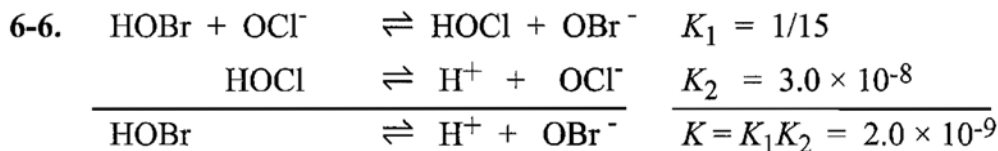


Chapter 6 Homework



$$\text{6-8. } K = e^{-(59.0 \times 10^3 \text{ J/mol}) / (8.314472 \text{ J/(K}\cdot\text{mol)})(298.15 \text{ K})} = 5 \times 10^{-11}$$

$$\begin{aligned}
 \text{6-10. (a) } K = P_{\text{H}_2\text{O}} &= e^{-\Delta G^\circ / RT} = e^{-(\Delta H^\circ - T\Delta S^\circ) / RT} \\
 &= e^{-\{[(63.11 \times 10^3 \text{ J/mol}) - (298.15 \text{ K})(148 \text{ J K}^{-1} \text{ mol}^{-1})] / (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})\}} \\
 &= 4.7 \times 10^{-4} \text{ bar}
 \end{aligned}$$

$$\text{(b) } P_{\text{H}_2\text{O}} = 1 = e^{-(\Delta H^\circ - T\Delta S^\circ) / RT} \Rightarrow \Delta H^\circ - T\Delta S^\circ \text{ must be zero.}$$

$$\Delta H^\circ - T\Delta S^\circ = 0 \Rightarrow T = \frac{\Delta H^\circ}{\Delta S^\circ} = 426 \text{ K} = 153^\circ\text{C}$$

6-11. (a) Let's designate the equilibrium constant at temperature T_1 as K_1 and the equilibrium constant at temperature T_2 as K_2 .

$$K_1 = e^{-\Delta G^\circ / RT_1} = e^{-(\Delta H^\circ - T_1\Delta S^\circ) / RT_1} = e^{-\Delta H^\circ / RT_1} \cdot e^{\Delta S^\circ / R}$$

$$\text{Similarly, } K_2 = e^{-\Delta H^\circ / RT_2} \cdot e^{\Delta S^\circ / R}$$

$$\text{Dividing } K_1 \text{ by } K_2 \text{ gives } \frac{K_1}{K_2} = e^{-(\Delta H^\circ / R)(1/T_1 - 1/T_2)}$$

$$\Rightarrow \Delta H^\circ = \left(\frac{1}{T_2} - \frac{1}{T_1} \right)^{-1} R \ln \frac{K_1}{K_2}$$

Putting in $K_1 = 1.479 \times 10^{-5}$ at $T_1 = 278.15 \text{ K}$ and

$K_2 = 1.570 \times 10^{-5}$ at $T_2 = 283.15 \text{ K}$ gives $\Delta H^\circ = +7.82 \text{ kJ/mol}$.

$$\text{(b) } K = e^{-\Delta H^\circ / RT} \cdot e^{\Delta S^\circ / R}$$

$$\ln K = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

$$\begin{array}{cccc}
 y & & m & x & b \\
 & & & & \\
 & & & &
 \end{array}$$

A graph of $\ln K$ vs. $1/T$ will have a slope of $-\Delta H^\circ / R$

6-14. $[\text{Cu}^+][\text{Br}^-] = K_{\text{sp}}$

$$[\text{Cu}^+][0.10] = 5 \times 10^{-9} \Rightarrow [\text{Cu}^+] = 5 \times 10^{-8} \text{ M}$$

6-16. If we let $x = [\text{Cu}^{2+}]$, then $[\text{SO}_4^{2-}] = \frac{1}{4}x$.

$$K = [\text{Cu}^{2+}]^4 [\text{OH}^-]^6 [\text{SO}_4^{2-}] = (x)^4 (1.0 \times 10^{-6})^6 \left(\frac{1}{4}x\right) = 2.3 \times 10^{-69}$$

$$\Rightarrow x = [\text{Cu}^{2+}] = \left(\frac{(4)(2.3 \times 10^{-69})}{(1.0 \times 10^{-6})^6}\right)^{1/5} = 3.9 \times 10^{-7} \text{ M}$$

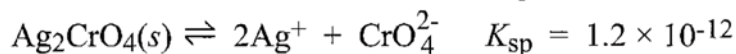
6-17. (a) $[\text{Zn}^{2+}]^2[\text{Fe}(\text{CN})_6^{4-}] = (0.00010)^2[\text{Fe}(\text{CN})_6^{4-}] = 2.1 \times 10^{-16}$

$$\Rightarrow [\text{Fe}(\text{CN})_6^{4-}] = 2.1 \times 10^{-8} \text{ M}$$

(b) $[\text{Zn}^{2+}]^2[\text{Fe}(\text{CN})_6^{4-}] = (5.0 \times 10^{-7})^2[\text{Fe}(\text{CN})_6^{4-}] = 2.1 \times 10^{-16}$

$$\Rightarrow [\text{Fe}(\text{CN})_6^{4-}] = 8.4 \times 10^{-4} \text{ M}$$

6-20. $\text{BaCrO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{CrO}_4^{2-} \quad K_{\text{sp}} = 2.1 \times 10^{-10}$



The stoichiometries are not identical, so it is not clear that the salt with lower K_{sp} will precipitate first. Let's try each possibility. Suppose that BaCrO_4 precipitates first. The concentration of CrO_4^{2-} that will reduce Ba^{2+} to 0.1% of its initial concentration is

$$[\text{Ba}^{2+}][\text{CrO}_4^{2-}] = [1.0 \times 10^{-5}][\text{CrO}_4^{2-}] = 2.1 \times 10^{-10} \Rightarrow [\text{CrO}_4^{2-}] = 2.1 \times 10^{-5} \text{ M.}$$

Will this much chromate precipitate 0.010 M Ag^+ ? We test by evaluating the reaction quotient for Ag_2CrO_4 :

$$Q = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (0.010)^2(2.1 \times 10^{-5}) = 2.1 \times 10^{-9} > K_{\text{sp}} \text{ for } \text{Ag}_2\text{CrO}_4$$

Since $Q > K_{\text{sp}}$ for Ag_2CrO_4 , Ag^+ will precipitate.

Let's try the reverse calculation. If Ag_2CrO_4 precipitates first, the concentration of CrO_4^{2-} that will reduce Ag^+ to $1.0 \times 10^{-5} \text{ M}$ is

$$[\text{Ag}^+]^2[\text{CrO}_4^{2-}] = [1.0 \times 10^{-5}]^2[\text{CrO}_4^{2-}] = 1.2 \times 10^{-12} \Rightarrow [\text{CrO}_4^{2-}] = 0.012 \text{ M.}$$

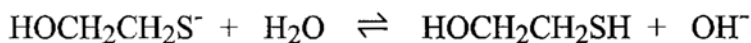
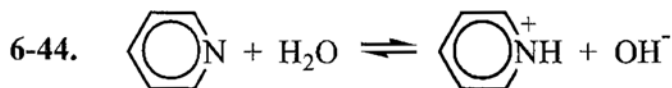
This concentration of CrO_4^{2-} exceeds the concentration required to precipitate 99.90% of Ba^{2+} . Neither Ag^+ nor Ba^{2+} can be 99.90% precipitated without precipitating the other ion.

6-25. $[Zn^{2+}] = K_{sp}/[OH^-]^2 = 2.93 \times 10^{-3} \text{ M}$
 $[ZnOH^+] = \beta_1[Zn^{2+}][OH^-] = \beta_1 K_{sp}/[OH^-] = 9 \times 10^{-6} \text{ M}$
 $[Zn(OH)_2(aq)] = \beta_2[Zn^{2+}][OH^-]^2 = \beta_3 K_{sp}[OH^-] = 6 \times 10^{-6} \text{ M}$
 $[Zn(OH)_3^-] = \beta_3[Zn^{2+}][OH^-]^3 = \beta_3 K_{sp}[OH^-] = 8 \times 10^{-9} \text{ M}$
 $[Zn(OH)_4^{2-}] = \beta_4[Zn^{2+}][OH^-]^4 = \beta_4 K_{sp}[OH^-]^2 = 9 \times 10^{-14} \text{ M}$

6-30. Dissolved CO_2 from the atmosphere lowers the pH by reacting with water to form carbonic acid. Water can be distilled under an inert atmosphere to exclude CO_2 , or most CO_2 can be removed by boiling the distilled water.

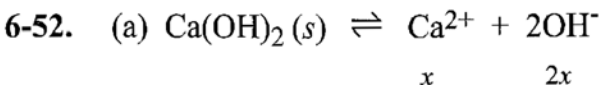
6-33. (a) HI (b) H_2O

6-39. $[La^{3+}][OH^-]^3 = K_{sp} = 2 \times 10^{-21}$
 $[OH^-]^3 = K_{sp} / (0.010) \Rightarrow [OH^-] = 5.8 \times 10^{-7} \text{ M} \Rightarrow \text{pH} = 7.8$



6-50. $K_{a1} = \frac{K_w}{K_{b3}} = 7.04 \times 10^{-3}$ $K_{a2} = \frac{K_w}{K_{b2}} = 6.25 \times 10^{-8}$
 $K_{a3} = \frac{K_w}{K_{b1}} = 4.3 \times 10^{-13}$

6-51. Add the two reactions and multiply their equilibrium constants to get $K = 2.9 \times 10^{-6}$.



$x(2x)^2 = K_{sp} = 10^{-5.19} \Rightarrow x = 1.2 \times 10^{-2} \text{ M}$

(b) Since some Ca^{2+} reacts with OH^- to form $CaOH^+$, the K_{sp} reaction will be drawn to the right, and the solubility of $Ca(OH)_2$ will be greater than we would expect just on the basis of K_{sp} .