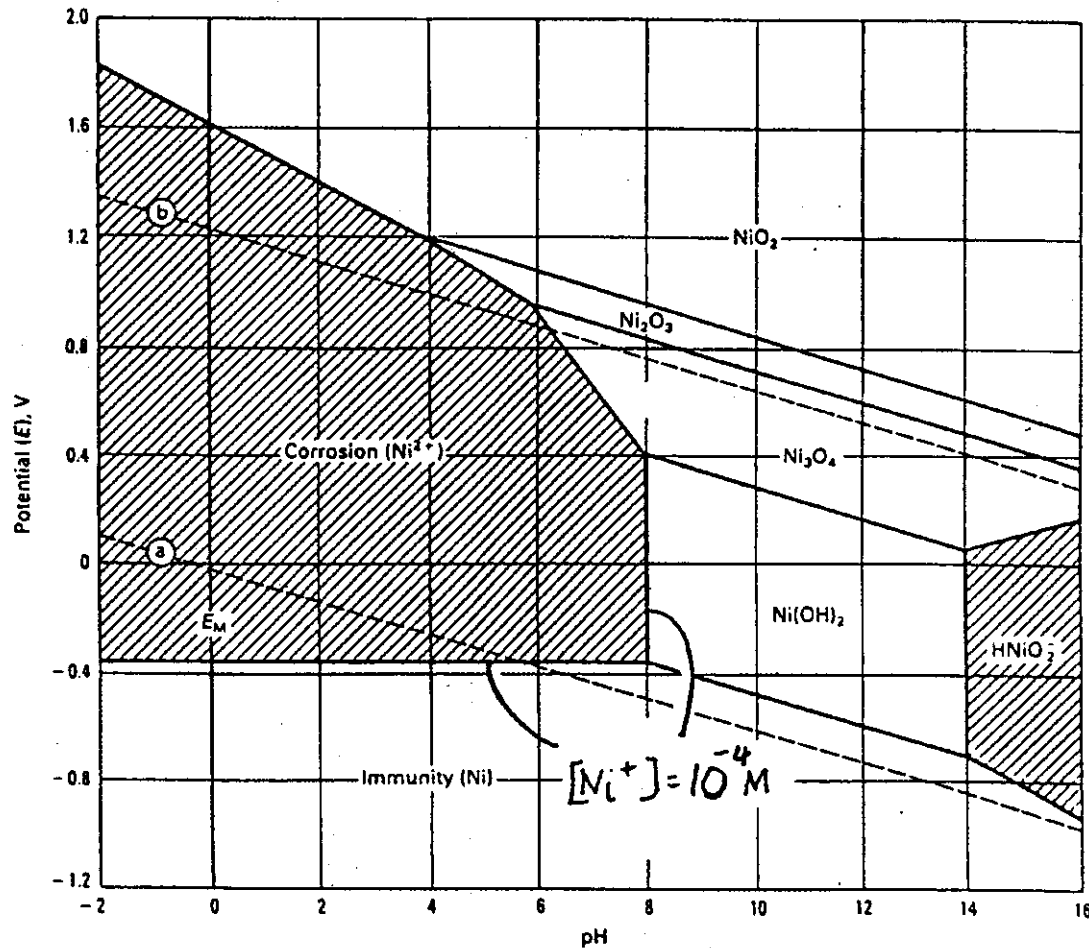
Since
$$K = \frac{[\text{Ni(OH)}_2]}{[\text{NiO}][\text{H}_2\text{O}]}$$

and $[\text{H}_2\text{O}] = 1$

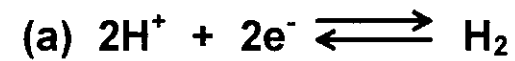
$$[\text{Ni(OH)}_2] = [\text{NiO}]$$

Note the stability lines for H_2O





Note the stability lines for H₂O



E-pH diagram for nickel.

The Nernst Equation gives . . .

$$(a) \quad E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^0 + \frac{0.059}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}}$$

By definition...

$$E_{\text{H}^+/\text{H}_2}^0 = 0$$

$$E_{\text{H}^+/\text{H}_2} = -0.059\text{pH} - \frac{0.059}{2} \log P_{\text{H}_2}$$

We usually consider case when $P_{\text{H}_2} = 1 \text{ atm}$

line (a) on Pourbaix diagram . . . $E_{\text{H}^+/\text{H}_2} = -0.059 \text{ pH}$

(b) Similarly...

$$E_{\text{O}_2} = E_{\text{O}_2}^0 + \frac{0.059}{2} \log \frac{(P_{\text{O}_2})^{\frac{1}{2}} [\text{H}^+]^2}{[\text{H}_2\text{O}]}$$

