Previous Class Problem

1a) Add 10 mg/L of iron chloride ($FeCl_3$) in pure water. Can $Fe(OH)_{3(s)}$ precipitate?

Step 1: Calculate TOTFe and TOTCl in M

Step 2: Assume $Fe(OH)_{3(s)}$ DOES NOT precipitate, i.e. all iron stays dissolved.

Step 3: Calculate pH of this hypothetical system

Species: Fe^{3+} and its four OH complexes, H_2O, H^+, OH^-, Cl^-

Components: Fe^{3+},(H_2O), H^+, Cl^-

Mass balance: $TOTFe = [Fe^{3+}] + [Fe(OH)^{2+}] + [Fe(OH)_2^+] + [Fe(OH)_{3(aq)}] + [Fe(OH)_4^-]$

$= [Fe^{3+}](1 + \beta_1^*/[H^+] + \beta_2^*/[H^+]^2 + \beta_3^*/[H^+]^3 + \beta_4^*/[H^+]^4)$, where $\log\beta^*$ values are taken from the Table

$= [Fe^{3+}]\, f([H^+])$

Metal-Complexation Reactions with OH^-

Table 8.2 Stability constants for complexation of metals by OH^-

	i	Log K_i	Log $^*K_i$	Log β_i	Log $^*\beta_i$
Ag^+	1	2.00	−12.00	2.00	−12.00
	2	2.00	−12.00	4.00	−24.00
Co^{2+}	1	4.80	−9.20	4.80	−9.20
	2	4.90	−9.10	9.70	
	3	1.10	−12.90	10.80	
Cr^{3+}	1	10.00	−4.00	10.00	
	2	8.38	−5.62	18.38	
	3	6.87	−7.13	25.25	
	4	2.98	−11.02	28.23	
Cu^{2+}	1	6.00	−8.00	6.00	
	2	8.32	−5.68	14.32	
	3	0.78	−13.22	15.10	
	4	1.30	−12.70	16.40	
Fe^{2+}	1	4.50	−9.50	4.50	
	2	2.93	−11.07	7.43	
	3	3.57	−10.43	11.00	−31.00
Fe^{3+}	1	11.81	−2.19	11.81	−2.19
	2	10.52	−3.48	22.33	−5.67
	3	6.07	−7.93	28.40	−13.60
	4	6.00	−8.00	34.40	−21.60

Reactions in terms of OH^-

K_i: $Fe^{3+} + OH^- = Fe(OH)^{2+}$

β_i: $Fe^{3+} + 2OH^- = Fe(OH)_2^+$

Listing all reactions and constants sequentially

$pK_1^* = 2.19$: $Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$

$pK_2^* = 3.48$: $Fe(OH)^{2+} + H_2O = Fe(OH)_2^+ + H^+$

$pK_3^* = 7.93$: $Fe(OH)_2^+ + H_2O = Fe(OH)_{3(aq)} + H^+$

$pK_4^* = 8.00$: $Fe(OH)_{3(aq)} + H_2O = Fe(OH)_4^- + H^+$

Reactions in terms of H^+

K_i^*: $Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$

β_i^*: $Fe^{3+} + 2H_2O = Fe(OH)_2^+ + H^+$

Listing all reactions and constants cumulatively (in terms of component Fe^{3+})

$p\beta_1^* = 2.19$: $Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$

$p\beta_2^* = 5.67$: $Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$

$p\beta_3^* = 13.6$: $Fe^{3+} + 3H_2O = Fe(OH)_{3(aq)} + 3H^+$

$p\beta_4^* = 21.6$: $Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$

Previous Class Problem (contd.)

Rearranging, $[Fe^{3+}] = TOTFe / f([H^+]) = 10^{-4.21} / f([H+])$

Charge balance: $[H^+]+3[Fe^{3+}]+2[Fe(OH)^{2+}]+ [Fe(OH)_2^+] = [OH^-] + [Fe(OH)_4^-] + [Cl^-]$

Each of the other Fe-OH complexes are also a function of $[H^+]$ from their complexation reactions with $[H^+]$

Listing all reactions and constants

$p\beta_1^* = 2.19$:	**$Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$**
$p\beta_2^* = 5.67$:	**$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$**
$p\beta_3^* = 13.6$:	**$Fe^{3+} + 3H_2O = Fe(OH)_{3(aq)} + 3H^+$**
$p\beta_4^* = 21.6$:	**$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$**

Solve for $[H^+]$ graphically (plotting sums of cations and anions and finding intersection) or numerically (using Excel Solver)

pH = 3.97 (remember, this is hypothetical!)

Previous Class Problem (contd.)

Step 4: Calculate the ion activity product (Q) for $Fe(OH)_{3(s)}$

$$\mathbf{Fe(OH)_{3(s)} + 3H^+ = Fe^{3+} + 3H_2O}$$

$$\boxed{Q = \frac{[Fe^{3+}]}{[H^+]^3} = \frac{10^{-6.6}}{(10^{-3.97})^3} = 10^{5.21} >> K_{sp}(= 10^{4.89})}$$

Yes, $Fe(OH)_{3(s)}$ will precipitate!

1b) If solid precipitates, find how much?

