Eh-pH diagram

Often called
Pourbaix diagram

Lecture in hydrometallurgy

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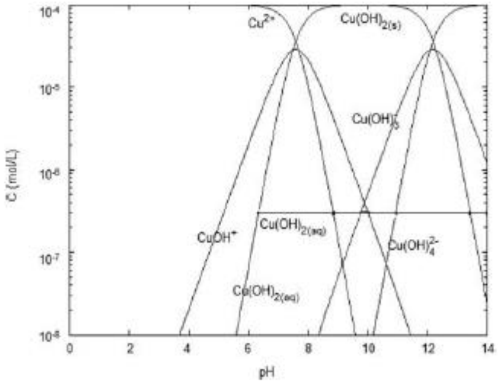
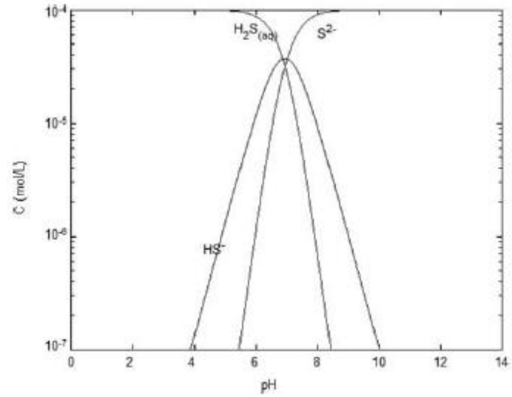
Content:

- The red-ox potential of a solution
  - How to measure it
- The use of Eh-pH diagrammes
- How to construct Eh-pH diagrammes

Short history

- First Eh-pH diagram presented by M. Pourbaix in 1949
- Applies mainly to dilute aqueous solutions
- Is dependent upon the knowledge of speciation
- Has proven valuable in leaching in particular
- Eh-pH diagrams do not exclude the use of speciation plots as a function of pH, e.g.:





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The red-ox potential of a solution

- Key equation is Nernst:

$$E = E^0 - \frac{RT}{nF} lnQ,$$

  F is Faraday's constant, Q is activity ratio of products relative to reactants

  – E.g.: $Fe^{3+} + e^- \leftrightarrow Fe^{2+}$, $Q = \{Fe^{2+}\}/\{Fe^{3+}\}$ & n=1

