

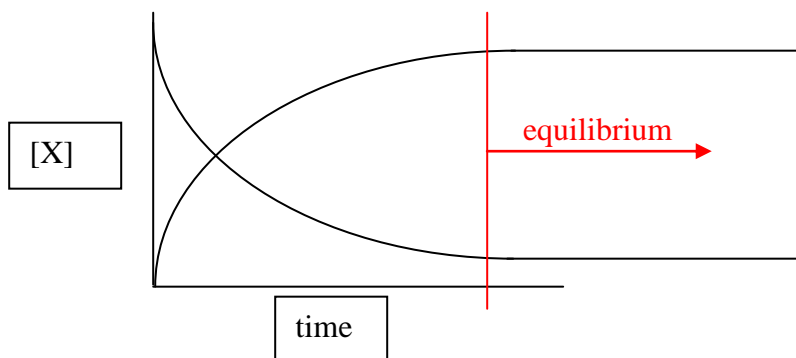
AP Chemistry

Unit 7- Homework Problems

Equilibrium and K_{sp}

Nature of the Equilibrium State

1. Draw on this graph where equilibrium has been reached.



2. What are three qualities of any equilibrium equation?

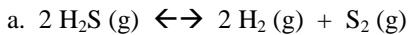
- Reversible
- Dynamic
- Occur when there are a stable ratio of products: reactants

3. For a general equation: $aA + bB \rightleftharpoons cC + dD$, write the equation for K_c .

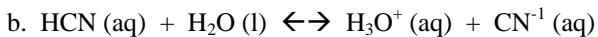
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Developing K_{eq}

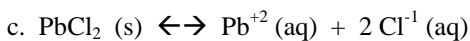
1. For each of the equations below, write the expression for K_c :



$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2}$$

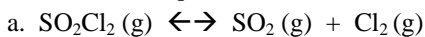


$$K_c = \frac{[\text{H}_3\text{O}^+] [\text{CN}^-]}{[\text{HCN}]}$$

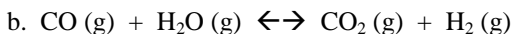


$$K_c = [\text{Pb}^{+2}] [\text{Cl}^-]^2$$

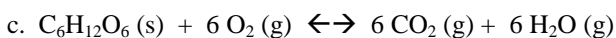
2. For each of the equations below, write the expression for K_p :



$$K_p = \frac{P_{\text{SO}_2} P_{\text{Cl}_2}}{P_{\text{SO}_2\text{Cl}_2}}$$



$$K_p = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}$$



$$K_p = \frac{P_{\text{CO}_2}^6 P_{\text{H}_2\text{O}}^6}{P_{\text{O}_2}^6}$$

3. Put the following K values in order of increasing product-favored ability.

a. $K = 4 \times 10^{-5}$

b. $K = 2 \times 10^{-9}$

c. $K = 7 \times 10^{-5}$

d. $K = 3 \times 10^{-3}$

$$b < a < c < d$$

Equilibrium Mathematics

1. The equation: $\text{C}(\text{s}) + 2 \text{H}_2\text{O}(\text{g}) \leftrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$ has a value of $K_c = 2.5 \times 10^{-6}$

What is the value of K_c for: $\text{CO}(\text{g}) + \text{H}_2(\text{g}) \leftrightarrow \text{C}(\text{s}) + 2 \text{H}_2\text{O}(\text{g})$?

$$K_c = (2.5 \times 10^{-6})^{-1} = 4 \times 10^5$$

What is the value of K_c for: $2 \text{C}(\text{s}) + 4 \text{H}_2\text{O}(\text{g}) \leftrightarrow 2 \text{CO}(\text{g}) + 2 \text{H}_2(\text{g})$

$$K_c = (2.5 \times 10^{-6})^2 = 6.25 \times 10^{-12}$$

2. The equation: $\text{H}_2\text{O}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$ has a value of $K_p = 4.9 \times 10^{-3}$

What is the value of K_p for: $2 \text{H}_2\text{O}(\text{g}) \leftrightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$?

$$K_p = (4.9 \times 10^{-3})^2 = 2.4 \times 10^{-5}$$

What is the value of K_p for: $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \leftrightarrow \text{H}_2\text{O}(\text{g})$?

$$K_p = (4.9 \times 10^{-3})^{-1} = 204$$

3. The equation: $2 \text{NH}_3(\text{g}) \leftrightarrow \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g})$ has a value of $K_c = 2.7 \times 10^{-4}$

At STP, What is the value for K_p ?

