1. How much water would it take to dissolve 3.0 g of $CaSO_4 \cdot \frac{1}{2} H_2O$ if its $K_{sp} = 3.1 \times 10^{-7}$? You may disregard the water formed in the dissolving process.

$$CaSO_4 \cdot \frac{1}{2} H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {SO_4}^{2-}(aq) + \frac{1}{2} H_2O(l)$$

	$CaSO_4$	Ca^{2+}	${SO_4}^{2-}$
I	—	0	0
C	—	+x	+x
E	—	x	x

$$K_{sp} = [Ca^{2+}][{SO_4}^{2-}] = x^2$$
$$x = \sqrt{3.1 \times 10^{-7}} = 5.57 \times 10^{-4} \tfrac{\text{mol}}{\text{L}}$$
$$V = 3.0\,\text{g} \times \frac{1\,\text{mol}}{145.15\,\text{g}} \times \frac{1\,\text{L}}{5.57 \times 10^{-4}\,\text{mol}}$$
$$= \boxed{37.1\,\text{L}}$$

2. (a) The solubility of AgCl(s) in 6.5×10^{-3} M $AgNO_3$ is 2.5×10^{-8} M at 298 K. What is the K_{sp} of AgCl?

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

	AgCl	Ag^+	Cl^-
I	-	6.5×10^{-3}	0
C	-	+x	+x
E	-	6.5×10^{-3} + x	x

$$[Ag^+] = 6.5 \times 10^{-3}\,\text{M}$$
$$[Cl^-] = 2.5 \times 10^{-8}\,\text{M}$$

$$K_{sp} = [Ag^+][Cl^-]$$
$$= (6.5 \times 10^{-3}\,\text{M})(2.5 \times 10^{-8}\,\text{M})$$
$$= 1.6 \times 10^{-10}$$

(b) Find the ΔS° for dissolving AgCl in water, given a reported $\Delta H^\circ_{\text{sol}}$ of 61 kJ/mol.

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_{sp}$$
$$\Delta S^\circ = \frac{\Delta H^\circ + RT \ln K_{sp}}{T}$$
$$\Delta S^\circ = \frac{61\ \frac{\text{kJ}}{\text{mol}} \cdot \frac{1{,}000\,\text{J}}{1\,\text{kJ}} + (8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}})(298\,\text{K}) \ln(1.6 \times 10^{-10})}{298\,\text{K}}$$
$$= 17.2\ \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

(c) True or False: "As the salt dissolves, heat is released, which increases the temperature of the solution, causing more salt to dissolve in solution." Briefly justify your answer.

False, the reaction is endothermic not exothermic

3. A small amount of $Ag_2C_2O_4(s)$ is added to 100 mL of a solution that is 4×10^{-3} M $Sr(NO_3)_2(aq)$. A single precipitate is present after the addition of $Ag_2C_2O_4(s)$. What is the precipitate?

$$K_{sp}(Ag_2C_2O_4) = 3.5 \times 10^{-11} \qquad K_{sp}(SrC_2O_4) = 5 \times 10^{-8}$$

$Ag_2C_2O_4(s) \rightleftharpoons 2\,Ag^+(aq) + {C_2O_4}^{2-}(aq)$ $\qquad$ $SrC_2O_4(s) \rightleftharpoons Sr^{2+}(aq) + {C_2O_4}^{2-}(aq)$

	$Ag_2C_2O_4$	Ag^+	${C_2O_4}^{2-}$
I	—	0	0
C	—	+2x	+x
E	—	2x	x

	SrC_2O_4	Sr^{2+}	${C_2O_4}^{2-}$
I	—	4.0×10^{-3}	0
C	—	+x	+x
E	—	4.0×10^{-3} + x	x

$$K_{sp} = [Ag^+]^2[{C_2O_4}^{2-}] \qquad K_{sp} = [Sr^{2+}][{C_2O_4}^{2-}]$$
$$3.5 \times 10^{-11} = (2x)^2 x \qquad 5 \times 10^{-8} = (4.0 \times 10^{-3} + \cancel{x})(x)$$
$$x = 2.06 \times 10^{-4}\,\text{M} \qquad x = 1.25 \times 10^{-5}\,\text{M}$$

SrC_2O_4 precipitates out first. Cannot compare K_{sp}

4. $AgBr\,(s)$ (MW = 187.77 g/mol) is used in black and white film. Once an image is formed, excess $AgBr\,(s)$ needs to be removed but it is not very soluble in water ($K_{sp} = 5.3 \times 10^{-13}$).

(a) What is the solubility of AgBr?

	$AgBr\,(s)$	Ag^+	Br^-
I	—	0	0
C	-s	+s	+s
E	—	s	s

$$K_{sp} = [Ag^+][Br^-] = s^2$$
$$s = \sqrt{5.3 \times 10^{-13}}$$
$$= 7.3 \times 10^{-7}\,\text{M}$$

(b) To increase the solubility of AgBr, $Na_2S_2O_3$ is added to water and the following equilibrium takes place:

$$Ag^+(aq) + 2\,{S_2O_3}^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) \quad K_f = ?$$

This leads to an overall equilibrium of:

$$AgBr\,(s) + 2\,{S_2O_3}^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq) \quad K = 15$$

Determine the value of K_f.

$$\begin{array}{rcll} AgBr & \rightleftharpoons & Ag^+ + Br^- & K_{sp} \\ Ag^+ + 2\,{S_2O_3}^{2-} & \rightleftharpoons & [Ag(S_2O_3)_2]^{3-} & K_f \\ \hline AgBr + 2\,{S_2O_3}^{2-} & \rightleftharpoons & [Ag(S_2O_3)_2]^{3-} + Br^- & K \end{array}$$

$$K = K_{sp} \cdot K_f \implies K_f = \frac{K}{K_{sp}} = \frac{15}{5.3 \times 10^{-13}} = \boxed{2.8 \times 10^{13}}$$

5.

$$\mathrm{AgBr(s)} + 2\,\mathrm{S_2O_3^{2-}(aq)} \rightleftharpoons [\mathrm{Ag(S_2O_3)_2}]^{3-}\mathrm{(aq)} + \mathrm{Br^-(aq)} \quad K = 15$$

This system is at equilibrium, and $\mathrm{AgBr(s)}$ is added. Immediately:

(a) Q: ☐ increases ☐ decreases ■ stays the same

(b) K: ☐ increases ☐ decreases ■ stays the same

(c) ΔG_{toeq}: ☐ is positive ☐ is negative ■ equals 0

This system is at equilibrium, and $\mathrm{Na_2S_2O_3 \cdot 5\,H_2O(s)}$ is added. Immediately:

(a) Q: ☐ increases ■ decreases ☐ stays the same

(b) K: ☐ increases ☐ decreases ■ stays the same

(c) ΔG_{toeq}: ☐ is positive ■ is negative ☐ equals 0

Homework Problem 26

1. The K_{sp} of $\mathrm{Ba(NO_3)_2}$ at 298 K is 4.63×10^{-3}. At 350 K it is 9.96×10^{-3}.
   (a) What is the solubility of $\mathrm{Ba(NO_3)_2}$ at 350 K?

   (b) What is the sign of ΔH_{sol} of $\mathrm{Ba(NO_3)_2}$?

   (c) 10.0 mL of a solution that is 0.005 M $\mathrm{Ba^{2+}(aq)}$ is mixed with 20.0 mL of 0.25 M $\mathrm{NO_3^-(aq)}$ at 298 K. Then a single crystal of solid $\mathrm{Ba(NO_3)_2}$ is added. Will $\mathrm{Ba(NO_3)}$ dissolve, precipitate, or do nothing? Show work to justify your answer.