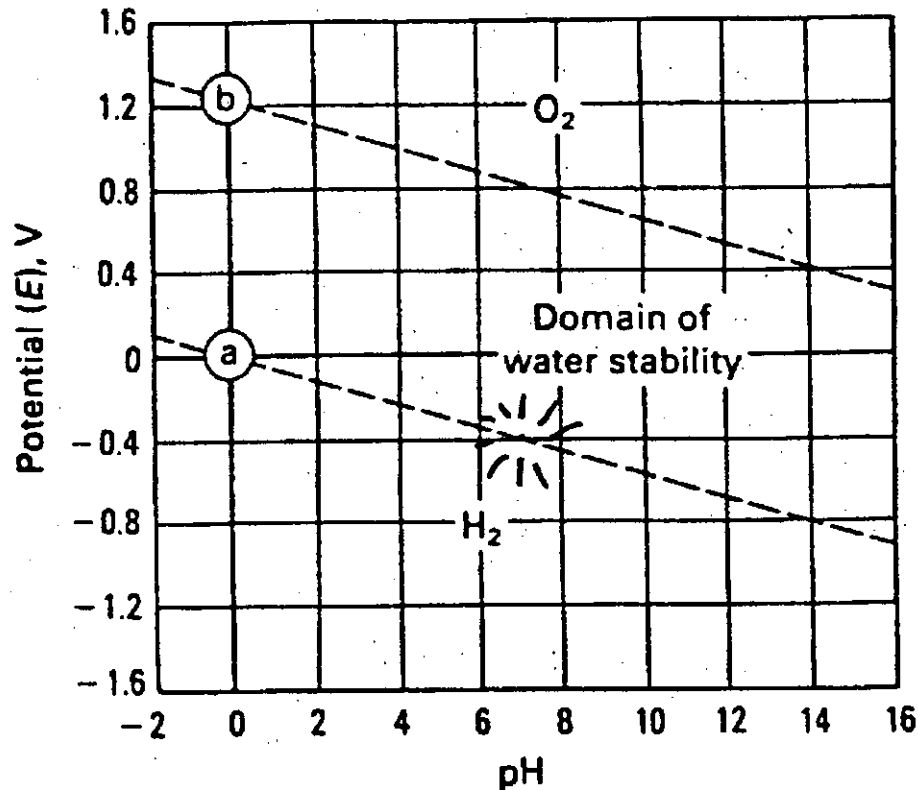
$$E_{\text{O}_2}^0 = 1.23 \text{ V}$$

$$[\text{H}_2\text{O}] = 1$$

and $P_{\text{O}_2} = 1 \text{ atm (for diagram)}$

line (b) is . . .

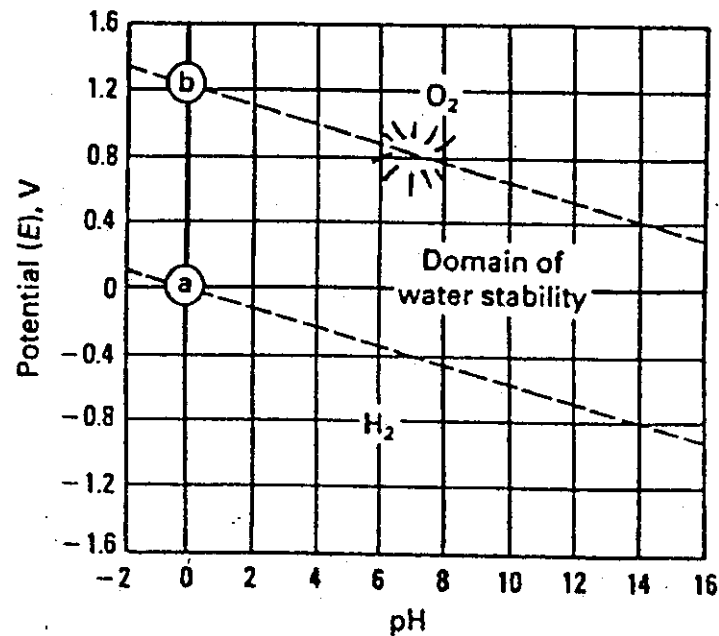
$$E_{\text{O}_2} = 1.23 - 0.059 \text{ pH}$$



If we have an electrode (say Pt) in water at pH 7 equilibrated with H₂ at 1 atm., the potential of the Pt will be ~ -400 mV. If we then LOWER the potential (to -600 mV, say) water will decompose and liberate H₂ to try and achieve a new equilibrium at a higher p_{H₂} and/or... higher pH.