$$K_p = K_c (\text{RT})^{\Delta n} = (2.7 \times 10^{-4})[(0.0821)(273 \text{ K})]^2 = 0.136$$

At STP, What is the value of K_c for: $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \leftrightarrow \text{NH}_3(\text{g})$?

$$K_c = (2.7 \times 10^{-4})^{-1/2} = 60.9$$

4. The equation: $\text{N}_2\text{O}_4(\text{g}) \leftrightarrow 2 \text{NO}_2(\text{g})$ has a value of $K_p = 3.2 \times 10^{-4}$

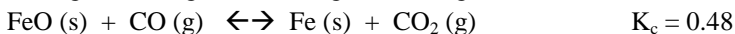
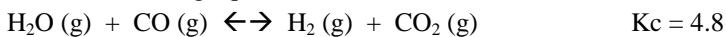
What is the value for K_c at 300 K??

$$K_p = K_c (\text{RT})^{\Delta n} \quad 3.2 \times 10^{-4} = K_c [(0.0821)(300 \text{ K})]^1 = 1.30 \times 10^{-5}$$

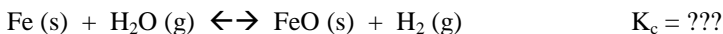
What is the value for K_c for: $\text{NO}_2(\text{g}) \leftrightarrow \frac{1}{2} \text{N}_2\text{O}_4(\text{g})$

$$K_c = (1.30 \times 10^{-5})^{-1/2} = 277$$

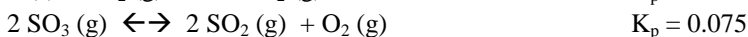
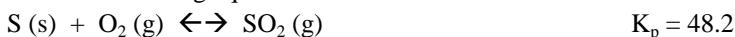
5. Given the following equations:



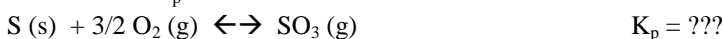
Calculate the K_c value for:



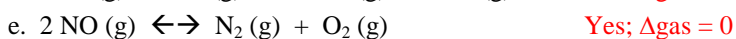
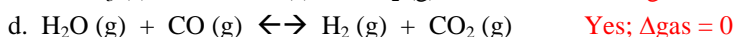
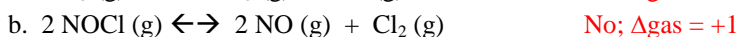
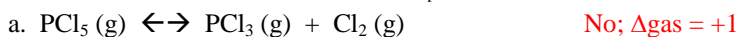
6. Given the following equations:



Calculate the K_p value for:



7. Which of the following equations has $K_c = K_p$



K_c and K_p Calculations

At Equilibrium

1. For the reaction: $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

At equilibrium $[\text{N}_2\text{O}_4] = 0.25 \text{ M}$ & $[\text{NO}_2] = 0.175 \text{ M}$. Calculate K_c

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \quad K_c = \frac{[0.25]}{[0.175]^2} \quad K_c = 8.16$$

2. For the reaction: $2 \text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g})$ $K_p = 32$

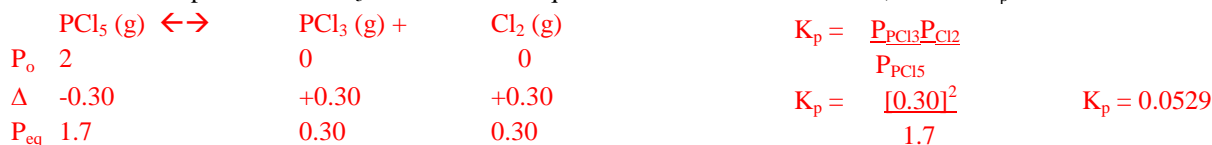
At equilibrium $P_{\text{NH}_3} = 0.64 \text{ atm}$ & $P_{\text{N}_2} = 1.18 \text{ atm}$. Calculate P_{H_2}

$$K_p = \frac{P_{\text{N}_2} P_{\text{H}_2}^3}{P_{\text{NH}_3}^2} \quad 32 = \frac{(1.18) P_{\text{H}_2}^3}{(0.64)^2} \quad P_{\text{H}_2} = 2.23$$

Dissociation

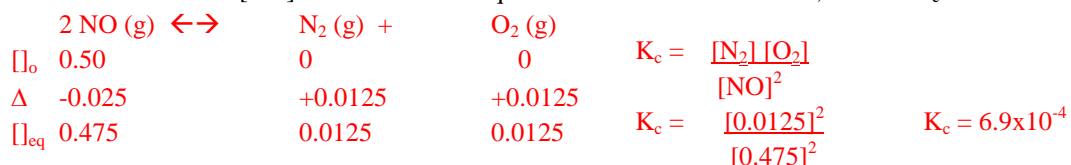
3. For the reaction: $\text{PCl}_5(\text{g}) \leftrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

If the initial pressure of PCl_5 is 2 atm and at equilibrium it is 15% dissociated, what is K_p ?



