Analytical chemistry (5th Edition)

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1 Chapter 9

1.

$$
\begin{aligned}
K_{sp} &= 9.1 * 10^{-6} mol/L \\
\frac{[CaSO_4]}{[Ca^{2+}][SO_4^{2-}]} &= 200 \\
[CaSO_4] &= 200 * K_{sp} = 1.82 * 10^{-3} mol/L \\
\frac{[CaSO_4]}{[CaSO_4] + [Ca^{2+}]} &= \frac{[CaSO_4]}{[CaSO_4] + \sqrt{K_{sp}}} = 37.6\%
\end{aligned} \tag{1}
$$

2.

- $$
\begin{aligned}
k_{sp} &= 4 * 10^{-15} \\
[OH^-] &= \sqrt{\frac{K_{sp}}{c_M * 0.99}} = 2.01 * 10^{-7} mol/L \\
pH &= 7.3
\end{aligned} \tag{2}
$$

- $$
\begin{aligned}
[OH^-] &= \sqrt{\frac{K_{sp}}{c_M * 0.5}} = 2.82 * 10^{-7} mol/L \\
pH &= 7.45
\end{aligned} \tag{3}
$$

- $$
\begin{aligned}
[OH^-] &= \sqrt{\frac{K_{sp}}{c_M * 0.01}} = 2 * 10^{-6} mol/L \\
pH &= 8.3
\end{aligned} \tag{4}
$$

3.

- $$I = \frac{1}{2}\Sigma c * z^2 = 0.1$$
$$\gamma_{Ba} = 0.38$$
$$\gamma_{SO_4^{2-}} = 0.36 \tag{5}$$
$$K_{sp}^{;} = \frac{K_{sp}}{\gamma_{Ba} * \gamma_{SO_4^{2-}}} = 8.04 * 10^{-10}[Ba^{2+}] = 2.83 * 10^{-5} mol/L$$

- $$I = \frac{1}{2}\Sigma c * z^2 = 0.3$$
$$\gamma_{Ba} = 0.26$$
$$\gamma_{SO_4^{2-}} = 0.22 \tag{6}$$
$$K_{sp}^{;} = \frac{K_{sp}}{\gamma_{Ba} * \gamma_{SO_4^{2-}}} = 1.92 * 10^{-9}[Ba^{2+}] = 0.1 mol/L$$
$$[SO_4^{2-}] = 1.92 * 10^{-8} mol/L$$

4.

- $$K_{sp} = 2.7 * 10^{-11}$$
$$K_a = 6.6 * 10^{-4}$$
$$\delta = \frac{K_a}{K_a + [H^+]} = 0.062$$
$$Let:$$
$$[Ca^{2+}] = s \tag{7}$$
$$c_F = 2s$$
$$[F^-] = 2s\delta$$
$$[Ca^{2+}][F^-]^2 = K_{sp}$$
$$[Ca^{2+}] = 1.2 * 10^{-3} mol/L$$

- $$\begin{gathered} K_{sp} = 1.1 * 10^{-10} \\ K_{a2} = 1.0 * 10^{-2} \\ \delta = \frac{K_a}{K_a + [H^+]} = 0.005 \\ Let: \\ [Ba^{2+}] = s \\ c_{SO_4^{2-}} = s \\ [SO_4^{2-}] = s\delta \\ [Ba^{2+}][SO_4^{2-}] = K_sp \\ [Ba^{2+}] = 1.48 * 10^{-4} mol/L \end{gathered} \tag{8}$$

- $$\begin{gathered} K_{sp} = 1.6 * 10^{-8} \\ K_a = 1.0 * 10^{-2} \\ \delta = \frac{K_a}{K_a + [H^+]} = 0.091 \\ [Pb^{2+}] = s \\ c_{SO_4^{2-}} = s \\ [SO_4^{2-}] = s\delta \\ [Pb^{2+}][SO_4^{2-}] = K_sp \\ [Pb^{2+}] = 4.2 * 10^{-4} mol/L \end{gathered} \tag{9}$$