The water E-pH diagram at 1 atm.

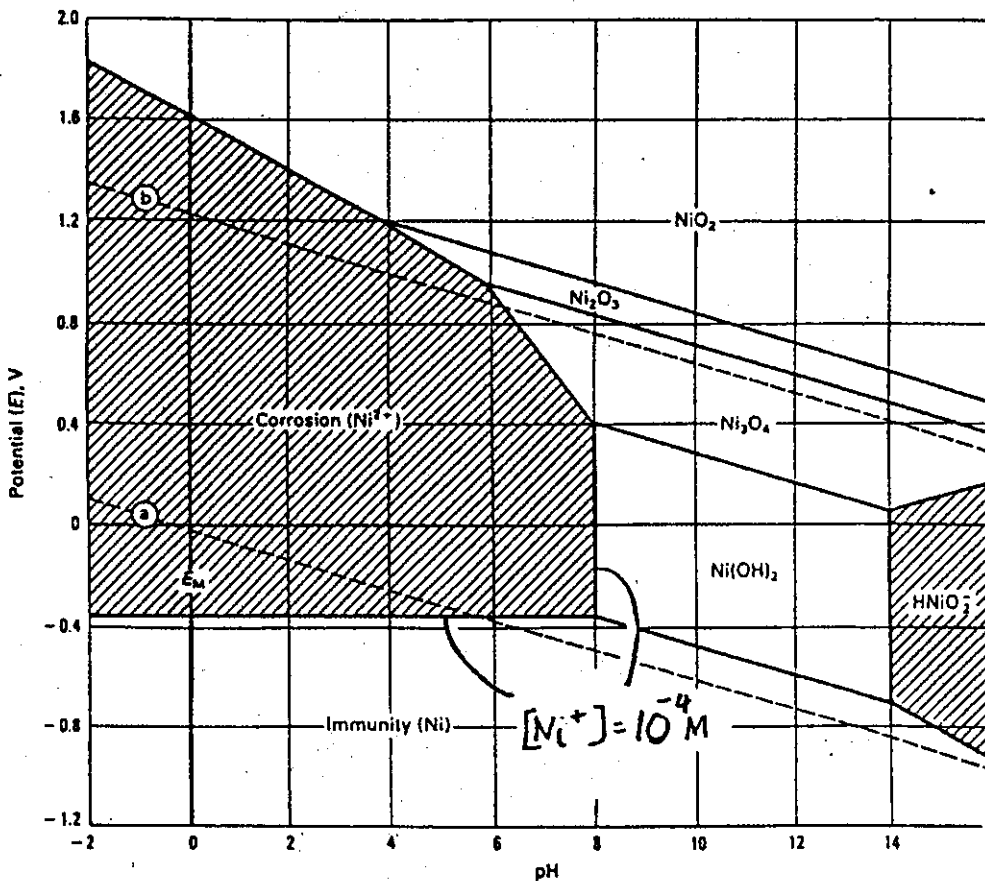
Similarly . . . on H₂O stability line at pH 7 and ~ +800 mV (in equilibrium with 1 atm. O₂) and we RAISE the potential, water will decompose and liberate O₂ to try and achieve new equilibrium at a higher pO₂ and/or lower pH.



The water E-pH diagram at 1 atm.

Use of Pourbaix Diagrams

Consider Ni metal corroding in an acid solution (pH 0) containing 10^{-4} M (strictly... g.ion/L) Ni^{2+} in equilibrium with 1 atm. H_2 gas.



E-pH diagram for nickel.

Potential of the anodic “regions”
= -0.37 V.

Potential of the cathodic “regions”
= 0 V

Since the $\text{Ni} \rightarrow \text{Ni}^{2+}$ reaction is more active than the $\text{H}^+ \rightarrow \frac{1}{2}\text{H}_2$ reaction, the former can “drive” the latter . . . i.e., Ni will displace H_2 from solution. The surface will attain a “mixed” potential E_M between the two equilibrium potentials, and corrosion will proceed.

If, now, pH raised to $\sim 6-8$ (say pH7) then $\text{Ni} \rightarrow \text{Ni}^{2+}$ is more noble than H^2 evolution reaction, will not corrode via H^+ reduction.

NOTE: If solution also contains dissolved O₂ at 1 atm., then an additional cathodic reaction is:



along line (b): this is also possible at pH 6-8, but will become slower at higher pH, since not much H⁺ is available. A mixed potential will be established.

At pH 8-14, stable species are solid Ni(OH)₂, Ni₃O₄ . . . corrosion will tend to produce protective layers. . . metal passivates.

At pH > 14 , corrosion (stable species IONIC HNiO₂⁻ at quite low potentials).

What happens if we put Ni metal into acid solution (say pH 0 in equilibrium with 1 atm H₂) containing ZERO concentration Ni²⁺?

DISCUSS

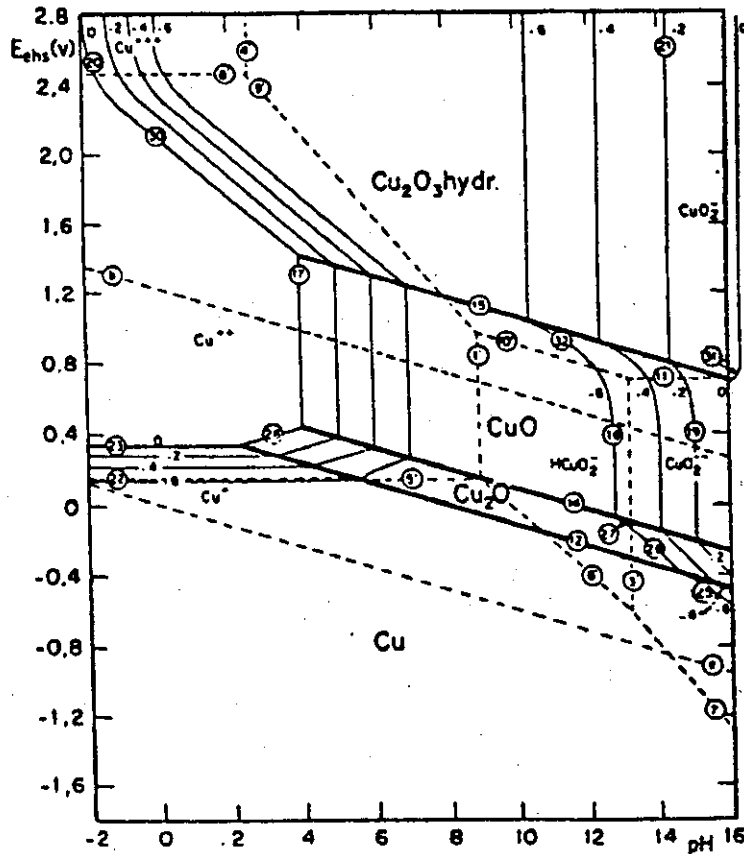
Remembering Nernst Equation . . . $E = E^0 + \frac{RT}{2F} \ln (\text{Ni}^{2+})$

Although potential very low initially ($E \rightarrow -\infty$), some Ni²⁺ generated in liquid film next to metal . . . potential rises as [Ni²⁺] increases.

