Environmental Chemistry

Precipitation and dissolution, redox: solution

1) Iron precipitation

$FePO_4 = Fe^{3+} + PO_4^{3-}$	$K_{s0} = 10^{-26} = [Fe^{3+}]\,[PO_4^{3-}]$	eq. 1
$Fe(OH)_3 = Fe^{3+} + 3OH^-$	$K_{s0} = 10^{-38.7} = [Fe^{3+}]\,[OH^-]^3$	eq. 2
$H_3PO_4 = H_2PO_4^- + H^+$	$K = 10^{-2.1} = [H_2PO_4^-]\,[H^+]\,[H_3PO_4]^{-1}$	eq. 3
$H_2PO_4^- = HPO_4^{2-} + H^+$	$K = 10^{-7.2} = [HPO_4^{2}]\,[H^+]\,[H_2PO_4^-]^{-1}$	eq. 4
$HPO_4^{2-} = PO_4^{3-} + H^+$	$K = 10^{-12.3} = [PO_4^{3-}]\,[H^+]\,[HPO_4^{2-}]^{-1}$	eq. 5

$[PO_4^{3-}]_{tot} = 10^{-4}\ M = [PO_4^{3-}] + [HPO_4^{2}] + [H_2PO_4^-] + [H_3PO_4]$ eq. 6

Use eqs. 3-5 to express concentrations of $[HPO_4^{2}]$, $[H_2PO_4^-]$ and $[H_3PO_4]$:

$[PO_4^{3-}]_{tot} = [PO_4^{3-}]\,(1 + [H^+]10^{12.3} + [H^+]^2 10^{19.5} + [H^+]^3 10^{21.6})$

Solve for $[PO_4^{3-}]$:

$[PO_4^{3-}] = [PO_4^{3-}]_{tot}\,(1 + [H^+]10^{12.3} + [H^+]^2 10^{19.5} + [H^+]^3 10^{21.6})^{-1}$ eq. 7

Solve eq. 1 for $[Fe^{3+}]$ and insert eq. 7:

$[Fe^{3+}]$ in eq. 1 = $5.16 * 10^{-17}$ M

Solve eq. 2 for $[Fe^{3+}]$ and insert eq. 7:

$[Fe^{3+}]$ in eq. 2 = $2 * 10^{-18}$ M

Iron hydroxide will precipitate, as evidenced from the lower concentration of [Fe3+] in equilibrium with $Fe(OH)_3$ than $FePO_4$.

2) Oxidation numbers

NO_3^- :	N(+V)	O(-II)		
N_2O :	N(+I)	O(-II)		
SCN^- :	S(-I)	N(-III)	C(+III)	(S–C≡N)

(since S and C have nearly the same electronegativity, it is assumed that each of them gets one electron of the shared bond)

SO_3^{2-} :	S(+IV)	O(-II)	
SO_4^{2-} :	S(+VI)	O(-II)	
CH_4 :	C(-IV)	H(+I)	
CO_2 :	C(+IV)	O(-II)	
CH_3OH :	C(-II)	O(-II)	H(+I)
C_6H_6 :	C(-I)	H(+I)	
C_6H_5OH	C(-0.667)	O(-II)	H(+I)

3) Reduction potentials

a)

$2(O_2 + 4H^+ + 4e^- = 2H_2O)$

$-(NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O)$

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

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

$\Delta E^0 = 1.19 – 0.88 = \underline{0.31\ V}$

b) For O_2/H_2O:

$E^0{}_{(pH = 7)} = E^0 – 0.059/n * \log Q = E^0 – 0.059/4 * \log (1/([O_2]*[H^+]^4))$

$= 1.19 – 0.059/4 * \log (1/(1*[10^{-7}]^4)) = 0.78\ V$

For NH_4^+/NO_3^-:

$E^0{}_{(pH = 7)} = E^0 – 0.059/n * \log Q = E^0 – 0.059/8 * \log([NH_4^+]/([NO_3^-]*[H^+]^{10}))$

$= 0.88 – 0.059/8 * \log(1/(1*[10^{-7}]^{10})) = 0.36\ V$

$\Delta E°(pH=7) = 0.78 - 0.36 = \underline{0.42\ V}$

c) $\Delta G = -n F \Delta E = -8 * 96485$ Coulomb/mol $* 0.42$ V $= -324$ kJ/mol

d) The process is called nitrification. It is thermodynamically possible (ΔE positive, ΔG negative). However, it is kinetically controlled and – in abiotic systems – practically not occurring on a relevant time span because the reaction is very slow (remember that thermodynamics and kinetics are two different aspects). It is nevertheless an important process in the environment because it is microbially mediated, i.e. bacteria catalyze the reaction. It occurs in