- E^0 is reduction potential at T= 298.15 K and 0.1 M
- At equilibrium, Q = K

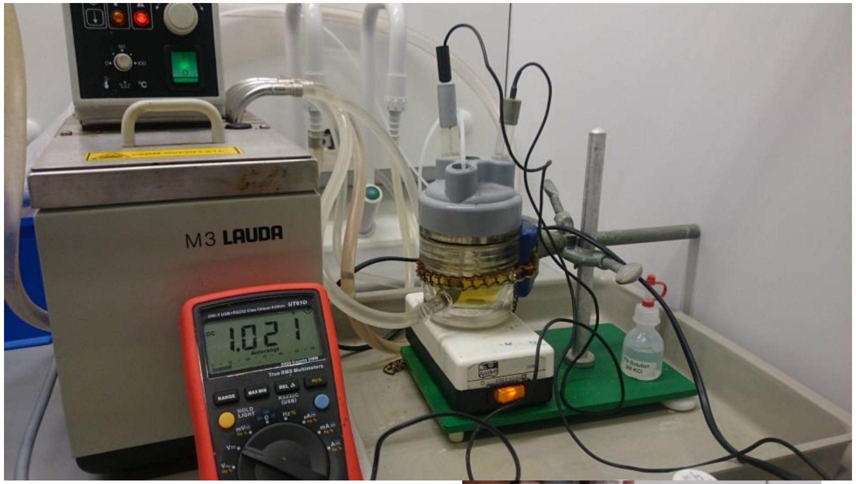
The red-ox potential of a solution

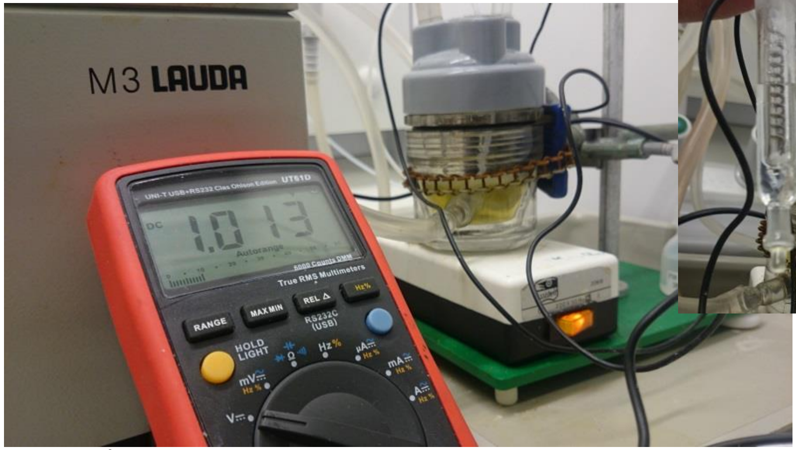
- Consider the dissolution of Ag in HNO_3:
  - $Ag^+ + e^- \rightarrow Ag$, $E^0 = 0.7996$ V
    $NO_3^- + 4H^+ + 3e^- \rightarrow NO + H_2O$, $E^0 = 0.957$ V
- The Ag|AgCl-electrode is often used for reference as AgCl is a stable salt:
  - $AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^-(aq)$, $E^0 = 0.22233$ V
  - In saturated KCl @ 25°C $E = 0.197$ V

- Example: Solubility product of AgCl:
  $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$
- Divide into the two half cell reactions above and use Nernst eq.: $\Delta E = 0 = \Delta E^0 - (RT/F)\ln(\{Ag^+\}\{Cl^-\})$
- $\ln K_{sp} = (0.2223-0.7996)F/RT \Rightarrow pK_{sp} = -\log K_{sp} = 9.76$ @ 25°C

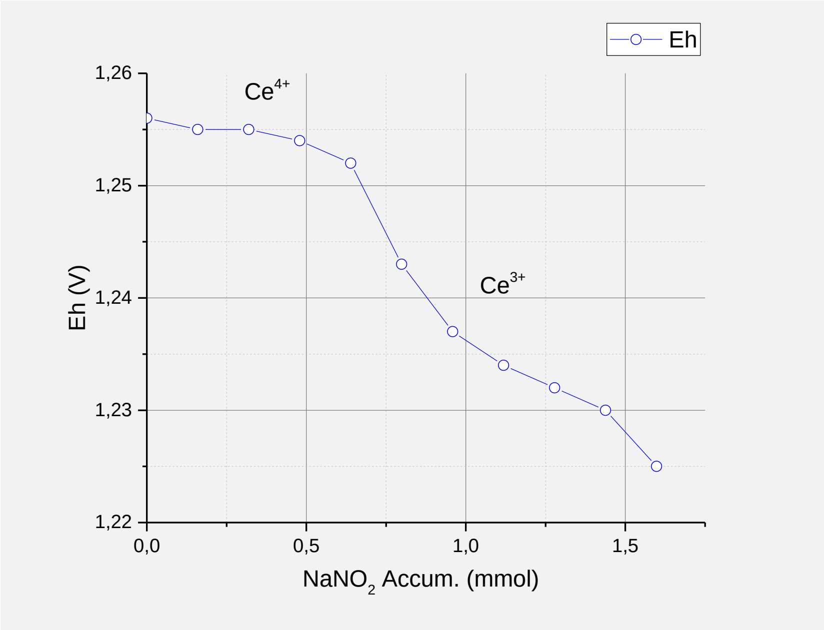
How to measure Eh

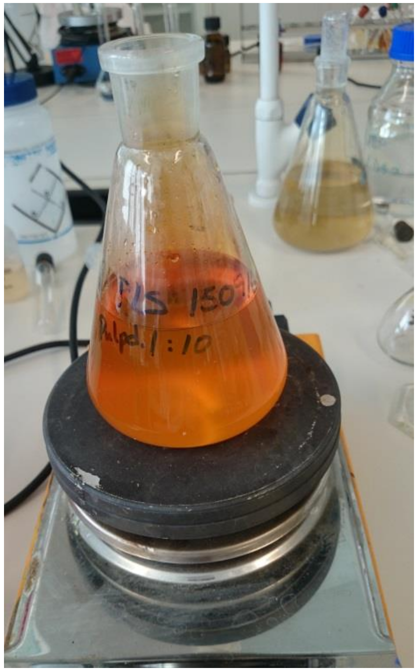
- A useful cell:
  Ag|AgCl|3M KCl|solution|Pt
  ΔV between Ag and Pt
- Important parameters:
  - Dissolved O_2 – flush w. Ar
  - Temperature – keep constant
  - Stirring - homogeneity





