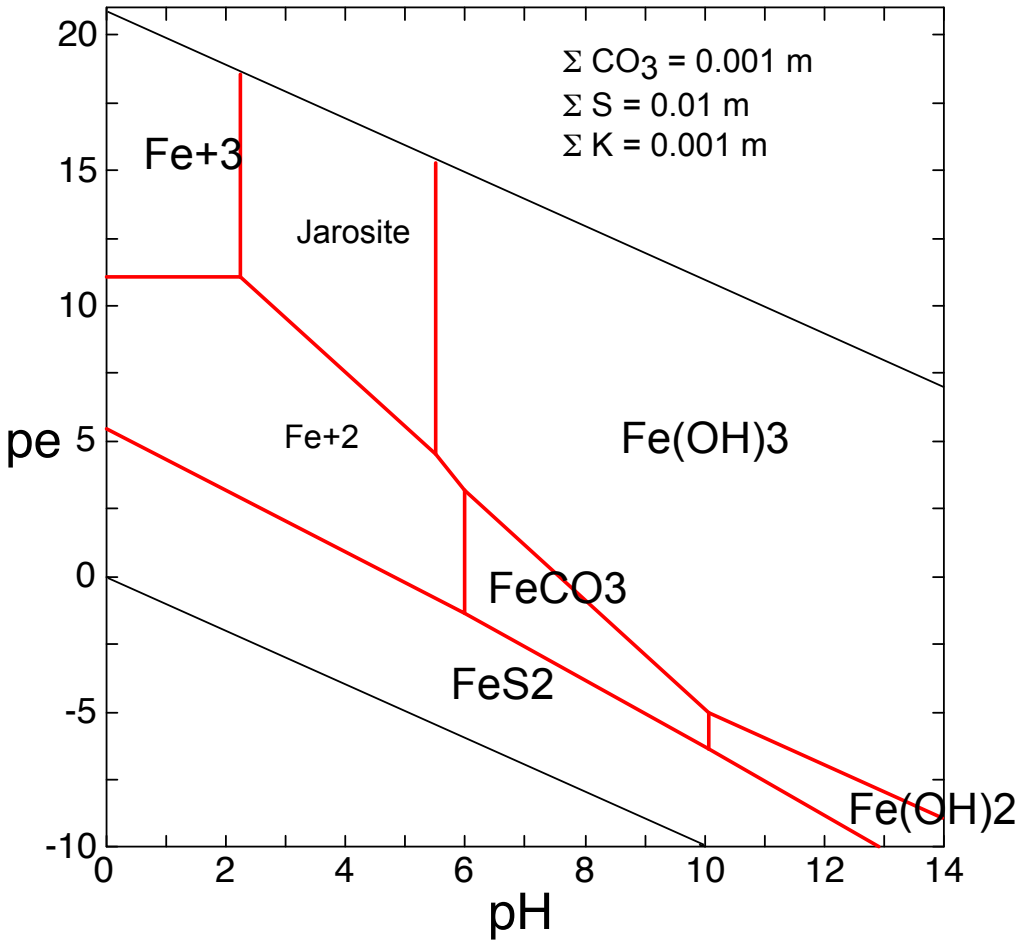
Chemistry for Earth Sciences
Practical 5: Redox Equilibria and the Phase Rule
(WORKED SOLUTIONS)

1. In the pe-pH diagram below, the possible species and phases are

Fe^{+3} (aqueous)
$Fe(OH)_3$ (solid)
FeS_2 (pyrite)
$FeCO_3$ (siderite)
$Fe(OH)_2$ (solid)
$KFe_3(OH)_6(SO_4)_2$ (Jarosite)

Try to work out which species/phases occupy which stability fields

Solution:



2. Near a sulfide ore body, the minerals pyrite (FeS_2), chalcopyrite ($CuFeS_2$) bornite (Cu_5FeS_4), and covellite (CuS) are present. How many components are in this assemblage? How many degrees of freedom does the phase assemblage have?

Solution: there are three components (Fe, Cu and S), four phases and, therefore f = 3-4+2 = 1 degree of freedom (i.e., at a given pressure, this phase assemblage can exist only at 1 temperature).

3. Consider the system $(Mg,Ca)CO_3(s)$ + aqueous solution (with $H_2O + Mg^{+2}$ $Ca^{+2} + CO_3^{-2} + H_2CO_3 + HCO_3^- + OH^- + H^+$) + $CO_2(g)$. Note that the notation $(Mg,Ca)CO_3$ means that the phase is a solid solution between $MgCO_3$ and $CaCO_3$. How many phases, components and degrees of freedom does this system have?

Solution: There are three phases ((Mg,Ca)CO3(s) + aqueous solution + gas) and we need 4 components to describe every species/phase. This gives f= 4-3+2 = 3 degrees of freedom. If we fix P and T, we have 1 degree of freedom. This extra degree of freedom could be PCO2 (P = partial pressure), pH or Mg/Ca.
If we know one of these, we then know the others.

4. Consider the redox reaction

$$CH_2O + 3NO_3^- = CO_2 + H_2O + 3NO_2^-$$

Which species is being oxidized and which is being reduced? What is the change in oxidation state for C and the change for N? Can you decompose this reaction into two half-reactions?

Solution: Carbon is being oxidized from 0 to +4. Nitrogen is being reduced from +5 to +3. The half-reactions are:

CH2O + H2O = CO2 + 4e- + 4H+

NO3- + 2e- + 2H+ = NO2- + H2O

5. The pK for the reaction

$$MnO_2(s) + 4H^+ + 2e- = Mn^{2+} + 2H_2O$$

Is -41.4. Calculate the pe when $MnO_2(s)$ is present, the pH is 6.5 and the concentration of dissolved Mn^{+2} is 10^{-5} m.

Solution:

pK = p[Mn+2] – 4pH -2pe

-41.4 = 5-4(6.5) – 2pe to give pe = 10.2

6. Balance the following redox reactions and work out the two half-reactions:

a) $CH_4 + O_2 = CO_2(g) + H_2O(g)$

b) $Fe(OH)_3 + H_2S = FeS + S + H_2O$

c) $CH_2O = CH_4 + CO_2$

d) $CH_2O + NO_3^- + H^+ = CO_2 + H_2O + NH_4^+$

e) Nitrogen fixation:
$NH_4^+ + O_2 = NO_3^- + H^+ + H_2O$

Solution:

a) $CH_4 + O_2 = CO_2(g) + 2H_2O(g)$

$CO_2 + 4e^- + 4H^+ = CH_4$
$O_2 + 4e^- + 4H^+ = 2H_2O$

b) $Fe(OH)_3 + 3/2\ H_2S = FeS + 1/2\ S + 3\ H_2O$

$Fe(OH)_3 + e^- + H^+ + H_2S = FeS + 3H_2O$
$1/2\ S + e^- + H^+ = 1/2\ H_2S$

c) $CH_2O = CH_4 + CO_2$

$CH2O + 4e^- + 4H^+ = CH4 + H2O$
$CO_2 + 4e^- + 4H^+ = CH_2O + H_2O$

d) $2CH_2O + NO_3^- + 2H^+ = 2CO_2 + H_2O + NH_4^+$

$2CO_2 + 8e^- + 8H^+ = 2CH_2O + 2H_2O$
$NO_3^- + 8e^- + 10H^+ = NH_4^+ + 3H_2O$

e) $NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$

$NO_3^- + 8e^- + 10H^+ = NH_4^+ + 3H_2O$
$2\ O_2 + 8e^- + 8H^+ = 4H_2O$