- $$\begin{gathered} K_{sp} = 6 * 10^{-36} \\ [S^{2-}] = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} = 9.23 * 10^{-22} mol/L \\ [Cu^{2+}] = \frac{K_{sp}}{[S^{2-}]} = 6.5 * 10^{-15} mol/L \end{gathered} \tag{10}$$

5.

$$
\begin{aligned}
c_{BaCl_2} &= 0.01 mol/L \\
c_{HCl} &= 0.07 mol/L \\
I = \frac{1}{2}\Sigma c * z^2 &= \frac{1}{2} * (0.01 * 2^2 + 0.02 + 0.07 + 0.07) = 0.1 \\
\gamma_{Ba} &= 0.38 \\
\gamma_{SO_4} &= 0.36 \\
K_{a2,H_2SO_4} &= 1.0 * 10^{-2} \\
\delta = \frac{K_a}{K_a + [H^+]} &= 0.125 \\
[SO_4^{2-}] = \frac{K_{sp}}{\delta * \gamma_{Ba} * \gamma_{SO_4} * [Ba^{2+}]} &= 6.43 * 10^{-7} mol/L
\end{aligned}
\tag{11}
$$

6.

- $$
\begin{aligned}
K_{sp} &= 6 * 10^{-36} \\
ignore [OH^-] & \\
\alpha_S &= 1 + \beta_1 * [H^+] + \beta_2 * [H^+]^2 \\
[H^+] &= 1 * 10^{-7} mol/L \\
\alpha_S &= 2.5 * 10^7 \\
K_{sp}^{,} = \alpha_S * K_{sp} &= 1.5 * 10^-28 \\
Let: & \\
[Cu^{2+}] &= s \\
c_S &= s \\
[S^{2-}] = \frac{1}{\alpha} * c_S & \\
[Cu^{2+}][S^{2-}] &= K_{sp} \\
[Cu^{2+}] &= 2.2 * 10^{-14} mol/L
\end{aligned}
\tag{12}
$$

- $$
\begin{aligned}
&K_{sp} = 2 * 10^{-10} \\
&\text{Consider} [OH^-] : \\
&MnS + H_2O = Mn^{2+} + OH^- + HS^- \\
&K = [Mn^{2+}][OH^-][HS^-]/[MnS] = \frac{K_w * K_{sp}}{K_{a2}} \\
&\text{Let} : \\
&[Mn^{2+}] = [OH^-] = [HS^-] = s \\
&s = 6.6 * 10^{-4} mol/L
\end{aligned} \tag{13}
$$

7. $$
\begin{aligned}
&K_{sp,AgBr} = 5 * 10^{-13} \\
&K_{sp,AgCl} = 1.8 * 10^{-10} \\
&\frac{[Br^-]}{[Cl^-]} = 2.8 * 10^{-3} \\
&\text{Let} : \\
&[Cl^-] = n \\
&[Br^-] = 2.8 * 10^{-3} * n \\
&[Ag^+] = [Cl^-] + [Br^-] \\
&n = 1.34 * 10^{-5} mol/L \\
&[Ag^+] = (1 + 2.8 * 10^{-3}) * n = 1.34 * 10^{-5} mol/L
\end{aligned} \tag{14}
$$

8. - $$
\begin{aligned}
&K_{sp} = 2.3 * 10^{-9} \\
&K_{a1} = 6.5 * 10^{-2} \\
&K_{a2} = 6.1 * 10^{-5} \\
&\alpha = 1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1} K_{a2}} = 2.64 \\
&K_{sp}^{,} = K_{sp} * \alpha [Ca^{2+}] = \sqrt{K_{sp}^{,}} = 7.8 * 10^{-5} mol/L
\end{aligned} \tag{15}
$$

- $$\begin{aligned}
[H^+] &= 10^{-3} mol/L \\
\alpha &= 1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1}K_{a2}} = 17.64 \\
c_{H_2C_2O_4} &= 0.01 mol/L \\
[C_2O_4^{2-}] &= \frac{0.01}{17.64} = 5.67 * 10^{-4} mol/L \\
[Ca^{2+}] &= \frac{K_{sp}}{[C_2O_4^{2-}]} = 4.0 * 10^{-6} mol/L
\end{aligned} \tag{16}$$

9.

$$\begin{aligned}
K_{sp} &= 2.9 * 10^{-9} mol/L \\
K_{a1} &= 4.2 * 10^{-7} \\
k_{a2} &= 5.6 * 10^{-11} \\
Consider &[OH^-]: \\
CO_3^{2-} + H_2O &= HCO_3^- + OH^- \\
K = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} &= \frac{K_{sp} * K_w}{K_{a2}} = 5.2 * 10^{-13} \\
Let &: \\
[OH^-] &= [Ca^{2+}] = [CO_3^{2-}] = s \\
[Ca^{2+}] &= 8.0 * 10^{-5} mol/L
\end{aligned} \tag{17}$$

10.

$$\begin{aligned}
\alpha_{Ag(NH_3)_x} &= 1 + \beta_1 * [NH_3] + \beta_2 * [NH_3]^2 \\
K_{sp}^{,} &= \frac{K_{sp}}{\alpha_{Ag(NH_3)_x}} \\
[Ag^+] &= 0.01 mol/L \\
[Cl^-] &= 0.01 mol/L \\
K_{sp}^{,} &= [Ag^+] * [Cl^-] \\
[NH_3] &= 0.22 mol/L
\end{aligned} \tag{18}$$

11.

$$
\begin{gathered}
K_{sp,AgI} = 9.3 * 10^{-17} \\
Ag(S_2O_3)x: \\
lg\beta_1 = 8.82 \\
lg\beta_2 = 13.46 \\
lg\beta_3 = 14.15 \\
[H^+] = 10^{-3} mol/L \\
c_{S_2O_3^{2-}} = 0.01 mol/L \\
c_{I^-} = 0.01 mol/L \\
\alpha_{Ag(S_2O_3)_x} = 1 + \beta_1 * c_{S_2O_3^{2-}} + \beta_2 * c^2_{S_2O_3^{2-}} + \beta_3 * c^3_{S_2O_3^{2-}} = 3.0 * 10^9 \\
K^{,}_{sp} = K_{sp} * \alpha_{Ag(S_2O_3)_x} = 2.79 * 10^{-7} \\
[Ag^+] = \frac{K^{,}_{sp}}{[I^-]} = 2.79 * 10^{-5} mol/L
\end{gathered}
\tag{19}
$$

20.

$$
\begin{gathered}
K_{sp} = 1.8 * 10^{-10} \\
lg\beta_1 = 3.04 \\
lg\beta_2 = 5.04 \\
\alpha_{AgCl_x} = 1 + \beta_1 * [Cl^-] + \beta_2 * [Cl^-]^2 = 1207 \\
[Ag^+] = \frac{K_{sp} * \alpha}{[Cl^-]} = 2.17 * 10^{-6} mol/L \\
Find: \\
[Ag^+] = \frac{K_{sp} * (1 + \beta_1 * [Cl^-] + \beta_2 * [Cl^-]^2)}{[Cl^-]} \\
Minimize: \\
[Cl^-] = 3.02 * 10^{-3} mol/L
\end{gathered}
\tag{20}
$$

21.

$$
\begin{gathered}
M = \frac{0.5}{0.1 * 23.36 * 10^{-3}} = 214.0 \\
x = 3
\end{gathered}
\tag{21}
$$

23.

- $$\begin{aligned} &MA_2: \\ &\alpha = 1 + \frac{[H^+]}{K_{a1}} + \frac{[H^+]^2}{K_{a1}K_{a2}} \\ &K_{sp}^{,} = K_{sp} * \alpha \end{aligned} \tag{22}$$

- $$[M^{2+}] = \frac{K_{sp}}{[A^-]^2} \tag{23}$$

- $$\begin{aligned} \alpha = 1 + \frac{[H^+]}{K_{a1}} + \frac{[H^+]^2}{K_{a1}K_{a2}} \\ [A^-] = \frac{K_{sp} * \alpha}{[M^{2+}]} \end{aligned} \tag{24}$$

- $$\begin{aligned} &Let: \\ &c_L = c \\ &\alpha = 1 + \beta * c \\ &K_{sp}^{,} = K_{sp} * \alpha \end{aligned} \tag{25}$$