Because of solid precipitation, will hypothetical pH calculated in part 1a change?

Yes, it will! Because $Fe(OH)_{3(s)}$ formation release H^+ and decrease TOTFe dissolved in the system. This impacts mass balance and charge balance.

Previous Class Problem (contd.)

Step 5: In the new charge balance,

$[H^+]+3[Fe^{3+}]+2[Fe(OH)^{2+}]+ [Fe(OH)_2^{+}] = [OH^-]+[Fe(OH)_4^{-}]+[Cl^-]$

we need to find $[Fe^{3+}] = g([H+])$. How?

Use the solubility relation at equilibrium with solid,

$$\mathbf{Fe(OH)_{3(s)} + 3H^+ = Fe^{3+} + 3H_2O}$$

$$\boxed{Q = \frac{[Fe^{3+}]}{[H^+]^3} = K_{sp}(=10^{4.89})}$$

Step 6: Using $[Fe^{3+}]$ and the complexation reactions, all Fe-OH complexes can be written in terms of $[Fe^{3+}]$ and $[H^+]$ in the charge balance equation.

Solve for $[H^+]$ graphically or numerically to get true pH

Previous Class Problem (contd.)

Step 7: At the new pH value, calculate $[Fe^{3+}]$ from K_{sp} relationship

Step 8: Find total dissolved iron remaining in solution

$$TOTFe_{diss} = [Fe^{3+}] + [Fe(OH)^{2+}] + [Fe(OH)_2^{+}] + [Fe(OH)_{3(aq)}] + [Fe(OH)_4^{-}]$$

$$= [Fe^{3+}](1 + \beta_1^*/[H^+] + \beta_2^*/[H^+]^2 + \beta_3^*/[H^+]^3 + \beta_4^*/[H^+]^4),$$

Step 9: Calculate molar concentration of solid precipitated

= TOTFe added (=$10^{-4.21}$ M) – TOT Fe_{diss} (from step 8)

Total Dissolved Solids (TDS) vs Annual RunOff

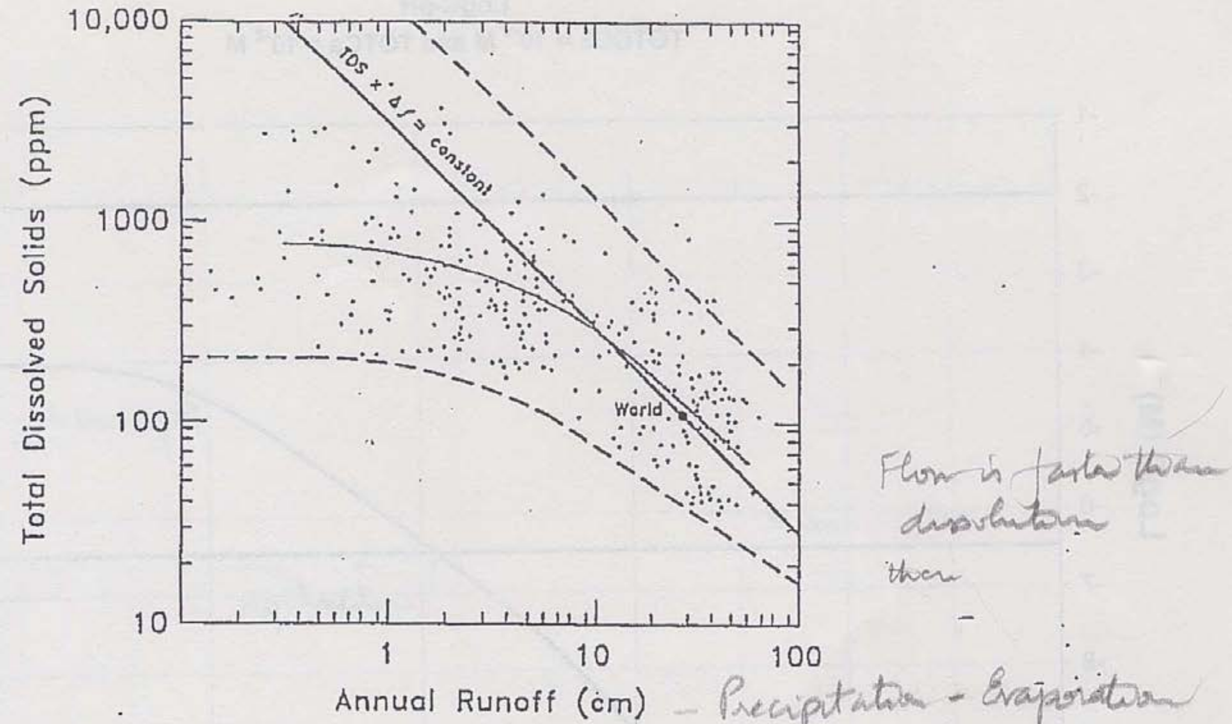

Figure 5.18 Total dissolved solids in river waters of the United States as a function of annual runoff. The dissolved load of rivers is a result of mineral dissolution. The observed relationship of dissolved solids concentration and runoff indicates that, at high flow, mineral dissolution rates are not transport limited, whereas at low flow, transport limitation appears to be important. From Holland 1978.[1]