4. For the reaction: $2 \text{NO}(\text{g}) \leftrightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g})$

If the initial $[\text{NO}] = 0.50 \text{ M}$ and at equilibrium it is 5% dissociated, what is K_c ?



5. For the equation: $\text{NH}_4\text{I}(\text{s}) \leftrightarrow \text{NH}_3(\text{g}) + \text{HI}(\text{g})$

The total pressure at equilibrium is 4.2 atm. What is K_p ?



$$K_p = P_{\text{NH}_3} P_{\text{HI}} = (2.1)^2 = 4.41$$

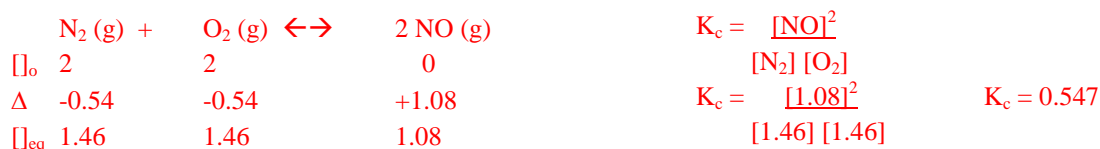
6. For the equation: $(\text{NH}_4)(\text{H}_2\text{NCO}_2)(\text{s}) \leftrightarrow 2 \text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$

The total pressure at equilibrium is 0.33 atm. What is K_p ?

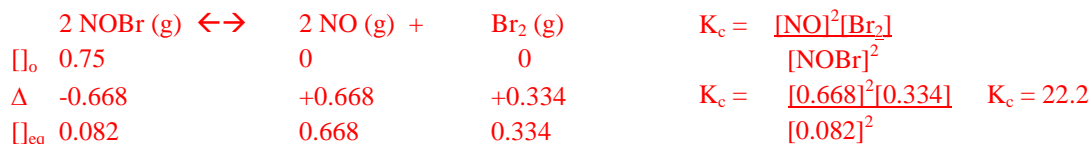


$$K_p = P_{\text{NH}_3}^2 P_{\text{CO}_2} = (0.22)^2 (0.11) = 5.32 \times 10^{-3}$$

7. For the equation: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{NO}(\text{g})$, you start with 2 M of each of the reactants. They react away to an extent of 27% to reach equilibrium. Calculate the value of K_c .



8. For the equation: $2 \text{NOBr}(\text{g}) \leftrightarrow 2 \text{NO}(\text{g}) + \text{Br}_2(\text{g})$, you start with 0.75 M of the NOBr. At equilibrium, the NOBr has reacted away by 89%. Calculate the value of K_c .



Q vs. K

9. For the reaction: $2 \text{NOCl}(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g})$ $K_c = 1.2 \times 10^{-3}$
 If the initial $[\text{NOCl}]_0 = 0.15 \text{ M}$, $[\text{NO}]_0 = 0.75 \text{ M}$, and $[\text{Cl}_2]_0 = 0.05 \text{ M}$, is the system at equilibrium?
 If not, which way will the reaction shift, left or right?

$$K_c = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2}$$

$$Q = \frac{[0.75]^2[0.05]}{[0.15]^2} \quad Q = 1.25 > 1.2 \times 10^{-3} \text{ so the reaction goes left}$$

10. For the reaction: $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ $K_c = 1.8 \times 10^{-5}$
 If the initial $[\text{NH}_3]_0 = 0.5 \text{ M}$, $[\text{NH}_4^+] = 0.0025 \text{ M}$, and $[\text{OH}^-] = 0.0025 \text{ M}$, is the system at equilibrium?
 If not, which way will the reaction shift, left or right?

$$K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$Q = \frac{[0.0025]^2}{[0.5]} \quad Q = 1.25 \times 10^{-5} < 1.8 \times 10^{-5} \text{ so the reaction goes right}$$

11. For the equation: $\text{CS}_2(\text{g}) + 3 \text{Cl}_2(\text{g}) \rightleftharpoons \text{S}_2\text{Cl}_2(\text{g}) + \text{CCl}_4(\text{g})$, $K_c = 4.8 \times 10^{-2}$. If you start with $[\text{CS}_2] = 0.025 \text{ M}$, $[\text{Cl}_2] = 0.175 \text{ M}$, $[\text{S}_2\text{Cl}_2] = 0.58 \text{ M}$, and $[\text{CCl}_4] = 0.042 \text{ M}$, is the reaction at equilibrium? If not, which way will the reaction go to reach equilibrium (left or right)?