24.

$$\begin{aligned} &Ag \sim SCN^- \\ &3Ag \sim AsO_4^{3-} \\ &w = \frac{\frac{0.100*45.45*10^{-3}}{3} * M_{As}}{0.5} = 22.70\% \end{aligned} \tag{26}$$

25.

$$\begin{aligned} M_{CaC_2O_4} * n_1 + M_{MgC_2O_4} * n_2 = 0.624 \\ M_{CaCO_3} * n_1 + M_{MgCO_3} * n_2 = 0.483 \\ n1 = 3.75 * 10^{-3} mol \\ n_2 = 1.28 * 10^{-3} mol \\ w_{CaC_2O_4} = 76.9\% \\ w_{MgC_2O_4} = 23.1\% \\ m_{CaO+MgO} = 0.261g \end{aligned} \tag{27}$$

26.

$$\begin{aligned} M_{Fe_2O_3} * n_1 + M_{Al_2O_3} * n_2 &= 0.5622 \\ M_{Fe} * 2n_1 + M_{Al_2O_3} * n_2 &= 0.4582 \\ n_1 &= 2.17 * 10^{-3} mol \\ n_2 &= 1.93 * 10^{-3} mol \\ w_{Fe} &= 43.11\% \\ w_{Al} &= 18.54\% \end{aligned} \tag{28}$$

27.

$$\begin{aligned} M_{AgCl} * n_1 + M_{AgBr} * n_2 &= 0.5046 \\ 0.105 * 28.34 * 10^{-3} &= n_1 + n_2 \\ n_1 &= 1.22 * 10^{-3} mol \\ n_2 &= 1.76 * 10^{-3} mol \\ w_{NaCl} &= 11.36\% \\ w_{NaBr} &= 28.87\% \end{aligned} \tag{29}$$

28.

$$\begin{aligned} n_{AgCl} &= \frac{1.4236}{35.453 + 107.868} = 9.93 * 10^{-3} mol \\ M_{NaCl} &= \frac{0.5805}{n_{AgCl}} = 58.46 \\ M_{Na} &= M_{NaCl} - M_{Cl} = 23.00 \end{aligned} \tag{30}$$

29.

$$\begin{aligned} w_S &= \frac{1.089 * M_S}{M_{BaSO_4}} = 14.93\% \\ n_S &= \frac{1.089}{M_{BaSO_4}} = 4.67 * 10^{-3} mol \\ n_M &= \frac{1.000}{214.33} = 4.66 * 10^{-3} mol \end{aligned} \tag{31}$$

30.

$$m = M_{AgCl} * (\frac{m_s * 0.6}{M_{AgBr}} + \frac{m_s * 0.4}{M_{AgCl}}) = 0.3666g \tag{32}$$

31.

$$\begin{gathered} M_{Fe} * x + M_O * y = 0.5434 \\ M_{Fe} * x = 0.3801 \\ \frac{x}{y} = \frac{2}{3} \\ Fe_2O_3 \end{gathered} \tag{33}$$

32.

$$\begin{gathered} M_{KCl} * n_1 + M_{NaCl} * n_2 = 0.5034 \\ n_1 + n_2 = \frac{0.2531}{M_{AgCl}} \\ n_1 = 1.11 * 10^{-3} mol \\ n_2 = 0.65 * 10^{-3} mol \\ w_{K_2O} = 10.36\% \\ w_{Na_2O} = 4.00\% \end{gathered} \tag{34}$$

33.

$$V = \frac{0.35}{M_{CaCO_3}} * M_{(NH_4)_2C_2O_4}/3\% = 14.5mL \tag{35}$$

34.

$$\begin{gathered} c_{I^-} = 0.025 mol/L \\ c_{Ag} = \frac{50mg}{143.3g/mol * 20 * 10^{-3} mL} = 0.017 mol/L \\ c_{NH_3} = 1.5 mol/L \\ K_{sp}^{,} = K_{sp} * (1 + 10^{7.40} * 1.5^2) = 4.69 * 10^{-9} mol/L \\ < c_{I^-} * c_{Ag^+} \end{gathered} \tag{36}$$