Example: Reduction of Ce(IV) with HNO_2





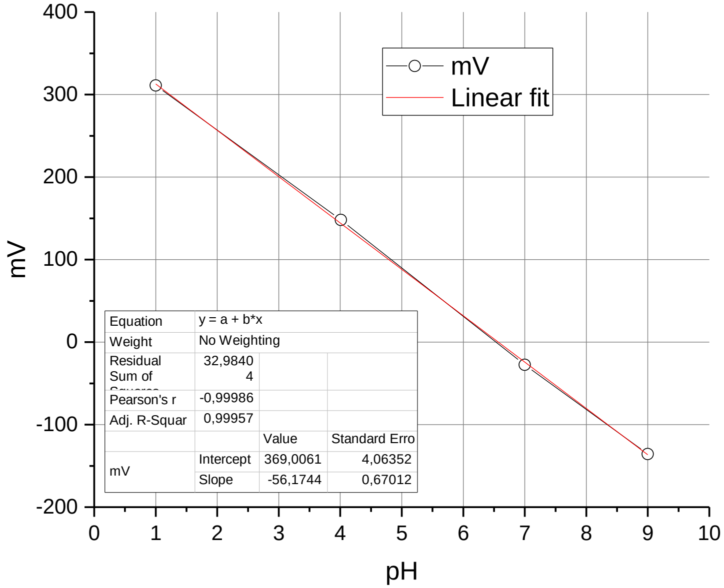
$$3HNO_2 \rightarrow 2NO + NO_3^- + H^+ + H_2O$$

The need for pH (or mV)

- In many redox-reactions acidity is imperative
  - $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$
  - $CuFeS_2 + 16Fe^{3+} + 8H_2O \leftrightarrow Cu^{2+} + 17Fe^{2+} + 2SO_4^{2-} + 16H^+$
  - $CuFeS_2 + 4Fe^{3+} \leftrightarrow Cu^{2+} + 5Fe^{2+} + 2S^0$
- In sulphidic ores it may be more easy to oxidize sulphide than produce H_2S.
  Often such ores are roasted first: $S^0 \rightarrow SO_2(g)$
  - $SO_2(g) + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3(g)$

How to measure pH

- Measure mV, not pH!
- pH < 0 is usually related with high uncertainty

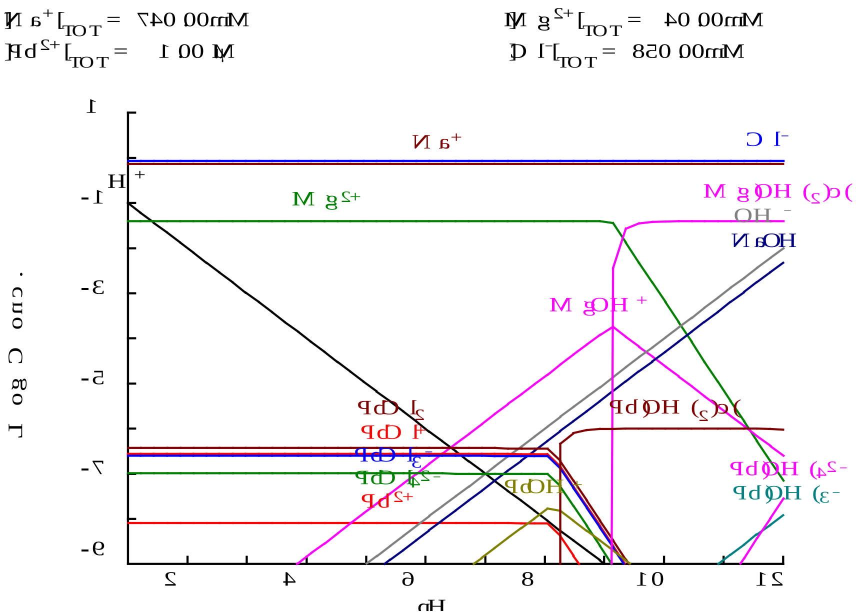


- Most pH-meters only use two or three buffers to construct the calibration curve
- Constructing the line manually, e.g. using Origin software, we can use as many buffers as we have
- Easier to measure mV

When to use Eh-pH diagrammes?