- Wastewater treatment (removal of ammonia)
- Surface waters, groundwaters (consumption of oxygen may lead to anoxic conditions)
- Soils (acidification of soils due to H+ production)

4) pe-pH diagram for As

The limits of the pe-pH stability diagram are given by the stability limits for water, as calculated in class:

$$pe = 20.6 – pH \qquad \text{eq. 1}$$

and

$$pe = -pH \qquad \text{eq. 2}$$

From the table, for As(5):

$$\log(K) = -6.76 = \log([HAsO_4^{2-}]) – pH – \log([H_2AsO_4^-])$$

If the activities of the As species are equal, then:

$$pH = 6.76 \qquad \text{eq. 3}$$

For As(3):

$$\log(K) = -9.23 = \log([H_2AsO_3^-]) – pH – \log([H_3AsO_3])$$

Again, if the As species activities are equal then:

$$pH = 9.23 \qquad \text{eq. 4}$$

For As(5)/As(3):

$$\log(K) = -21.14 = \log([H_2AsO_4^-]) - 3pH - 2pe - \log([H_3AsO_3])$$

For equal As species activities, this gives:

$$pe = 10.57 - \frac{3}{2} pH \qquad \text{eq. 5}$$

The boundaries between $HAsO_4^{2-}$ and H_3AsO_3, and $HAsO_4^{2-}$ and $H_2AsO_3^-$ are needed. For the $HAsO_4^{2-}$ / H_3AsO_3 boundary, the first and third reactions in the table give:

$$H_3AsO_3 + H_2O = HAsO_4^{2-} + 4H^+ + 2e^-$$

With log(K) = -21.14-6.76 = -27.9

Therefore, $-27.9 = \log([HAsO_4^{2-}]) - 4H^+ - 2pe - \log([H_3AsO_3])$

For equal As species activities:

$$pe = 13.95 - 2pH \qquad \text{eq. 6}$$

For the $HAsO_4^{2-}$/$H_2AsO_3^-$ boundary, the second and third equations in the table give, when added:

$$H_2AsO_3^- - + H_2O = H_2AsO_4^- + 2H^+ + 2e^-$$

with log(K) = 9.23 – 21.14 = -11.91

Now replace $H_2AsO_4^-$ using the first equation in the table:

$$H_2AsO_3^- + H_2O = HAsO_4^{2-} + 3H^+ + 2e^-$$

with log(K) = -11.91 – 6.76 = -18.67. Thus,

$$\log(K) = -18.67 = \log([HAsO_4^{2-}]) - 3\ pH - 2pe - \log([H_2AsO_3^-])$$

At equal As species activities:

$$pe = 9.335 - \frac{3}{2} pH \qquad \text{eq. 7}$$

Drawing the diagram

Eqs. 1-3 are a series of straight lines. The range of eqs. 1 and 2 is given as follows:

$$0 \leq pH \leq 14$$

Eq. 3 separates $H_2AsO_4^-$ and $HAsO_4^{2-}$. Its maximum value is at:

$$pe = 20.6 - 6.76 = 13.84 \qquad \text{eq. 8}$$

The minimum value for eq. 3 is at the $H_2AsO_4^-$ / H_3AsO_3 boundary. This occurs at (eq. 6):

$$pe = 13.95 - 2 \times 6.76 = 0.43 \qquad \text{eq. 9}$$

Eq. 4 separates H_3AsO_3 and $H_2AsO_3^-$. Its minimum value is at eq. 2, i.e.,

$$pe = -9.23 \qquad \text{eq. 10}$$

The maximum value of eq. 4 is at the $HAsO_4^{2-}$ / H_3AsO_3 boundary. From eq. 7 this is:

$$pe = 9.335 - 9.23 = -4.51 \qquad \text{eq. 11}$$

The maximum pH value of eq. 5 is given by eq. 3, i.e., at pH = 6.76. For this pH, eq. 5 gives the pe value:

$$pe = 10.57 - \frac{3}{2} \times 6.76 = 0.43 \qquad \text{eq. 12}$$

The range of eq. is, from above, pH = 6.76 and the intersection of eqs. 6 and 7. This intersection occurs at pH = (13.95 – 9.335) x 2 = 9.23.

Finally, eq. 7 then applies for:

$$7.995 \leq pH \leq 14$$

We obtain the following plot: