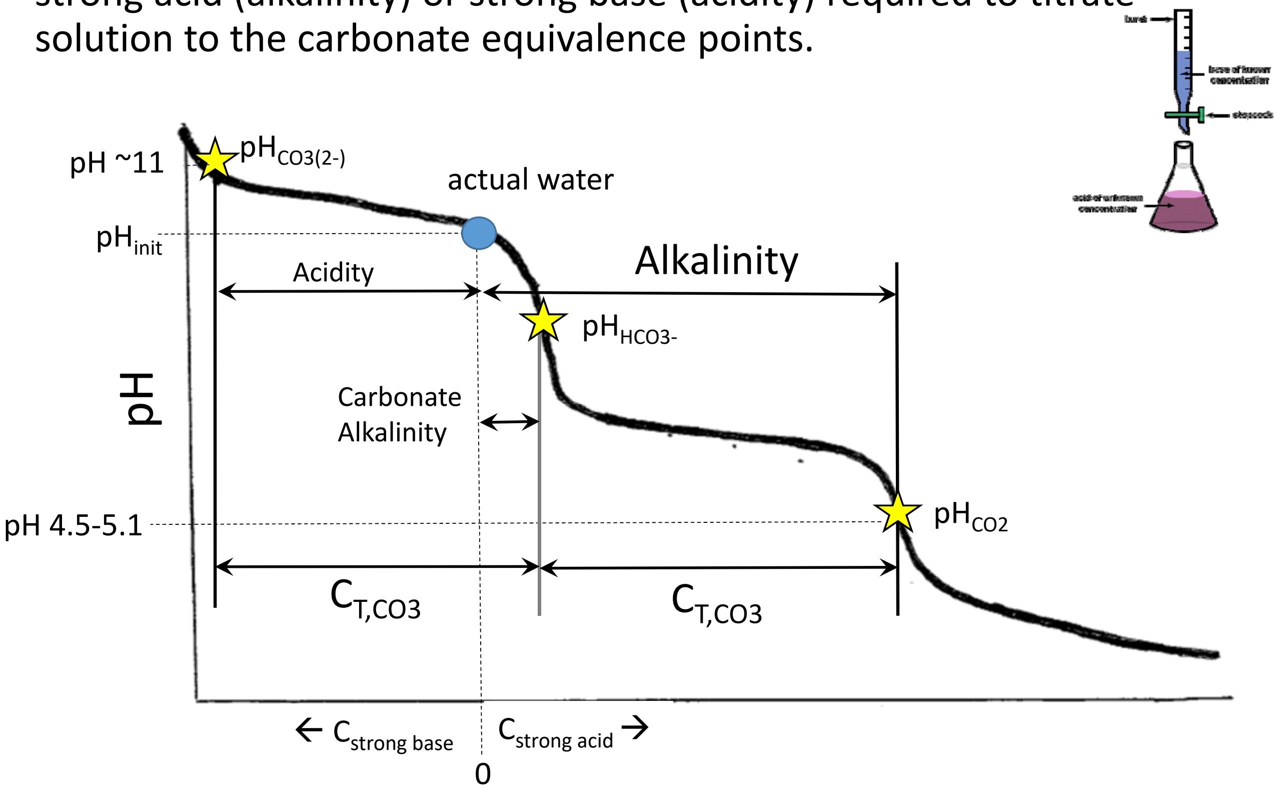
Advanced Water Quality

Class 16: Coordination Chemistry

Review of last week

- Analytical definitions of alkalinity and acidity = concentration of strong acid (alkalinity) or strong base (acidity) required to titrate solution to the carbonate equivalence points.



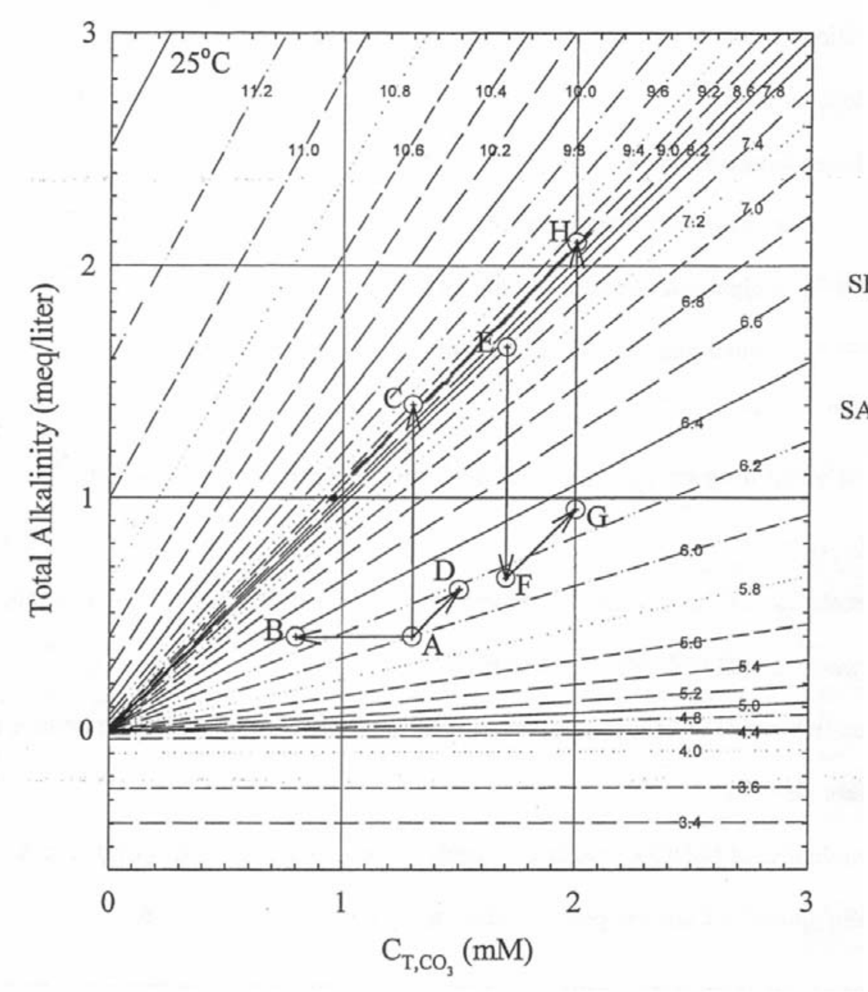
Chemical Definition of Alkalinity

If we assume carbonate acid/base chemistry dominates (90% of natural waters)

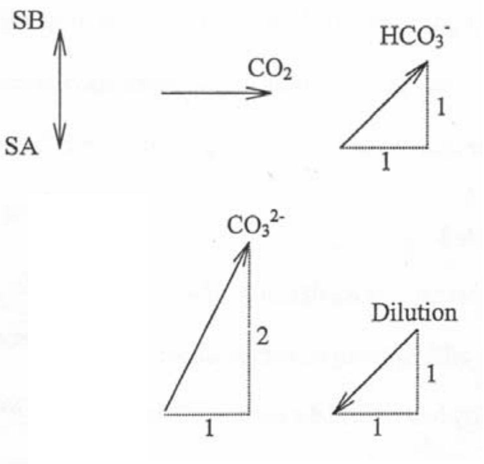
$$\underbrace{\text{Tot ALK (eq/L)}}_{\text{ANC to pH}_{CO2}} = \underbrace{\Sigma[BC] - \Sigma[SA]}_{\text{Inert ion “imbalance”}} = \underbrace{[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]}_{\text{Sum of titratable bases to pH}_{CO2}}$$

Implications of ALK = $\Sigma[BC] - \Sigma[SA]$

- No change in ALK when CO_2 transfers to/from water
- Increase ALK by adding a salt the increases $\Sigma[BC]$ more than $\Sigma[SA]$
- Decrease ALK by adding substance that increases $\Sigma[SA]$ more than $\Sigma[BC]$



Deffeyes Diagram



Prob 6: The sourcewater entering a drinking water treatment plant has pH 5.8 and alkalinity of 0.2 meq/L.
(a) What will be the new alkalinity and pH if 53 mg/L of soda ash (Na_2CO_3 -MW: 106) is added to the sourcewater?