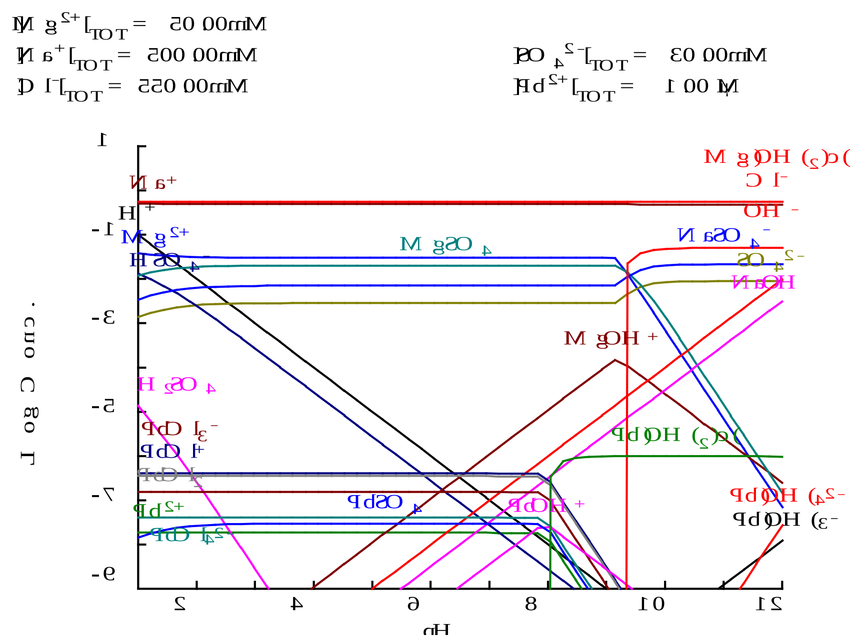
- When the metal has more than one oxidation state, e.g. Cu^{+} vs. Cu^{2+} or Fe^{2+} vs. Fe^{3+}.
- When combining two metals, e.g. Cu and Fe
- When the metal is hydrolysed
- When the metal forms strong complexes
- When anion has more than one oxidation state, e.g. CuS vs. $CuSO_4$