$\text{CS}_2(\text{g})$	$+$	$3 \text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{S}_2\text{Cl}_2(\text{g})$	$+$	CCl_4	$Q = \frac{[\text{S}_2\text{Cl}_2][\text{CCl}_4]}{[\text{CS}_2][\text{Cl}_2]^3}$	$Q = \frac{(0.58)(0.042)}{(0.025)(0.175)^3} = 2.3$
[] ₀ 0.025		0.175		0.58		0.042		

$Q > K_c$ so reaction goes left

Calculating Equilibrium Conditions

12. For the equation: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, you start with 0.25 atm of each of the products as well as the reactants. The K_p value is 0.125. Is the reaction at equilibrium? Prove it. What are the equilibrium pressures of all species?

$\text{PCl}_5(\text{s})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	$+$	$\text{Cl}_2(\text{g})$	$Q = \frac{P_{\text{PCl}_3}P_{\text{Cl}_2}}{P_{\text{PCl}_5}} \quad Q = \frac{(0.25)^2}{0.25} = 0.25$
P_0 0.25		0.25		0.25	$Q > K_p \quad 0.25 > 0.125$ so there are too many products so the reaction moves to the <i>left</i>
Δ +x		-x		-x	$K_p = \frac{P_{\text{PCl}_3}P_{\text{Cl}_2}}{P_{\text{PCl}_5}} \quad 0.125 = \frac{(0.25-x)^2}{(0.25+x)}$ $x = 0.055$
P_{eq} 0.25 + x		0.25 - x		0.25 - x	$P_{\text{PCl}_5} = 0.305 \quad P_{\text{PCl}_3} = P_{\text{Cl}_2} = 0.195$

13. For the equation: $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ $K_c = 0.235$
 If 2 moles of each of H_2O and CO are put into a 10 L container, what is the concentration of all species at equilibrium?

$\text{H}_2\text{O}(\text{g})$	$+$	$\text{CO}(\text{g})$	\rightleftharpoons	$\text{CO}_2(\text{g})$	$+$	$\text{H}_2(\text{g})$	$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{H}_2\text{O}][\text{CO}]}$	$0.235 = \frac{(x)^2}{(0.2-x)^2}$
P_0 0.2		0.2		0		0		
Δ -x		-x		+x		+x		
P_{eq} 0.2 - x		0.2 - x		x		x	$x = 0.065$	$[\text{CO}_2] = [\text{H}_2] = 0.065$ $[\text{H}_2\text{O}] = [\text{CO}] = 0.135$

14. For the equation: $\text{SO}_2\text{Cl}_2(\text{g}) \leftrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ $K_p = 4.8$

If enough SO_2Cl_2 is put into a container so its pressure is 8 atm, what is the equilibrium pressure of all species.
What is the total pressure?

	$\text{SO}_2\text{Cl}_2(\text{g})$	\leftrightarrow	$\text{SO}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$		
P_o	8		0		0		$K_p = \frac{P_{\text{SO}_2}P_{\text{Cl}_2}}{P_{\text{SO}_2\text{Cl}_2}}$
Δ	-x		+x		+x		$K_p = \frac{[x]^2}{8-x}$ $K_p = 4.25$
P_{eq}	8-x		x		x		



$$P_{\text{SO}_2} = P_{\text{Cl}_2} = 4.25$$

$$P_{\text{SO}_2\text{Cl}_2} = 3.75$$

$$P_{\text{tot}} = 3.75 + 4.25 + 4.25 = 12.25$$

15. For the equation: $\text{CaCO}_3(\text{s}) \leftrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ $K_p = 2.4$

If 200 g CaCO_3 is put into a 20 L container at 500 K, how many grams of it remain at equilibrium?