$[Na_2CO_3]$ = 53 mg/106 = 0.5 mM

At pH 5.8, ALK $\cong$ $[HCO_3^-]$ = $\alpha_1 C_{T,CO3}$ where α_1 = 0.22
$C_{T,CO3}$ = 9.1 x 10^{-4}M

$C_{T,\text{ final}}$ = 9.1 x 10^{-4}M + 5 x 10^{-4}M = 1.41 x 10^{-3} M

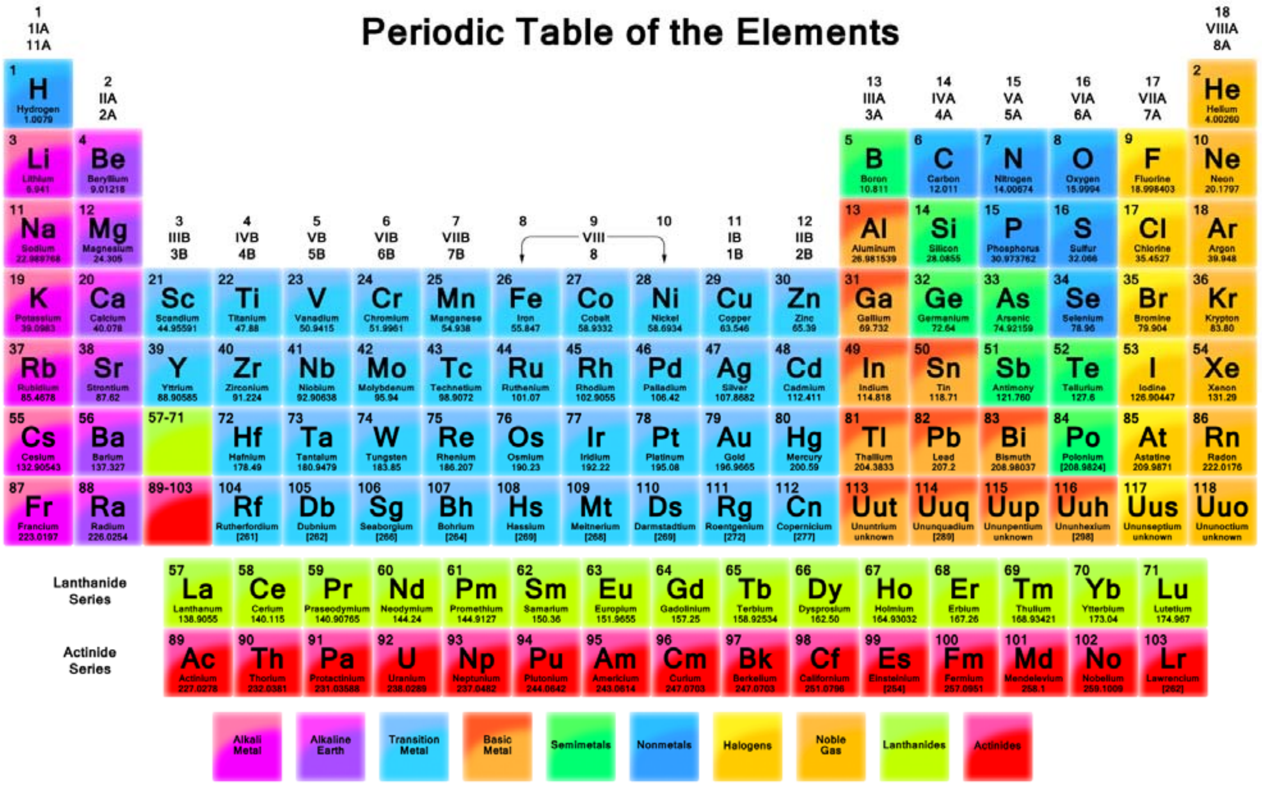
ALK_{final} = ALK_{init} + ALK_{Na2CO3} =0.2 meq/L + 2*0.5 meq/L = 1.2 x 10^{-3} M

pH = 7.1 from new C_T and ALK

Today's NEW Topic

- The aqueous chemistry of metal ions
  1. Coordination chemistry concepts and terms
  2. Factors affecting the strength of metal-ligand interactions
  3. Describing metal-ligand complexation equilibria complexes
     1. Metal-ligand complexation
     2. Metal ion hydrolysis – formation of dissolved $M(OH)_x^y$ complexes
     3. Solving complexation Equilibria

Coordination chemistry and metal speciation



Coordination chemistry

In aqueous systems, metal ions are present as coordination complexes with ligand molecules

(Free metal ion) **+** **(Ligand)** **→** **coordination complex**

positively charged

negatively charged or neutral

cationic, neutral or anionic

Metal	Ligand × CN	Coordination complex
Mg^{2+}	H_2O × 6	$Mg(H_2O)_6^{2+}$
Co^{2+}	Cl^- × 4	$CoCl_4^{2-}$
Ni^{2+}	OH^- × 1 + H_2O x 5	$Ni(OH)(H_2O)_5^+$
Pd^{2+}	PPh_3 × 2, Cl^- × 2	$Pd(PPh_3)_2Cl_2$
Mn^{7+}	O^{2-} × 4	MnO_4^-

Coordination number (CN): # of metal-ligand coordination bond from the central metal ion.

Metal Ion-Ligand Coordination Bonds

- Lewis acid (e$^-$ pair acceptor) – base (e$^-$ pair donor) interactions
- Ligands are Lewis bases (have free e$^-$ pair to donate to form coordination bond)

- Metal ions are Lewis acids (have empty orbitals to accept e$^-$ pair to form coordination bond)

Common ligands in environmental chemistry

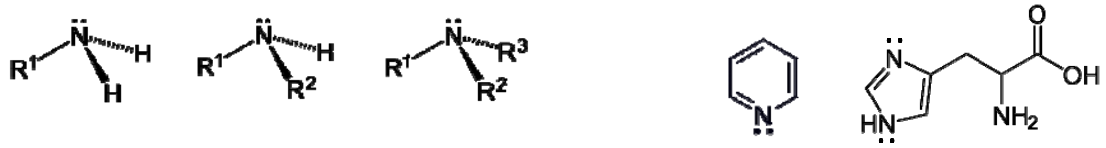
Halide ions: F^-, Cl^-, Br^-, I^-

O-donors: H_2O, OH^-, CO_3^{2-}, SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}

carboxylates (R-COO^-), phenolates (PhO^-)

N-donors: NH_3

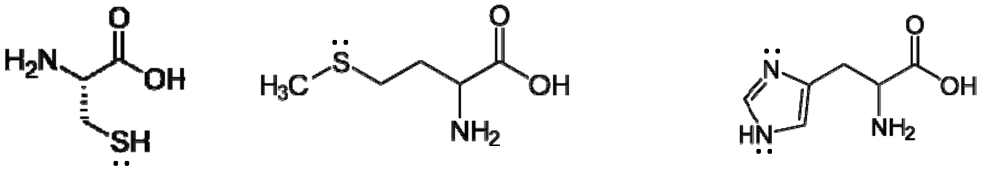
amines (R-NH_2, R_2NH, R_3N), heterocyclic N (e.g. pyridine, imidazole)



S-donors: H_2S, HS^-

cysteine, methionine

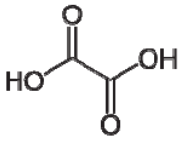
histidine



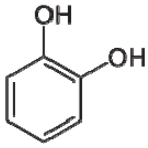
Ligands also classified by the number of metal binding sites they possess

- Monodentate – single binding site

- Multidentate – bond to metal simultaneously with multiple donor e^- pairs

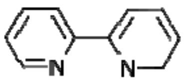


oxalate

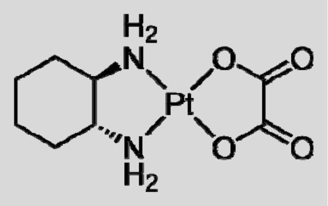


catechol

ethylenediamine (en)

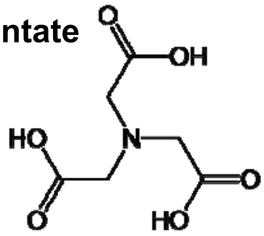


2,2'-bipyridine (bpy)

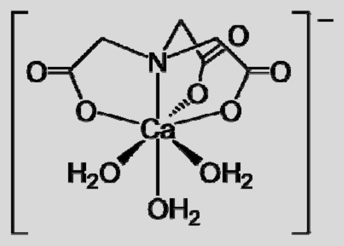


- Chelating agents – form very strong multidentate complexes with metal ions

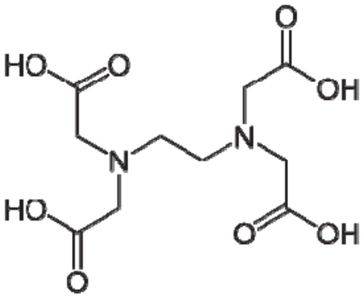
Tetradentate



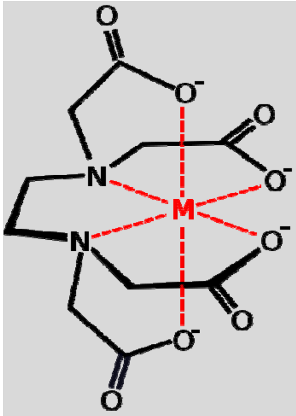
Nitrilotriacetic acid (NTA)



Hexadentate



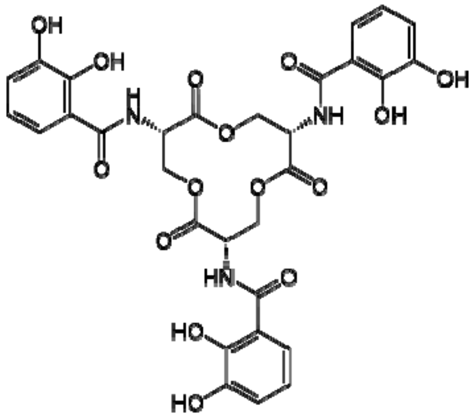
Ethylenediaminetetraacetic acid (EDTA)

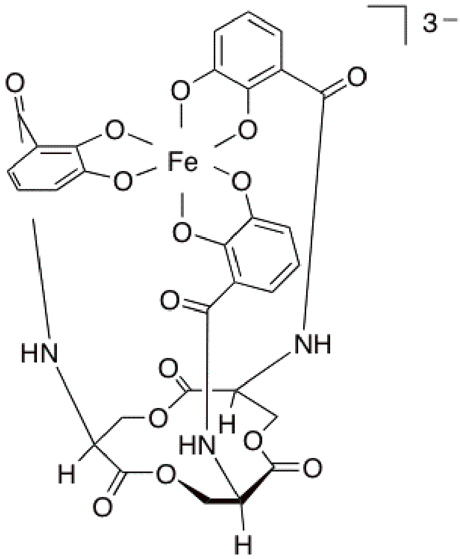


Multidentate ligands in nature

Siderophores (Greek: "iron carrier") are small, high-affinity iron chelating compounds secreted by microorganisms.

Enterobactin is the strongest siderophore known to bind Fe^{3+} ($K_{ent\text{-}Fe} = 10^{52}$, compared to $K_{EDTA\text{-}Fe} \sim 10^{25}$ compared to $K_{acetate}$-Fe $\sim 10^{4}$

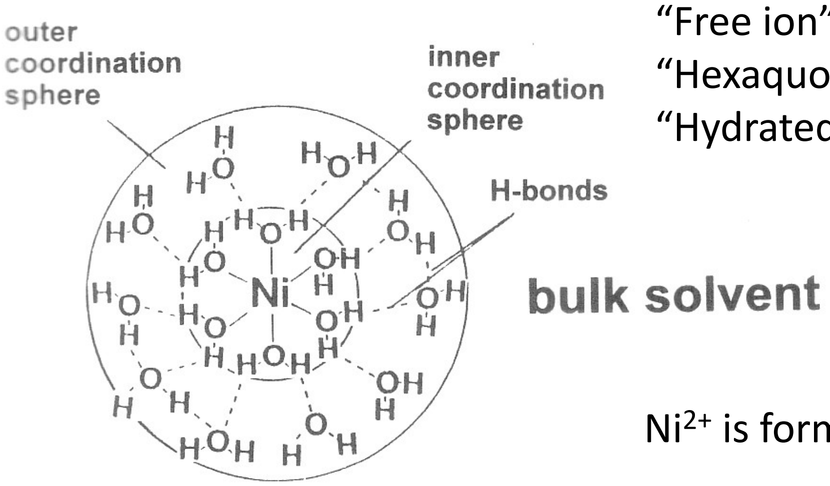




Fe(III)-Enterobactin

Metal ions in aqueous solution

- Typically represent metal ions such as Ni^{2+} as though they are bare ions
- Reality – Ni^{2+} is coordinated to multiple H_2O molecules by default