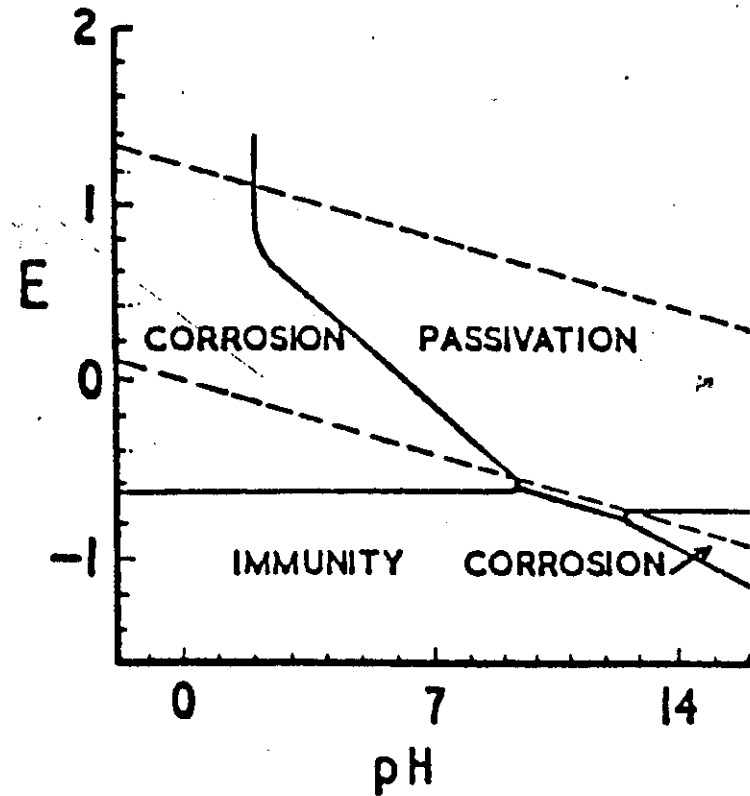
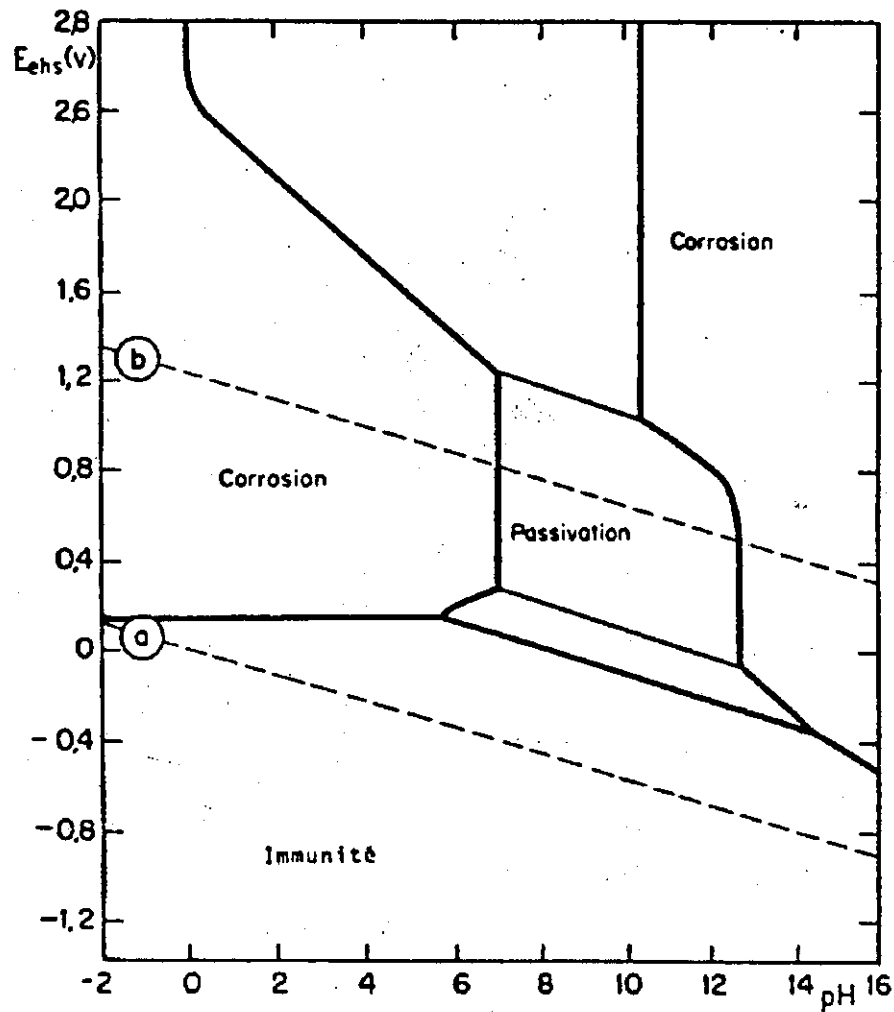
NOTE: For corrosion considerations, a metal ion concentration of 10^{-6} M (10^{-6} g-ion/L) is considered as indicative of conditions that apply in the liquid film next to the metal surface with no extraneous source of those ions . . . most Pourbaix diagrams consider this concentration for corrosion.

Pourbaix diagrams can be complex . . .

because there are many reactions that can be considered (not all of them occurring)...

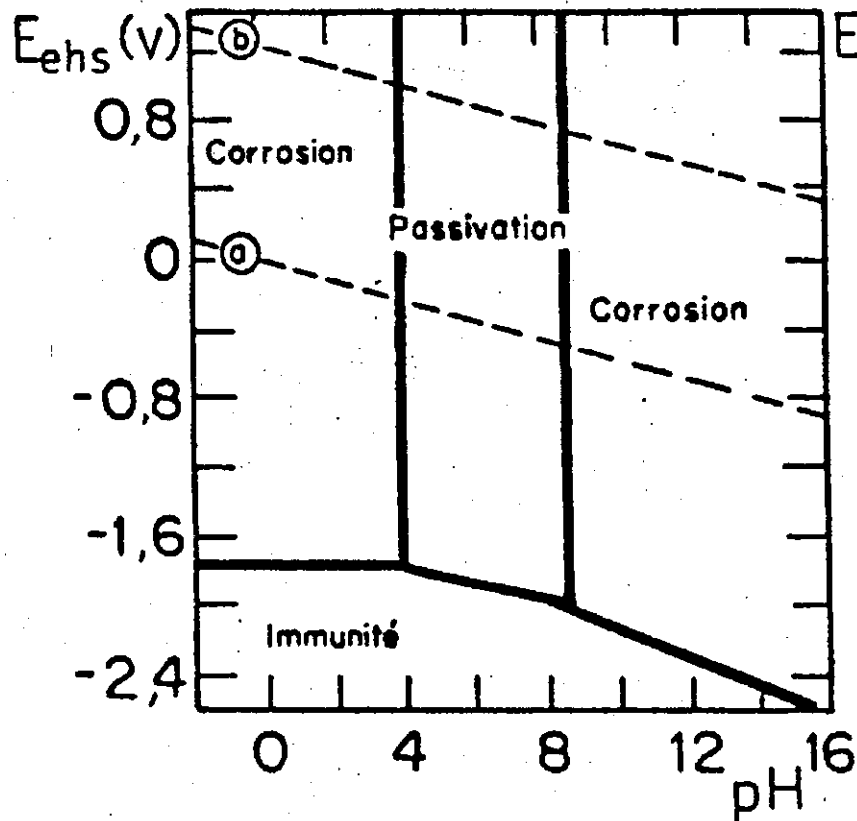


But, for indicating corrosion trends, we can use simplified versions . . .

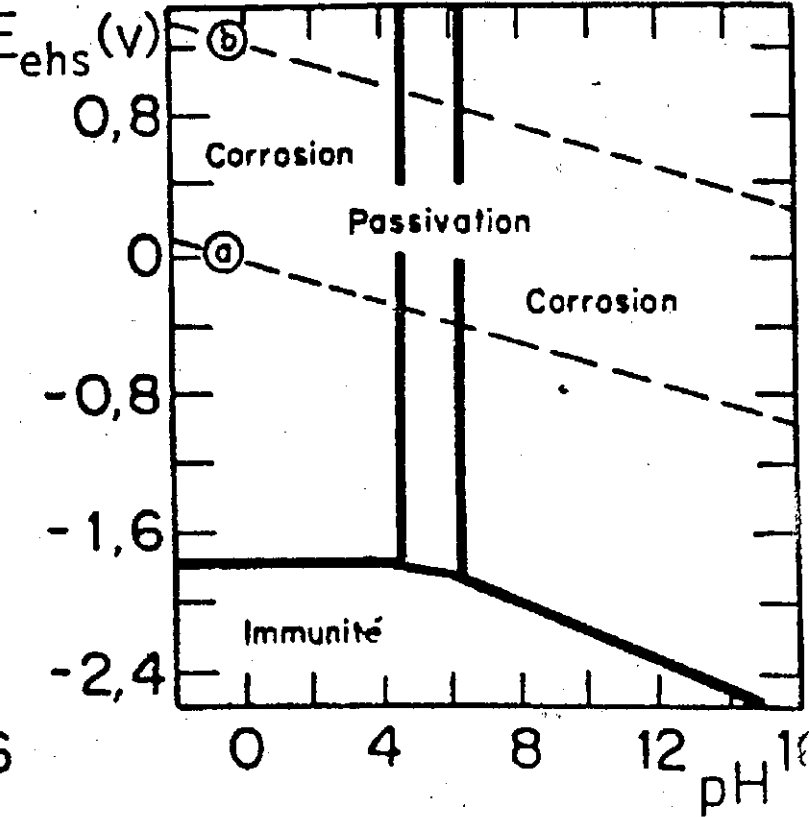


A simplified form of the Pourbaix Diagram for iron.

And for a reactive - but usually passivated metal such as Al ...



(a) Passivation par un film d'hydrargillite $Al_2O_3 \cdot 3H_2O$



(b) Passivation par un film de boëhmite $Al_2O_3 \cdot H_2O$

Chemical Reactions

Z = +2

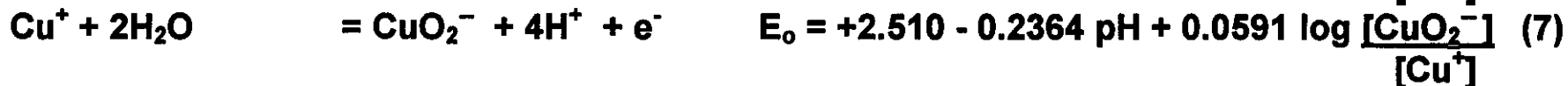
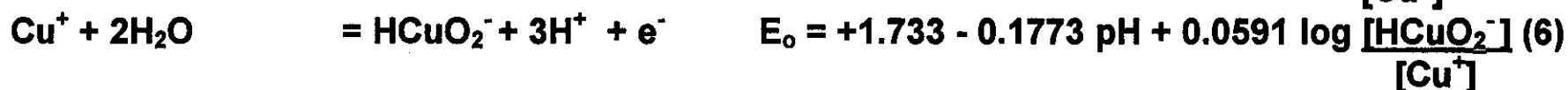
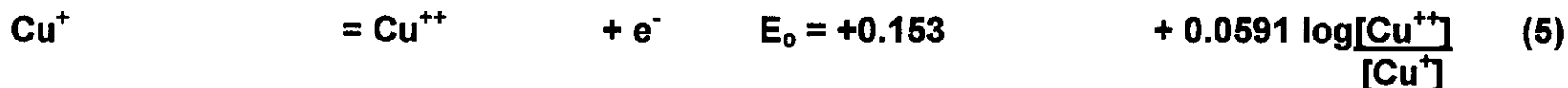