Solubility of lead in produced water (PW) and in sea water

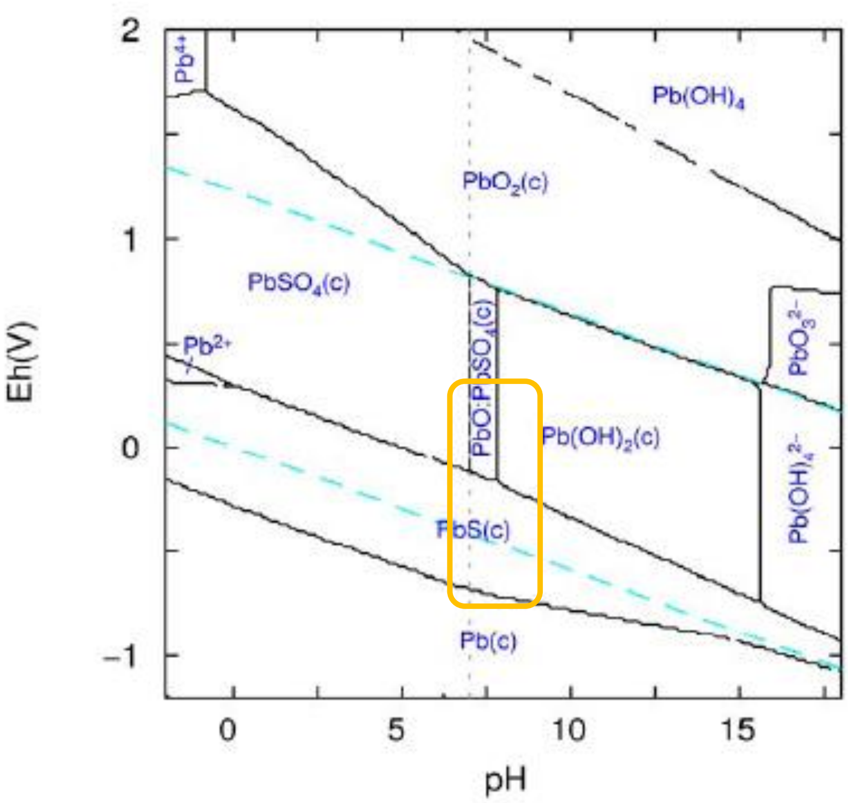


PW - Troll

Sea water



Stability of Pb in PW and sea water

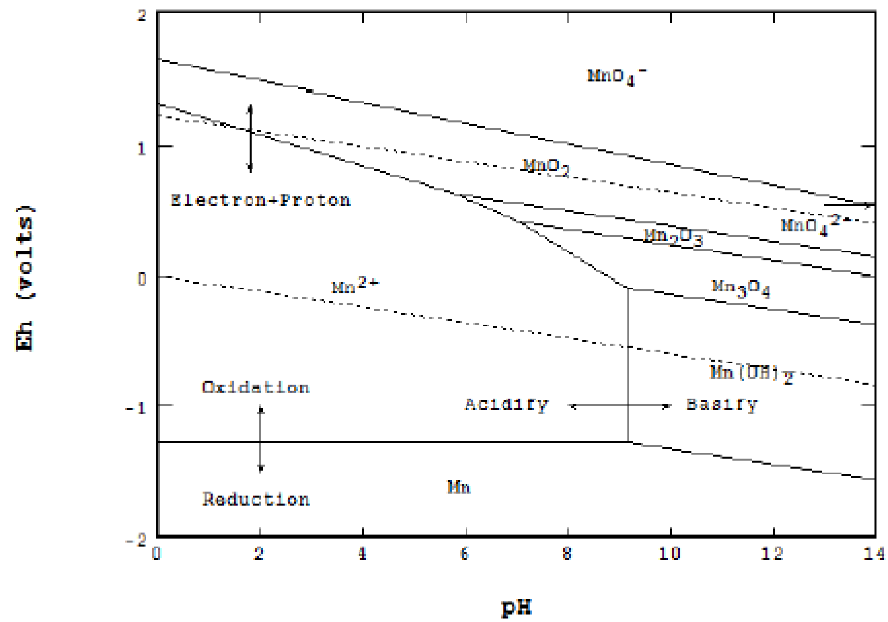


Eh-pH diagrams are usually much more instructive

Low probability that lead is in solution. It will probably be attached to particulates.

Metal has more than one oxidation state

- Mn as example:
  Mn-H_2O system



metals

Article

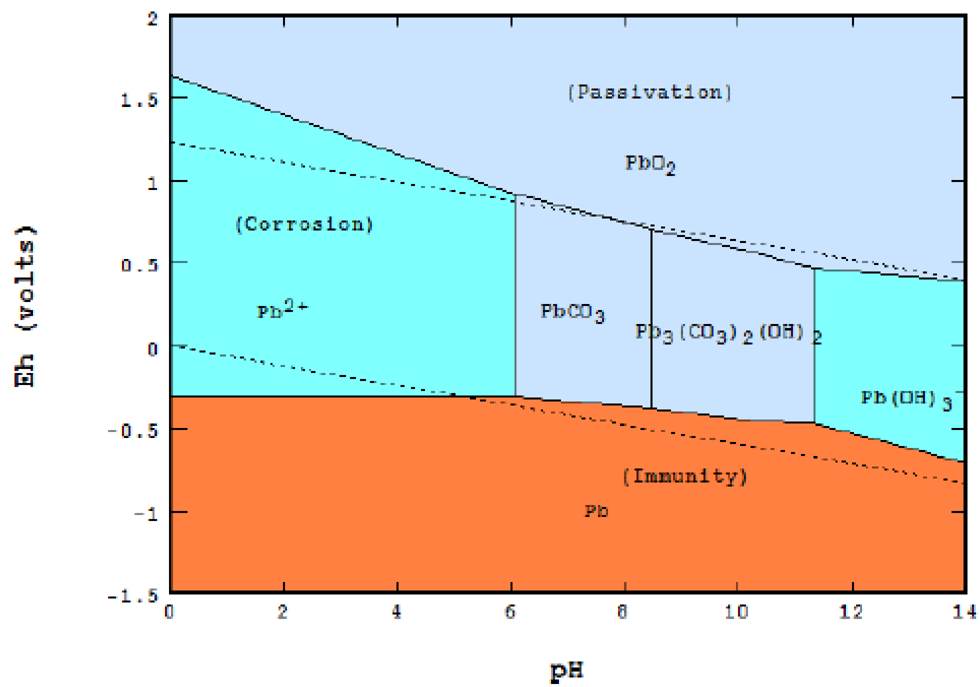
The Eh-pH Diagram and Its Advances

Hsin-Hsiung Huang

Received: 29 July 2015; Accepted: 28 December 2015; Published: 14 January 2016

Metal has more than one oxidation state – and/or forms stable salts/complexes

- Pb as example:
  $PbCO_3$-H_2O system



$[Pb] = 1 \times 10^{-6}$ and $[CO_3] = 0.001$ M.

metals

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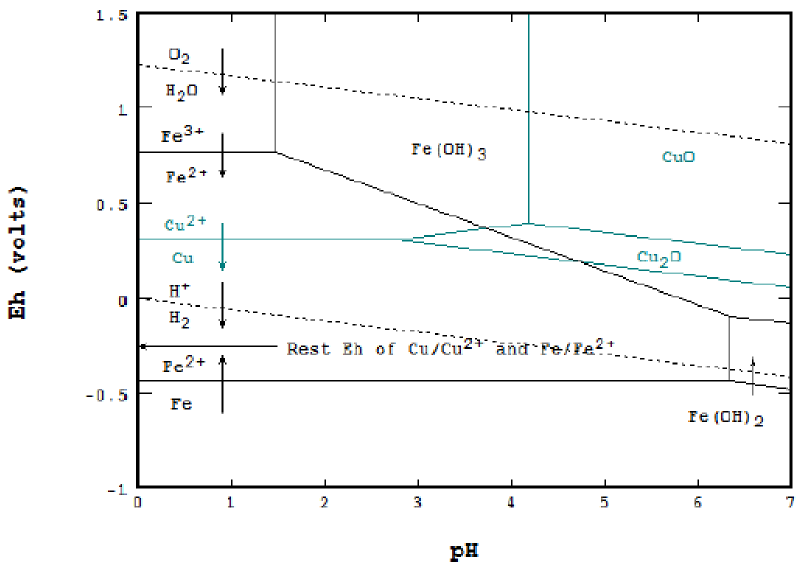
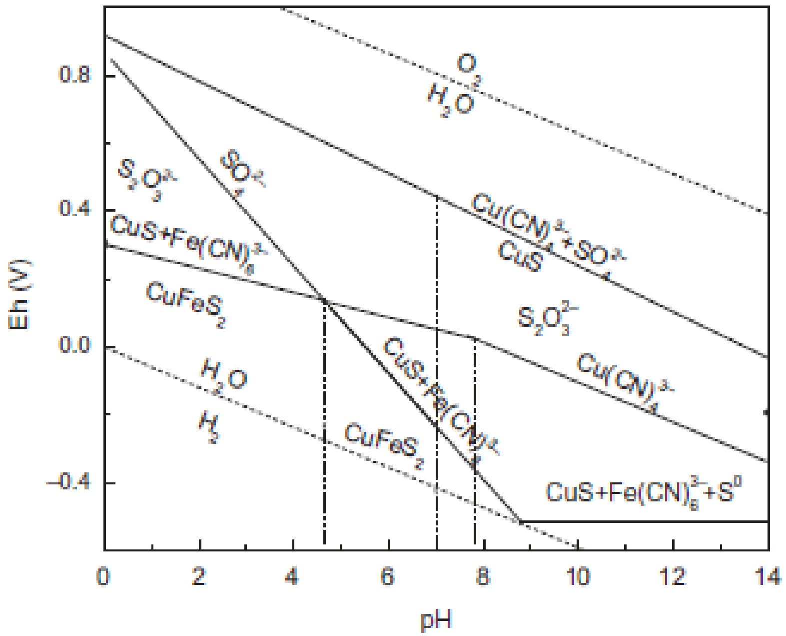
Combining two metals

- Chalcopyrite is an important source for Cu
  - $CuFeS_2$





Chalcopyrite–NaCN–H_2O System

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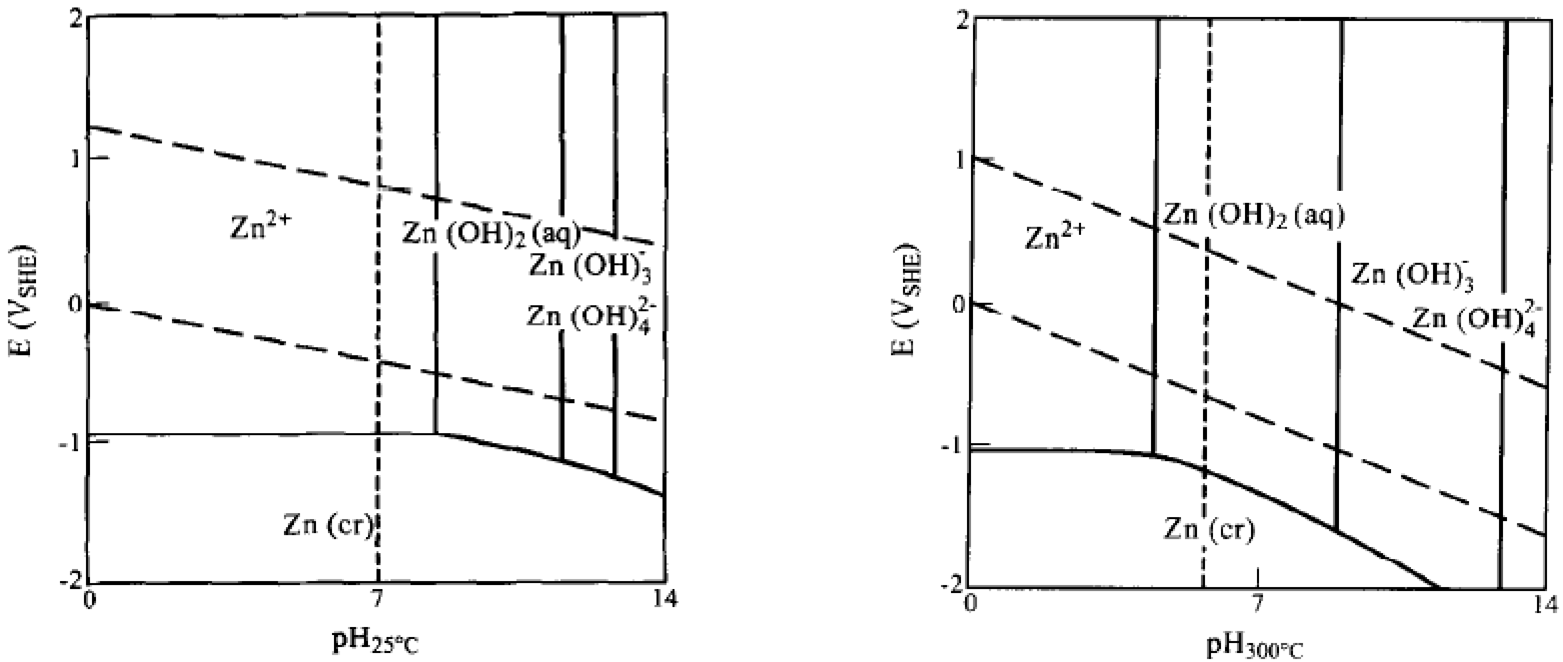
How to construct Eh-pH diagrammes

- Based on Ch.3.3 in M. Free: Hydrometallurgy
  1. Write out the species to be considered
  2. Write out chemical equilibria
  3. Calculate equations for equilibrium lines
  4. Activities are to be used, not concentrations

1. E.g.:
   Zn, ZnO, ε-$Zn(OH)_2$, Zn^{2+}, $ZnOH^{+}$, $Zn(OH)_2$, $Zn(OH)_3^{-}$, $Zn(OH)_4^{2-}$
2. E.g.:
   $Zn^{2+} + H_2O \leftrightarrow ZnOH^{+} + H^{+}$
   $Zn^{2+} + nOH^{-} \leftrightarrow Zn(OH)_n^{2-n}$
3. $E = E^0 - \frac{RT}{nF} \ln \frac{\{red\}}{\{ox\}}$

Published results on Zn:



B.Beverskog & I. Puigdomenech, Corrosion Science, Vol.39, No.1, 107-114 (1997)