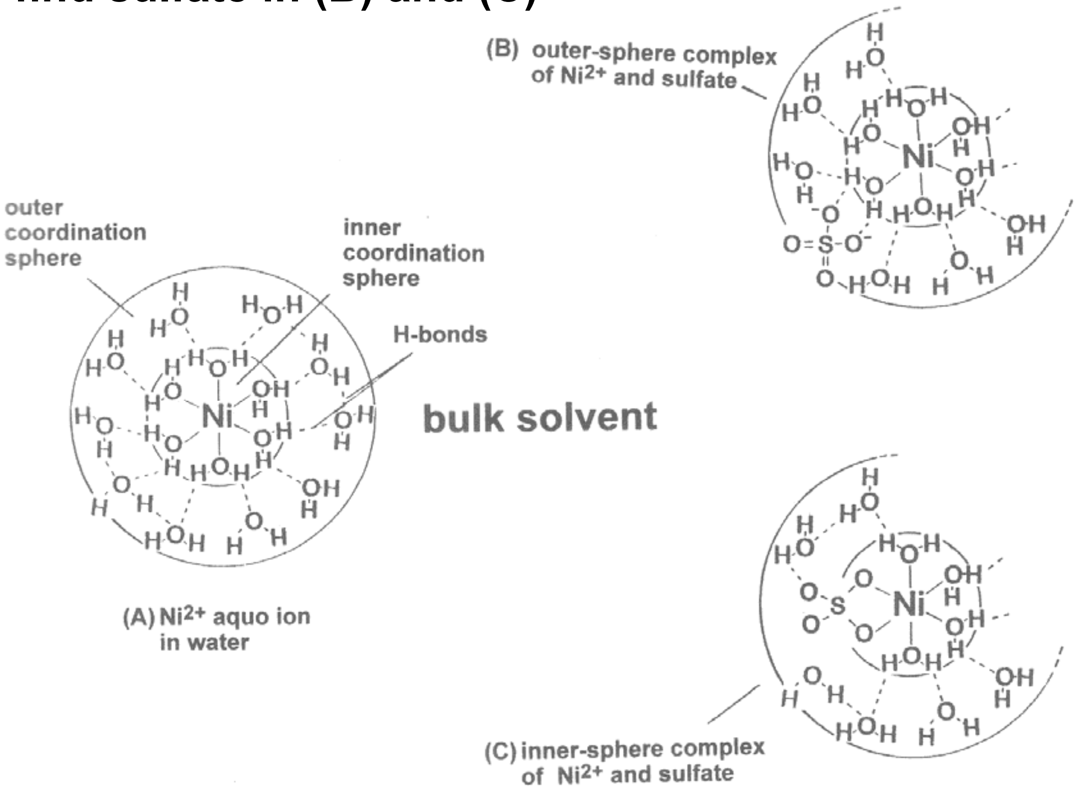
“Free ion” species
“Hexaquo” species
“Hydrated” species

Ni^{2+} is formally $Ni(H_2O)_6^{2+}$

From Martell & Hancock (1996) Metal Complexes in Aqueous Solutions

Outer- versus Inner-Sphere Complexes

-find sulfate in (B) and (C)



Metal-ligand complexation equilibria

- Ligand exchange with coordinated H_2O typically shown without formally showing the coordinated H_2O molecules

$$\mathrm{Cd(H_2O)_6^{2+} + Cl^- \rightleftharpoons CdCl(H_2O)_5^{+} + H_2O}$$

$$\mathrm{Cd^{2+} + Cl^- \rightleftharpoons CdCl^{+}}$$

$$K_1 \ and \ \beta_1 = \frac{[CdCl^+]}{[Cd^2+][Cl^-]} = 10^{1.98}$$

- Likewise, we can consider stepwise formation of higher order Cd(II) complexes with Cl^- (like stepwise deprotonation)

$$CdCl^+ + Cl^- \rightleftharpoons CdCl_2 \qquad K_2 = 10^{0.62}$$

$$CdCl_2 + Cl^- \rightleftharpoons CdCl_3^- \qquad K_3 = 10^{-0.2}$$

- Alternatively, we often find it useful to write the expressions in terms of complex formation from the "component" species:

$Cd^{2+} + Cl^- \rightleftharpoons CdCl^+$ $$K_1 = \beta_1 = \frac{[CdCl^+]}{[Cd^2+][Cl^-]} = 10^{1.98}$$

$Cd^{2+} + 2Cl^- \rightleftharpoons CdCl_2$ $$\beta_2 = \frac{[CdCl_2]}{[Cd^{2+}][Cl^-]^2} = 10^{2.6}$$

$Cd^{2+} + 3Cl^- \rightleftharpoons CdCl_3^-$ $$\beta_3 = \frac{[CdCl_3]}{[Cd^{2+}][Cl^-]^3} = 10^{2.4}$$

$$C_{T,Cd} = [Cd^{2+}]+[CdCl^+]+[CdCl_2]+[CdCl_3^-]$$

$$C_{T,Cl} = [Cl^-]+[CdCl^+]+2[CdCl_2]+3[CdCl_3^-]$$

- This is the form used by programs like Visual Minteq

Problem: Determine the concentration of each Cd species with 0.01 M Cd^{2+} is added to a salt brine containing 2.0 M Cl^-. *Neglect ionic strength and pH effects for this problem.*

Simplification:
$[Cl^-]$ is the dominant species of $C_{T,Cl}$ (thus it is 2.0 M)

Metal ion hydrolysis

- H_2O is the default ligand in aqueous solution

$$M(H_2O)_6^{2+} + H_2O \rightleftharpoons MOH(H_2O)_5^{+} + H_3O^{+}$$

- Hydrolysis = splitting of water ($H_2O \rightarrow OH^- + H^+$)
- Metal ion hydrolysis: metal ion promotes splitting of coordinated water molecules
- Metal ion hydrolysis stoichiometry: metal ions acting like Bronsted acids (i.e., H^+ donor)

- Metal ions promote hydrolysis of coordinated H_2O mCs because M-O bond weakens the O-H bond
  - makes coordinated H_2O more acidic than H_2O mCs in bulk solution
- Most metal ions can only promote donation of 1 proton from each coordinated water

$$Cu(H_2O)_6^{2+} + xH_2O^- \rightleftharpoons Cu(OH)_x(H_2O)_{6-x}^{2-x} + xH_3O^+$$

- Some metal ions have such strong M-O interactions that both H^+ are donated to solution, forming “oxyanion” metals:

$$CrO_4^{2-}, MnO_4^-, AsO_3^{3-}$$

Metal ion hydrolysis equilibria represented in different ways

1. Ligand exchange reaction between OH^- from bulk solution and a metal-coordinated H_2O molecule:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons FeOH(H_2O)_5^{2+} + H_3O^+$$

$$Fe(H_2O)_6^{3+} + OH^- \rightleftharpoons FeOH(H_2O)_5^{2+} + H_2O$$

$$Fe^{3+} + OH^- \rightleftharpoons FeOH^{2+}$$

$$K_1 = \frac{[FeOH^{2+}]}{[Fe^{3+}][OH^-]} = 10^{11.81}$$

2. Transfer of a H^+ from a coordinated H_2O molecule to a bulk H_2O molecule (reality):

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons FeOH(H_2O)_5^{2+} + H_3O^+$$

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$$

$$^*K_1 = \frac{[FeOH^{2+}][H^+]}{[Fe^{3+}]}$$

$^*K_1$ and K_1 values related by $K_w = [H^+][OH^-]$

$$^*K_1 = K_1K_w = \frac{[FeOH^{2+}]}{[Fe^{3+}][OH^-]} \times [H^+][OH^-]$$

$$^*K_1 = 10^{11.81}10^{-14} = 10^{-2.19}$$

Formation of complexes with multiple coordinated OH^- can be represented in successive steps (like acid-base pKa values)

$$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+$$

$$^*K_2 = \frac{\left[Fe(OH)_2{}^+\right][H^+]}{[FeOH^{2+}]} = 10^{-3.48}$$

Or we can represent as complex formation from component species (M^{n+}, H^+):

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+$$

$$^*\beta_2 = {}^*K_2 \times {}^*K_1 = \frac{[Fe(OH)_2{}^+][H^+]^2}{[Fe^{3+}]}$$

$$^*\beta_2 = 10^{-5.67}$$

Similarly, we can represent successive complexation of OH- (K_1, K_2, …) or complex formation from Mn+ and OH- (β_1, β_2, ….)

How does the percentage of hydrolyzed species vary with changing pH conditions?

$$^*\beta_x = \frac{[Fe(OH)_x{}^+][H^+]^x}{[Fe^{3+}]}$$

When pH increases,
- OH complex of metal increases.