	$\text{CaCO}_3(\text{s})$	\leftrightarrow	$\text{CaO}(\text{s})$	+	$\text{CO}_2(\text{g})$	
P_o					0	
Δ					+x	$K_p = 2.4 = P_{\text{CO}_2}$
P_{eq}					x	

$$P_{\text{CO}_2} = 2.4$$

$$PV = nRT$$



$$(2.4 \text{ atm})(20 \text{ L}) = n(0.0821 \text{ Latm/molK})(500 \text{ K})$$

$$n = 1.17 \text{ moles reacted away}$$

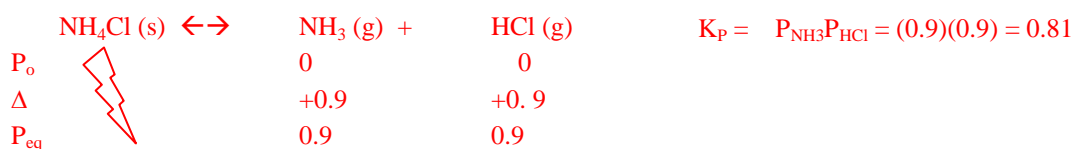
$$1.17 \text{ moles CaCO}_3 * (100.1 \text{ g/mole}) = 117 \text{ g reacted}$$

$$200 \text{ g to begin with} - 117 \text{ g reacted} = 83 \text{ g left}$$

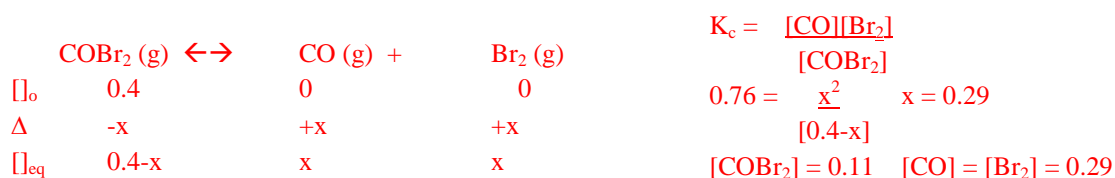
16. For the equation: $2 \text{KClO}_3(\text{s}) \leftrightarrow 2 \text{KCl}(\text{s}) + 3 \text{O}_2(\text{g})$, you start with some KClO_3 that decomposes into the products. At equilibrium, there is some solid remaining and the total pressure in the flask is 0.29 atm. Calculate the value of K_p .

	$2 \text{KClO}_3(\text{s})$	\leftrightarrow	$2 \text{KCl}(\text{s})$	+	$3 \text{O}_2(\text{g})$	
P_o					0	$K_p = P^3_{\text{O}_2} = 0.0244$
Δ					+0.29	
P_{eq}					0.29	

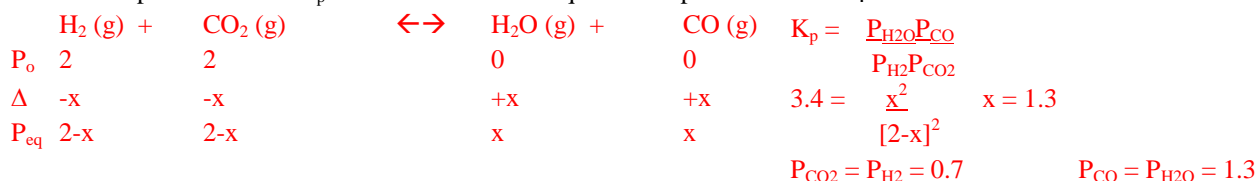
17. For the equation: $\text{NH}_4\text{Cl (s)} \leftrightarrow \text{NH}_3 \text{ (g)} + \text{HCl (g)}$, you start with some NH_4Cl that decomposes into the products. At equilibrium, there is some solid remaining and the total pressure in the flask is 1.8 atm. Calculate the value of K_p .



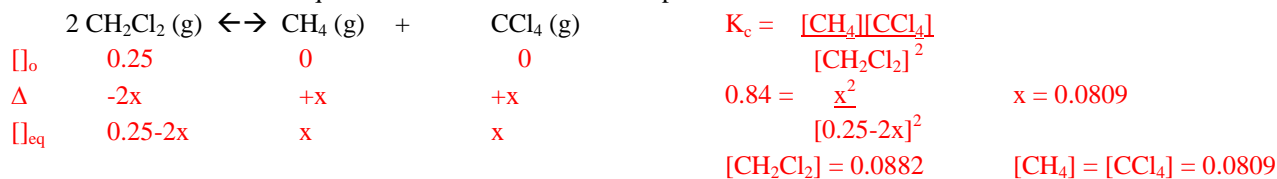
18. For the equation: $\text{COBr}_2 \text{ (g)} \leftrightarrow \text{CO (g)} + \text{Br}_2 \text{ (g)}$, you start with 4 moles in a 10 L vessel of COBr_2 . The reaction has a $K_c = 0.76$. What are the equilibrium concentrations of all species?



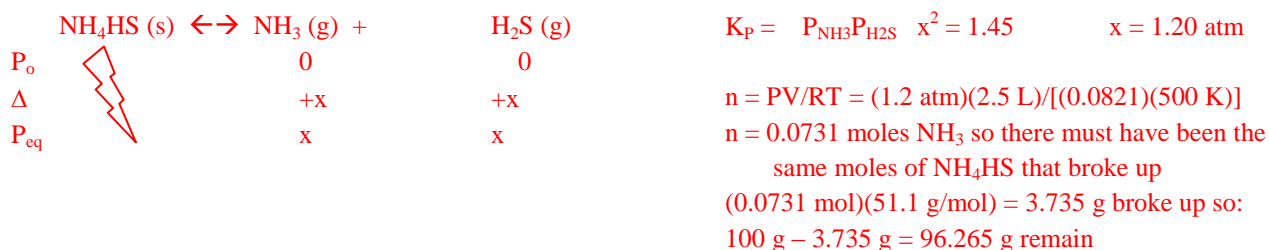
19. For the equation: $\text{H}_2 \text{ (g)} + \text{CO}_2 \text{ (g)} \leftrightarrow \text{H}_2\text{O (g)} + \text{CO (g)}$, you start with 2 atm of each of the reactants and none of the products. The $K_p = 3.4$. What are the equilibrium pressures of all species?



20. For the equation: $2 \text{CH}_2\text{Cl}_2 \text{ (g)} \leftrightarrow \text{CH}_4 \text{ (g)} + \text{CCl}_4 \text{ (g)}$, you start with 0.25 M of CH_2Cl_2 and is has a K_c value of 0.84. What are the equilibrium concentrations of all species?



21. For the equation: $\text{NH}_4\text{HS (s)} \leftrightarrow \text{NH}_3 \text{ (g)} + \text{H}_2\text{S (g)}$, you start with 100 grams of $\text{NH}_4\text{HS (s)}$ in a 2.5 L flask at 500 K. The K_p value is 1.45. How many grams of the solid remain at equilibrium?



LeChatelier's Principle

1. State LeChatelier's Principle. **A change in any factor that effects the equilibrium of a system will cause the system to shift in such a way to reduce or counteract that initial change.**

2. For the following reaction: $\text{Heat} + \text{CaCO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{Ca}^{+2}(\text{aq}) + 2 \text{HCO}_3^{-1}(\text{aq})$

What will be the effect of doing each of the following actions on the above equilibrium?

- | | | | |
|---|------|-------|-----------|
| a) Adding $\text{CaCO}_3(\text{s})$ | Left | Right | No Change |
| b) Removing $\text{Ca}^{+2}(\text{aq})$ | Left | Right | No Change |
| c) Removing $\text{CO}_2(\text{g})$ | Left | Right | No Change |
| d) Adding $\text{NaHCO}_3(\text{s})$ | Left | Right | No Change |
| e) Adding $\text{Ne}(\text{g})$ | Left | Right | No Change |
| f) Adding $\text{CO}_2(\text{g})$ | Left | Right | No Change |
| g) Increasing temperature | Left | Right | No Change |
| h) Decreasing volume | Left | Right | No Change |

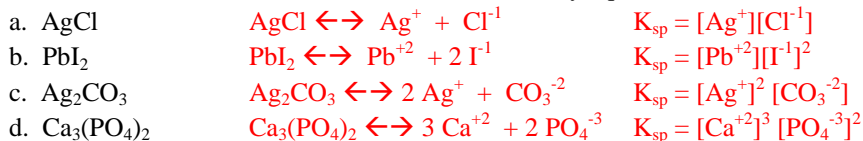
3. For the following reaction: $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{SO}_3(\text{g}) + \text{Heat}$

What will be the effect of doing each of the following actions on the above equilibrium?

- | | | | |
|---------------------------------------|------|-------|-----------|
| a) Decreasing temperature | Left | Right | No Change |
| b) Increasing $\text{O}_2(\text{g})$ | Left | Right | No Change |
| c) Decreasing $\text{SO}_2(\text{g})$ | Left | Right | No Change |
| d) Increasing volume | Left | Right | No Change |
| e) Increasing $\text{SO}_3(\text{g})$ | Left | Right | No Change |
| f) Adding $\text{N}_2(\text{g})$ | Left | Right | No Change |

K_{sp}

1. For each of the substances below, write the solubility equation as well as the K_{sp} equation.



Problem Solving with K_{sp}

1. Calculate the K_{sp} of CaCrO_4 if a saturated solution has $[\text{Ca}^{+2}] = 4.5 \times 10^{-5}$



2. Calculate the K_{sp} of $\text{Fe}(\text{OH})_3$ if a saturated solution has $[\text{Fe}^{+3}] = 4.2 \times 10^{-6}$



3. Calculate the solubility (moles/L) of PbCO_3 if $K_{sp} = 7.4 \times 10^{-14}$



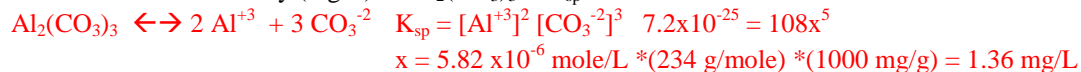
4. Calculate the solubility (moles/L) of Ag_2SO_4 if $K_{sp} = 1.2 \times 10^{-5}$



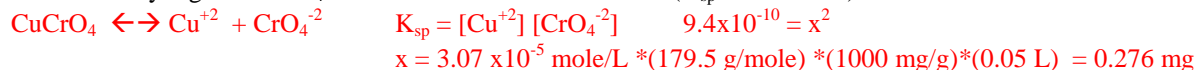
5. Calculate the solubility (mg/L) of FePO_4 if $K_{sp} = 9.4 \times 10^{-9}$



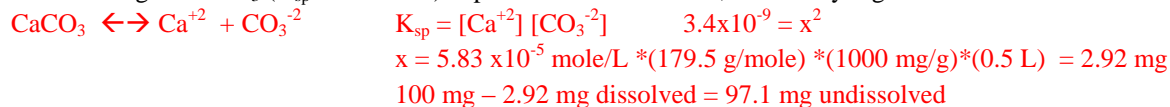
6. Calculate the solubility (mg/L) of $\text{Al}_2(\text{CO}_3)_3$ if $K_{sp} = 7.2 \times 10^{-25}$



7. How many mg of CuCrO_4 will dissolve in 50 mL of water ($K_{sp} = 9.4 \times 10^{-10}$)



8. If 100 mg of CaCO_3 ($K_{sp} = 3.4 \times 10^{-9}$) is put in 500 mL of water, how many mg remain undissolved?



9. Put the following substances in order of least soluble to most soluble.



Since they are all the same number of pieces, you can compare them directly by K_{sp} values. Thus:



10. Put the following substances in order of least soluble to most soluble.



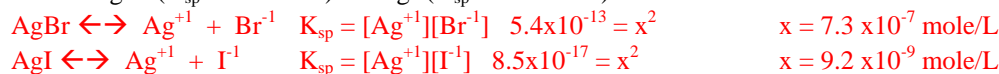
These substances have different number of ionic pieces so you can't compare K_{sp} values directly. If you do a solubility ICE table for each, the ultimate results will be as follows where x is the solubility:



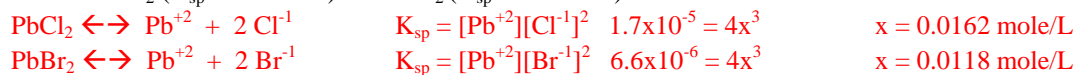
Thus $\text{AgBr} < \text{Pb}(\text{OH})_2 < \text{BaSO}_4 < \text{Zn}(\text{CN})_2$

11. Prove which of each of the substances below is the most soluble.

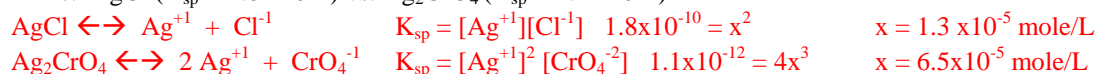
a. AgBr ($K_{sp} = 5.4 \times 10^{-13}$) vs. AgI ($K_{sp} = 8.5 \times 10^{-17}$)



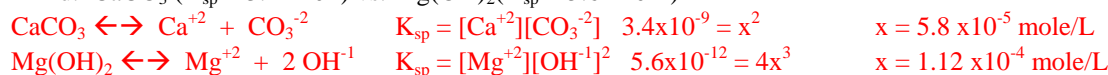
b. PbCl₂ ($K_{sp} = 1.7 \times 10^{-5}$) vs. PbBr₂ ($K_{sp} = 6.6 \times 10^{-6}$)



c. AgCl ($K_{sp} = 1.8 \times 10^{-10}$) vs. Ag₂CrO₄ ($K_{sp} = 1.1 \times 10^{-12}$)



d. CaCO₃ ($K_{sp} = 3.4 \times 10^{-9}$) vs. Mg(OH)₂ ($K_{sp} = 5.6 \times 10^{-12}$)



