Class problem

1a) Solid calcium fluoride ($CaF_{2(s)}$) is added to pure water so that at equilibrium some solid remains dissolved. Given that the solubility product is 3×10^{-11} $M^{3,}$ what is the equilibrium concentration of F^- in water?

Solubility product relation: $CaF_{2(s)} = Ca^{2+} + 2F^-$

Since some solid remains at equilibrium, the solubility relationship must be satisfied

$$[Ca^{2+}][F^-]^2 = 3 \times 10^{-11} \qquad (1)$$

Two unknowns, Ca^{2+} and F^-, and one equation?

Two options:

- use stoichiometry of dissolution
- charge balance (useful if we know all other constituents present)

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

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

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

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

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

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

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+})

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

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

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

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

Solubility Expressions

Listing all reactions and constants

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

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

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

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

At any state of the system,

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

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

Solubility Curve for $Fe(OH)_{3(s)}$

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

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