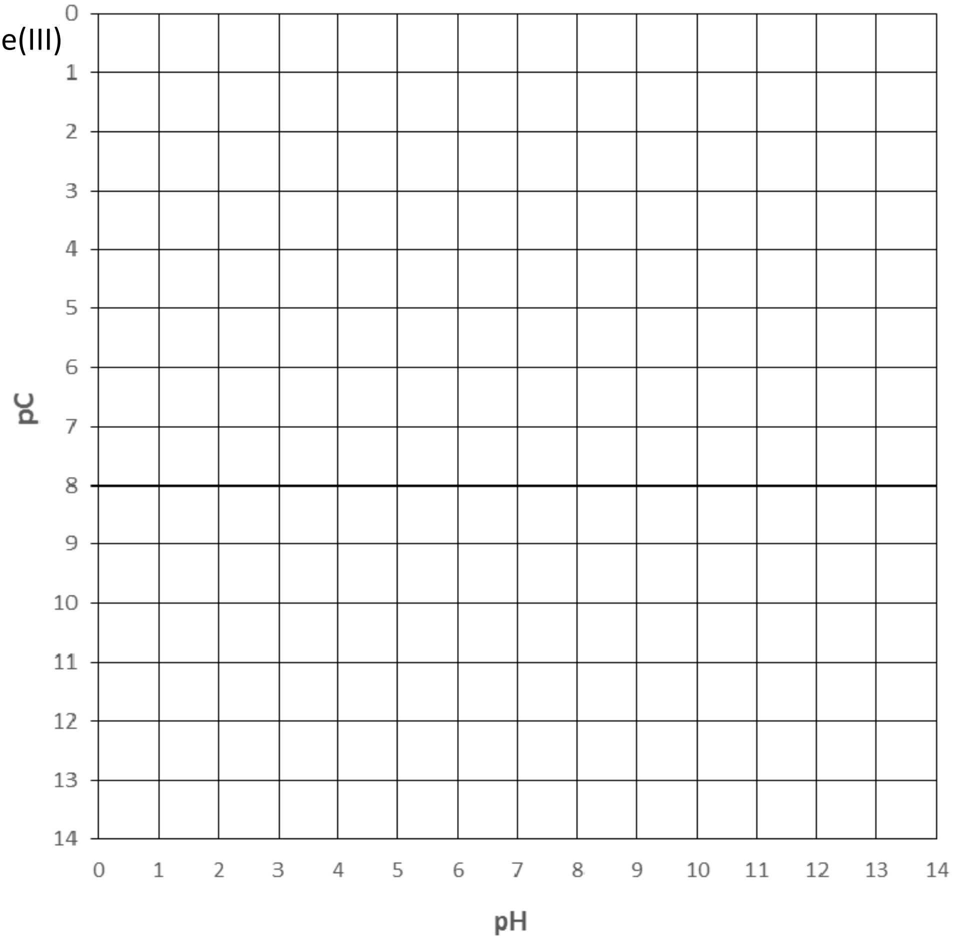
When pH decreases,
- OH complex of metal decreases.

Can generate “rough” pC-pH diagram for metal ion hydrolysis by same rules we previously learned using the p$^*K_i$ values

- Recall $^*K_i$ values are for successive proton donation steps

E.g., for 10^{-3} M Fe(III)

$^*K_1 = 10^{-2.19}$
$^*K_2 = 10^{-3.48}$
$^*K_3 = 10^{-7.93}$
$^*K_4 = 10^{-8.00}$



Can use mass balance with $^*\beta_i$ expressions to solve for $[Fe^{3+}]$ as a master variable at each pH condition, then use $^*\beta_i$ expressions to calculate $[Fe(OH)_x^y]$

$$C_{T,Fe(III)} = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2^{\ +}] + [Fe(OH)_3^{\ 0}] + [Fe(OH)_4^{\ -}]$$

$$C_{T,Fe(III)} = [Fe^{3+}]\left(1 + \frac{^*\beta_1}{[H^+]} + \frac{^*\beta_2}{[H^+]^2} + \frac{^*\beta_3}{[H^+]^3} + \frac{^*\beta_4}{[H^+]^4}\right)$$

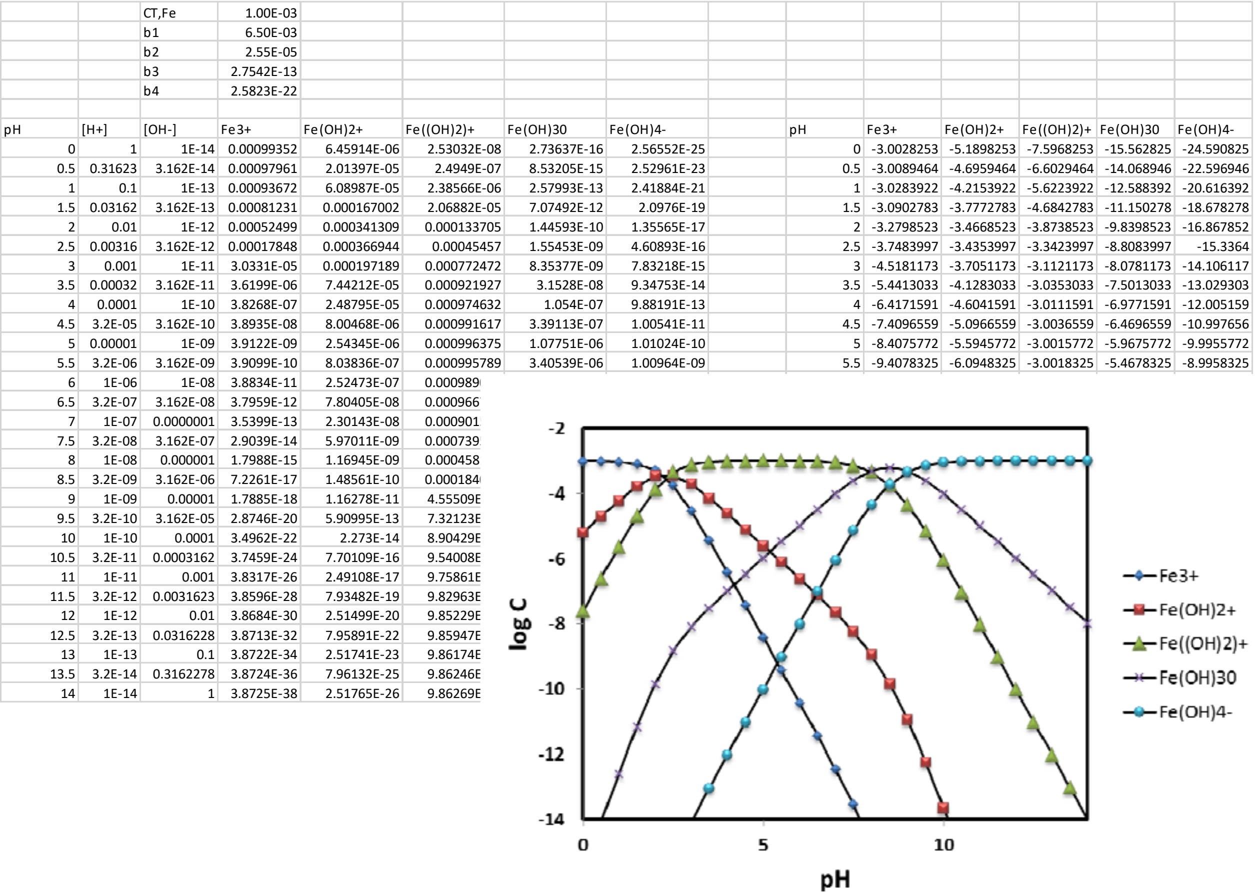
$$\therefore \quad [Fe^{3+}] = \frac{C_{T,Fe(III)}}{\left(1 + \frac{^*\beta_1}{[H^+]} + \frac{^*\beta_2}{[H^+]^2} + \frac{^*\beta_3}{[H^+]^3} + \frac{^*\beta_4}{[H^+]^4}\right)}$$

Plug this into Excel, vary pH, calculate $[Fe^{3+}]$

Then use $[Fe^{3+}]$ and $[H^+]$ at each pH condition to calculate $[Fe(OH)_x^y]$

$$[FeOH^{2+}] = \frac{^*\beta_1[Fe^{3+}]}{[H^+]} \qquad [Fe(OH)_3^{\ 0}] = \frac{^*\beta_3[Fe^{3+}]}{[H^+]^3}$$

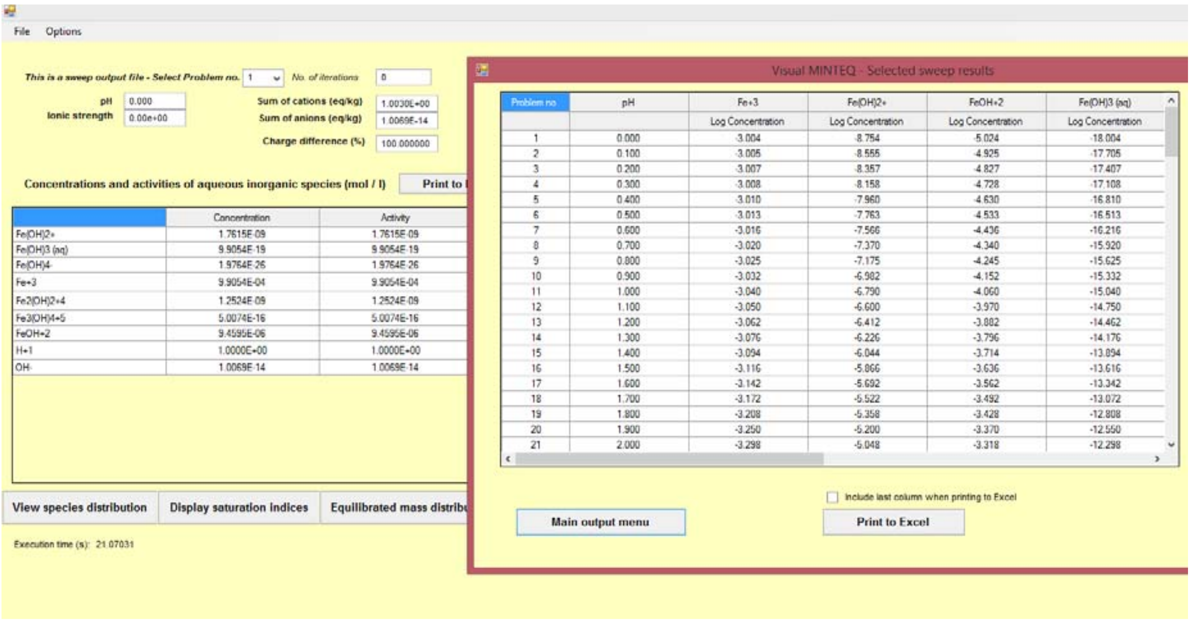
$$[Fe(OH)_2^{\ +}] = \frac{^*\beta_2[Fe^{3+}]}{[H^+]^2} \qquad [Fe(OH)_4^{\ -}] = \frac{^*\beta_4[Fe^{3+}]}{[H^+]^4}$$



		CT,Fe	1.00E-03
		b1	6.50E-03
		b2	2.55E-05
		b3	2.7542E-13
		b4	2.5823E-22

pH	[H+]	[OH-]	Fe3+	Fe(OH)2+	Fe((OH)2)+	Fe(OH)30	Fe(OH)4-
0	1	1E-14	0.00099352	6.45914E-06	2.53032E-08	2.73637E-16	2.56552E-25
0.5	0.31623	3.162E-14	0.00097961	2.01397E-05	2.4949E-07	8.53205E-15	2.52961E-23
1	0.1	1E-13	0.00093672	6.08987E-05	2.38566E-06	2.57993E-13	2.41884E-21
1.5	0.03162	3.162E-13	0.00081231	0.000167002	2.06882E-05	7.07492E-12	2.0976E-19
2	0.01	1E-12	0.00052499	0.000341309	0.000133705	1.44593E-10	1.35565E-17
2.5	0.00316	3.162E-12	0.00017848	0.000366944	0.00045457	1.55453E-09	4.60893E-16
3	0.001	1E-11	3.0331E-05	0.000197189	0.000772472	8.35377E-09	7.83218E-15
3.5	0.00032	3.162E-11	3.6199E-06	7.44212E-05	0.000921927	3.1528E-08	9.34753E-14
4	0.0001	1E-10	3.8268E-07	2.48795E-05	0.000974632	1.054E-07	9.88191E-13
4.5	3.2E-05	3.162E-10	3.8935E-08	8.00468E-06	0.000991617	3.39113E-07	1.00541E-11
5	0.00001	1E-09	3.9122E-09	2.54345E-06	0.000996375	1.07751E-06	1.01024E-10
5.5	3.2E-06	3.162E-09	3.9099E-10	8.03836E-07	0.000995789	3.40539E-06	1.00964E-09
6	1E-06	1E-08	3.8834E-11	2.52473E-07	0.000989		
6.5	3.2E-07	3.162E-08	3.7959E-12	7.80405E-08	0.000966		
7	1E-07	0.0000001	3.5399E-13	2.30143E-08	0.000901		
7.5	3.2E-08	3.162E-07	2.9039E-14	5.97011E-09	0.000739		
8	1E-08	0.000001	1.7988E-15	1.16945E-09	0.000458		
8.5	3.2E-09	3.162E-06	7.2261E-17	1.48561E-10	0.000184		
9	1E-09	0.00001	1.7885E-18	1.16278E-11	4.55509E		
9.5	3.2E-10	3.162E-05	2.8746E-20	5.90995E-13	7.32123E		
10	1E-10	0.0001	3.4962E-22	2.273E-14	8.90429E		
10.5	3.2E-11	0.0003162	3.7459E-24	7.70109E-16	9.54008E		
11	1E-11	0.001	3.8317E-26	2.49108E-17	9.75861E		
11.5	3.2E-12	0.0031623	3.8596E-28	7.93482E-19	9.82963E		
12	1E-12	0.01	3.8684E-30	2.51499E-20	9.85229E		
12.5	3.2E-13	0.0316228	3.8713E-32	7.95891E-22	9.85947E		
13	1E-13	0.1	3.8722E-34	2.51741E-23	9.86174E		
13.5	3.2E-14	0.3162278	3.8724E-36	7.96132E-25	9.86246E		
14	1E-14	1	3.8725E-38	2.51765E-26	9.86269E		

pH	Fe3+	Fe(OH)2+	Fe((OH)2)+	Fe(OH)30	Fe(OH)4-
0	-3.0028253	-5.1898253	-7.5968253	-15.562825	-24.590825
0.5	-3.0089464	-4.6959464	-6.6029464	-14.068946	-22.596946
1	-3.0283922	-4.2153922	-5.6223922	-12.588392	-20.616392
1.5	-3.0902783	-3.7772783	-4.6842783	-11.150278	-18.678278
2	-3.2798523	-3.4668523	-3.8738523	-9.8398523	-16.867852
2.5	-3.7483997	-3.4353997	-3.3423997	-8.8083997	-15.3364
3	-4.5181173	-3.7051173	-3.1121173	-8.0781173	-14.106117
3.5	-5.4413033	-4.1283033	-3.0353033	-7.5013033	-13.029303
4	-6.4171591	-4.6041591	-3.0111591	-6.9771591	-12.005159
4.5	-7.4096559	-5.0966559	-3.0036559	-6.4696559	-10.997656
5	-8.4075772	-5.5945772	-3.0015772	-5.9675772	-9.9955772
5.5	-9.4078325	-6.0948325	-3.0018325	-5.4678325	-8.9958325



This is a sweep output file - Select Problem no. 1 *No. of iterations* 0

pH 0.000
Ionic strength 0.00e+00
Sum of cations (eq/kg) 1.0030E+00
Sum of anions (eq/kg) 1.0069E-14
Charge difference (%) 100.000000

Concentrations and activities of aqueous inorganic species (mol / l)

	Concentration	Activity
Fe(OH)2+	1.7615E-09	1.7615E-09
Fe(OH)3 (aq)	9.9054E-19	9.9054E-19
Fe(OH)4-	1.9764E-26	1.9764E-26
Fe+3	9.9054E-04	9.9054E-04
Fe2(OH)2+4	1.2524E-09	1.2524E-09
Fe3(OH)4+5	5.0074E-16	5.0074E-16
FeOH+2	9.4595E-06	9.4595E-06
H+1	1.0000E+00	1.0000E+00
OH-	1.0069E-14	1.0069E-14

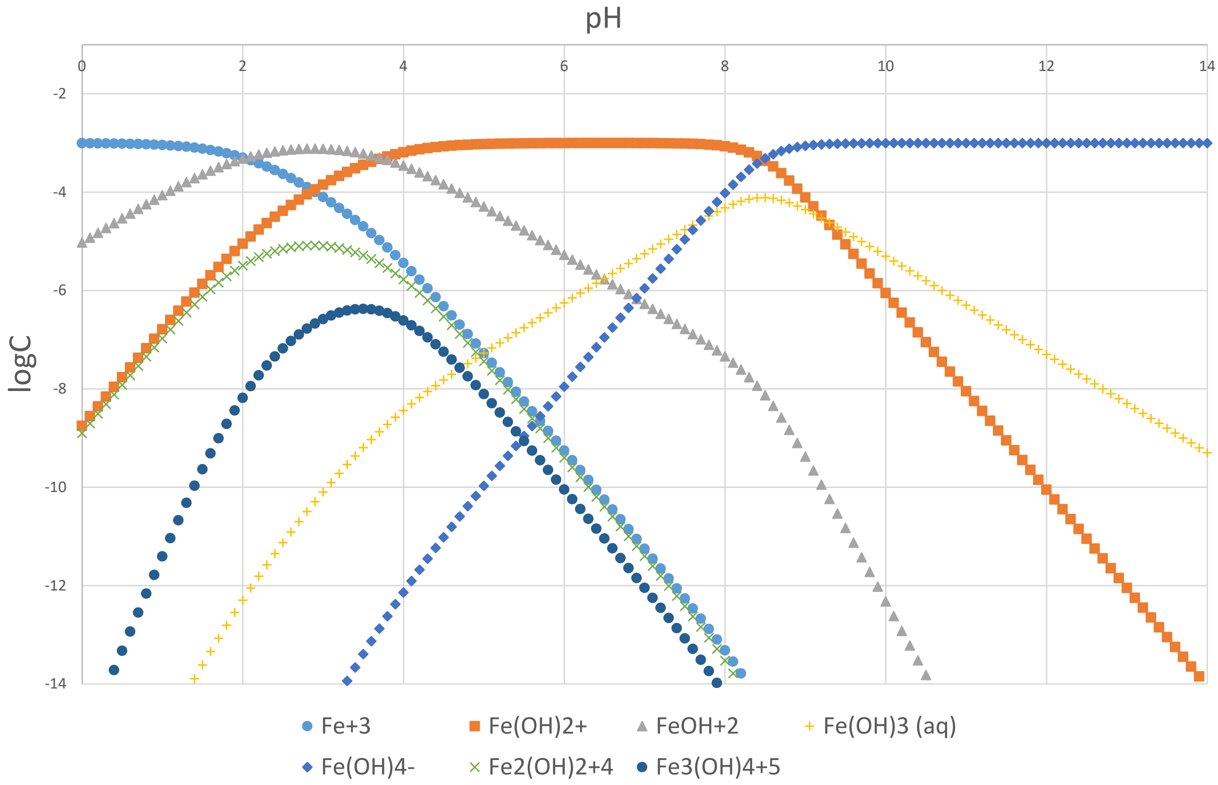
Execution time (s): 21.07031

Visual MINTEQ - Selected sweep results

Problem no	pH	Fe+3	Fe(OH)2+	FeOH+2	Fe(OH)3 (aq)
		Log Concentration	Log Concentration	Log Concentration	Log Concentration
1	0.000	-3.004	-8.754	-5.024	-18.004
2	0.100	-3.005	-8.555	-4.925	-17.705
3	0.200	-3.007	-8.357	-4.827	-17.407
4	0.300	-3.008	-8.158	-4.728	-17.108
5	0.400	-3.010	-7.960	-4.630	-16.810
6	0.500	-3.013	-7.763	-4.533	-16.513
7	0.600	-3.016	-7.566	-4.436	-16.216
8	0.700	-3.020	-7.370	-4.340	-15.920
9	0.800	-3.025	-7.175	-4.245	-15.625
10	0.900	-3.032	-6.982	-4.152	-15.332
11	1.000	-3.040	-6.790	-4.060	-15.040
12	1.100	-3.050	-6.600	-3.970	-14.750
13	1.200	-3.062	-6.412	-3.882	-14.462
14	1.300	-3.076	-6.226	-3.796	-14.176
15	1.400	-3.094	-6.044	-3.714	-13.894
16	1.500	-3.116	-5.866	-3.636	-13.616
17	1.600	-3.142	-5.692	-3.562	-13.342
18	1.700	-3.172	-5.522	-3.492	-13.072
19	1.800	-3.208	-5.358	-3.428	-12.808
20	1.900	-3.250	-5.200	-3.370	-12.550
21	2.000	-3.298	-5.048	-3.318	-12.298

☐ Include last column when printing to Excel

Visual Minteq - Hydrolysis of 10^{-3} M Fe(III)



Consider hydroxy complexes + complexes with other ligands (e.g., 1 mM Fe(III) + 1 mM phosphate)

$$C_{T,Fe(III)} = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2{}^{+}] + [Fe(OH)_3{}^{0}] + [Fe(OH)_4{}^{-}] + [\mathrm{FeH_2PO_4}{}^{2+}] + [\mathrm{FeHPO_4}{}^{+}]$$

$$C_{T,Fe(III)} = [Fe^{3+}]\left(1 + \frac{{}^{*}\beta_1}{[H^+]} + \frac{{}^{*}\beta_2}{[H^+]^2} + \frac{{}^{*}\beta_3}{[H^+]^3} + \frac{{}^{*}\beta_4}{[H^+]^4} + \beta_{FeH2P}[\mathrm{H}^+]^2[PO_4{}^{3-}] + \beta_{FeHP}[\mathrm{H}^+][PO_4{}^{3-}]\right)$$