Z = +3

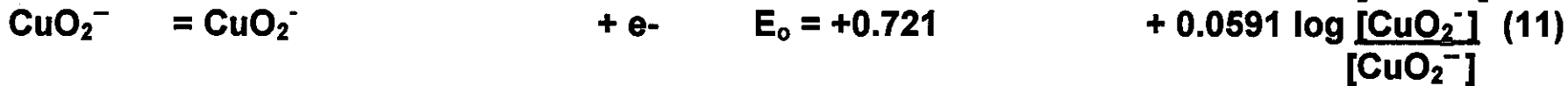
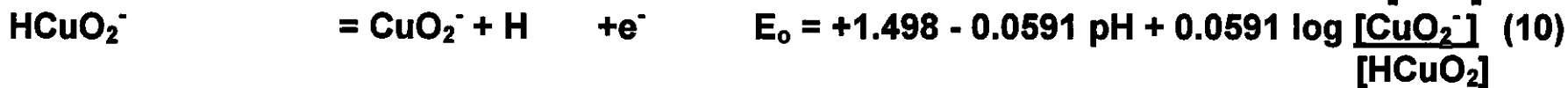
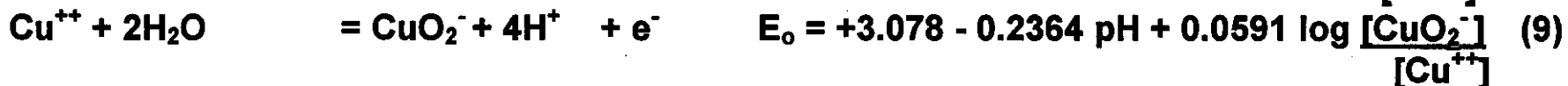
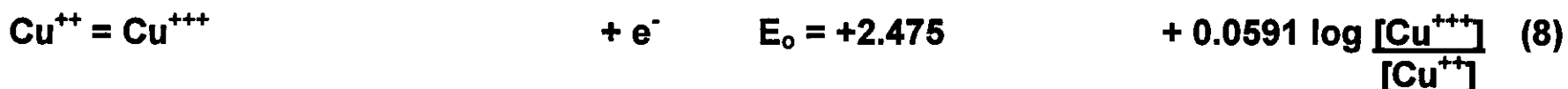


Electrochemical Reactions

Z = +1 → +2



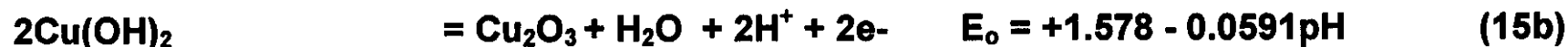
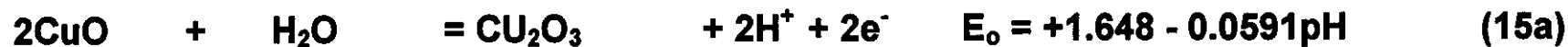
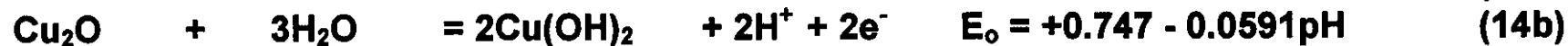
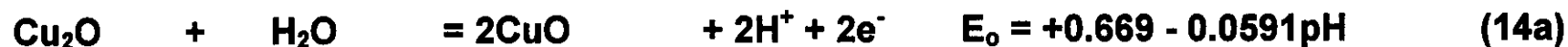
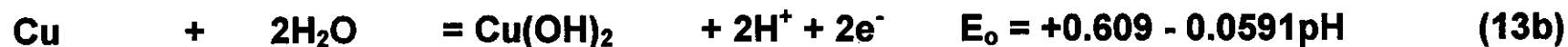
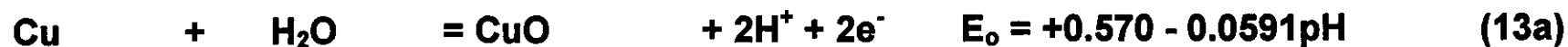
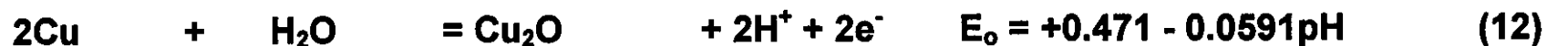
Z = +2 → +3