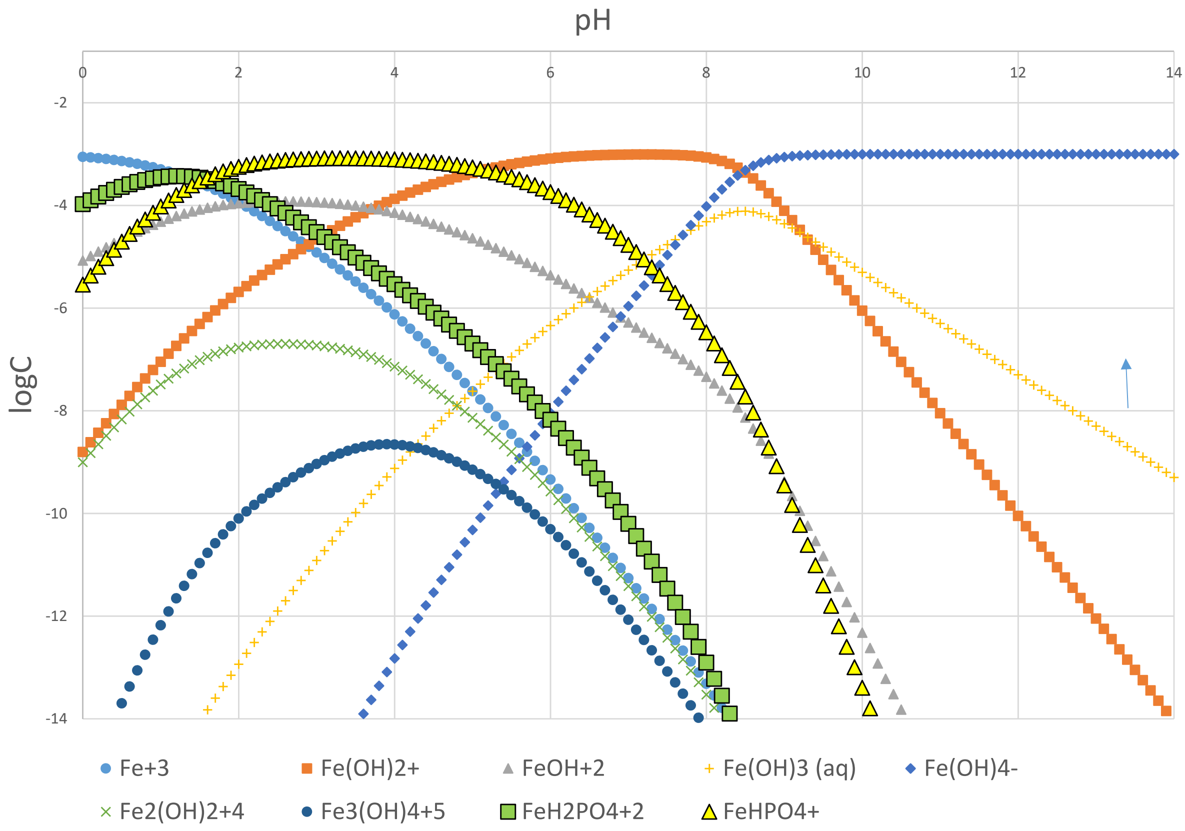
$$\therefore\ [Fe^{3+}] = \frac{C_{T,Fe(III)}}{\left(1 + \frac{{}^{*}\beta_1}{[H^+]} + \frac{{}^{*}\beta_2}{[H^+]^2} + \frac{{}^{*}\beta_3}{[H^+]^3} + \frac{{}^{*}\beta_4}{[H^+]^4} + \beta_{FeH2P}[\mathrm{H}^+]^2[PO_4{}^{3-}] + \beta_{FeHP}[\mathrm{H}^+][PO_4{}^{3-}]\right)}$$

$$[FeOH^{2+}] = \frac{{}^{*}\beta_1[Fe^{3+}]}{[H^+]} \qquad [Fe(OH)_4{}^{-}] = \frac{{}^{*}\beta_4[Fe^{3+}]}{[H^+]^4}$$

$$[Fe(OH)_2{}^{+}] = \frac{{}^{*}\beta_2[Fe^{3+}]}{[H^+]^2} \qquad [FeHPO_4{}^{+}] = \beta_{FeHP}[\mathrm{Fe}^{3+}][\mathrm{H}^+][PO_4{}^{3-}]$$

$$[Fe(OH)_3{}^{0}] = \frac{{}^{*}\beta_3[Fe^{3+}]}{[H^+]^3} \qquad [FeH_2PO_4{}^{2+}] = \beta_{FeH2P}[\mathrm{Fe}^{3+}][\mathrm{H}^+]^2[PO_4{}^{3-}]$$

Visual Minteq –
Hydrolysis of 10^{-3} M Fe(III) + 1 mM phosphate



Consider hydroxy complexes + complexes with other ligands (e.g., 1 mM Fe(III) + 1 mM phosphate)

$$C_{T,Fe(III)} = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2^{+}] + [Fe(OH)_3^{0}] + [Fe(OH)_4^{-}] + [\mathrm{FeH_2PO_4}^{2+}] + [\mathrm{FeHPO_4}^{+}]$$

$$C_{T,Fe(III)} = [Fe^{3+}]\left(1 + \frac{{}^*\beta_1}{[H^+]} + \frac{{}^*\beta_2}{[H^+]^2} + \frac{{}^*\beta_3}{[H^+]^3} + \frac{{}^*\beta_4}{[H^+]^4} + \beta_{FeH2P}[\mathrm{H}^+]^2[PO_4^{3-}] + \beta_{FeHP}[\mathrm{H}^+][PO_4^{3-}]\right)$$

$$\therefore\ [Fe^{3+}] = \frac{C_{T,Fe(III)}}{\left(1 + \frac{{}^*\beta_1}{[H^+]} + \frac{{}^*\beta_2}{[H^+]^2} + \frac{{}^*\beta_3}{[H^+]^3} + \frac{{}^*\beta_4}{[H^+]^4} + \beta_{FeH2P}[\mathrm{H}^+]^2[PO_4^{3-}] + \beta_{FeHP}[\mathrm{H}^+][PO_4^{3-}]\right)}$$

$$[FeOH^{2+}] = \frac{{}^*\beta_1[Fe^{3+}]}{[H^+]}$$

$$[Fe(OH)_2^{+}] = \frac{{}^*\beta_2[Fe^{3+}]}{[H^+]^2}$$

$$[Fe(OH)_3^{0}] = \frac{{}^*\beta_3[Fe^{3+}]}{[H^+]^3}$$

$$[Fe(OH)_4^{-}] = \frac{{}^*\beta_4[F}{[H^+}$$

$$[FeHPO_4^{+}] = \beta_{FeHP}[\mathrm{Fe}^{3+}$$

$$[FeH_2PO_4^{2+}] = \beta_{FeH2P}[\mathrm{Fe}\ ][\mathrm{H}\ ]\ [PO_4\ ]$$

How do I know $[PO_4^{3-}]$ as a function of pH?

Hint

- Is $C_{T,PO4}$ >> $C_{T,Fe(III)}$ or is PO_4^{3-} a very weakly binding ligand?

Yes: Try assuming that the presence of Fe(III) has no significant effect on the dominant PO_4^{3-} speciation, and calculate $[PO_4^{3-}]$ as a function of pH with no Fe(III) present (*a simple acid-base calculation*)

No: Sorry, but very difficult to solve manually, need to use an iterative tool like Visual Minteq to solve.

Summary

- The aqueous chemistry of metal ions
  1. Coordination chemistry concepts and terms
  2. Metal-ligand complexation equilibria
  3. Metal ion hydrolysis
  4. Solving metal ion complexation equilibrium problems.