Activities egales de deux formes dissoutes

| | | | |
|------------------------------------|---------|--------------------|-------|
| $\text{Cu}^{++} - \text{HCuO}_2^-$ | pH = | 8.91 | (1') |
| $\text{HCuO}_2^- - \text{CuO}_2^-$ | pH = | 13.15 | (3') |
| $\text{Cu}^{+++} - \text{CuO}_2^-$ | pH = | 2.57 | (4') |
| $\text{Cu}^+ - \text{Cu}^{++}$ | $E_o =$ | +0.153 | (5') |
| $\text{Cu}^+ - \text{HCuO}_2^-$ | $E_o =$ | +1.733 - 0.1773pH | (6') |
| $\text{Cu}^+ - \text{CuO}_2^-$ | $E_o =$ | +2.510 - 0.2364pH | (7') |
| $\text{Cu}^{++} - \text{Cu}^{+++}$ | $E_o =$ | +2.475 | (8') |
| $\text{Cu}^{++} - \text{CuO}_2^-$ | $E_o =$ | +3.078 - 0.2364pH | (9') |
| $\text{HCuO}_2^- - \text{CuO}_2^-$ | $E_o =$ | +1.4998 - 0.0591pH | (10') |
| $\text{CuO}_2^- - \text{CuO}_2^-$ | $E_o =$ | +0.721 | (11') |

Séparation des domaines de stabilité de corps condensés



Solubilities . . .

Chemical Reactions

| | | | | | | | |
|--------------------------|-------------------------|----------------------------|-----------------|-------------------------|------------|----------------|--------------|
| 2Cu^+ | $+ \text{H}_2\text{O}$ | $= \text{Cu}_2\text{O}$ | $+ 2\text{H}^+$ | $\log [\text{Cu}^+]$ | $= -1.68$ | $- \text{pH}$ | (16a) |
| Cu^+ | $+ \text{H}_2\text{O}$ | $= \text{Cu}(\text{OH})$ | $+ \text{H}^+$ | $\log [\text{Cu}^+]$ | $= -0.84$ | $- \text{pH}$ | (16b) |
| Cu^{++} | $+ \text{H}_2\text{O}$ | $= \text{CuO}$ | $+ 2\text{H}^+$ | $\log [\text{Cu}^{++}]$ | $= +7.89$ | $- 2\text{pH}$ | (17a) |
| Cu^{++} | $+ 2\text{H}_2\text{O}$ | $= \text{Cu}(\text{OH})_2$ | $+ 2\text{H}^+$ | $\log [\text{Cu}^{++}]$ | $= +9.27$ | $- 2\text{pH}$ | (17b) |
| CuO | $+ \text{H}_2\text{O}$ | $= \text{HCuO}_2^-$ | $+ \text{H}^+$ | $\log[\text{HCuO}_2^-]$ | $= -18.83$ | $+ \text{pH}$ | (18a) |
| $\text{Cu}(\text{OH})_2$ | | $= \text{HCuO}_2^-$ | $+ \text{H}^+$ | $\log[\text{HCuO}_2^-]$ | $= -17.52$ | $+ \text{pH}$ | (18b) |
| CuO | $+ \text{H}_2\text{O}$ | $= \text{CuO}_2^-$ | $+ 2\text{H}^+$ | $\log[\text{CuO}_2^-]$ | $= -31.98$ | $+ 2\text{pH}$ | (19a) |
| $\text{Cu}(\text{OH})_2$ | | $= \text{CuO}_2^-$ | $+ 2\text{H}^+$ | $\log[\text{CuO}_2^-]$ | $= -30.67$ | $+ 2\text{pH}$ | (19b) |
| 2Cu^{+++} | $+ 3\text{H}_2\text{O}$ | $= \text{Cu}_2\text{O}_3$ | $+ 6\text{H}^+$ | $\log[\text{Cu}^{+++}]$ | $= -6.09$ | $- 3\text{pH}$ | (20) |
| Cu_2O_3 | $+ \text{H}_2\text{O}$ | $= 2\text{CuO}_2^-$ | $+ 2\text{H}^+$ | $\log[\text{HCuO}_2^-]$ | $= -16.31$ | $+ \text{pH}$ | (21) |

Electrochemical Reactions