Common Ion Effect

1. Calculate the solubility (moles/L) of MgS ($K_{sp} = 5.2 \times 10^{-16}$) in:

a. Pure water



b. A 0.25 M solution of MgCl₂



2. Calculate the solubility (moles/L) of PbCl₂ ($K_{sp} = 1.7 \times 10^{-5}$) in:

a. Pure water



b. A 0.55 M solution of NaCl



3. Calculate the solubility (moles/L) of PbI₂ ($K_{sp} = 9.8 \times 10^{-9}$) in:

a. Pure water

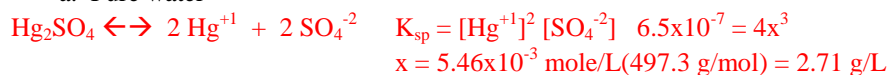


b. A 0.005 M solution of AlI₃

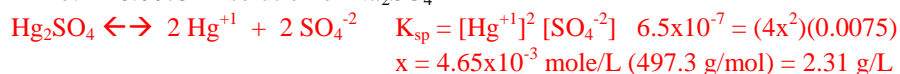


4. Calculate what mass of Hg₂SO₄ ($K_{sp} = 6.5 \times 10^{-7}$) will dissolve per liter in:

a. Pure water

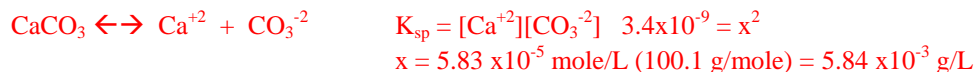


b. A 0.0075 M solution of Na₂SO₄

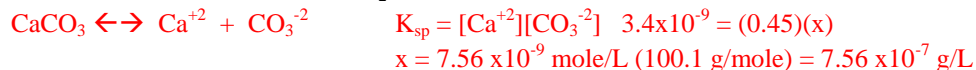


5. Calculate what mass of CaCO_3 ($K_{sp} = 3.4 \times 10^{-9}$) will dissolve per liter in:

a. Pure water

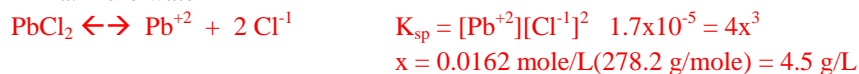


b. A 0.45 M solution of CaCl_2

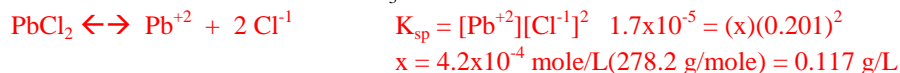


6. Calculate what mass of PbCl_2 ($K_{sp} = 1.7 \times 10^{-5}$) will dissolve per liter in:

a. Pure water



b. A 0.067 M solution of AlCl_3



7. AgBr will be the least soluble in 0.10 M:

a. NaBr b. CaBr_2 c. AlBr_3 d. Ag_2SO_4 e. AgNO_3

AlBr_3 will have the most concentrated $[\text{Br}^{-1}]$ or $[\text{Ag}^{+1}]$ since there are 3 Br^{-1} for every 1 AlBr_3 . Thus, AgBr will be least soluble in it.

8. MgF_2 will be least soluble in 0.25 M:

a. KF b. $\text{Mg}(\text{NO}_3)_2$ c. MgC_2O_4 d. BaF_2 e. LiF

BaF_2 will have the most concentrated $[\text{F}^{-1}]$ or $[\text{Mg}^{+2}]$ since there are 2 F^{-1} for every 1 BaF_2 . Thus, MgF_2 will be least soluble in it.

Precipitation

1. Will a ppt of CaCO_3 ($K_{sp} = 3.4 \times 10^{-9}$) form if $[\text{Ca}^{+2}] = 4 \times 10^{-6} \text{ M}$ and $[\text{CO}_3^{-2}] = 4 \times 10^{-3}$?

$$Q = [4 \times 10^{-6}][4 \times 10^{-3}] = 1.6 \times 10^{-8} \gg 3.4 \times 10^{-9} \text{ so yes, ppt}$$

2. Will a ppt of Ag_2CrO_4 ($K_{sp} = 1.1 \times 10^{-12}$) form if $[\text{Ag}^{+}] = 3 \times 10^{-4}$ and $[\text{CrO}_4^{-2}] = 2 \times 10^{-4}$?

$$Q = [3 \times 10^{-4}]^2 [2 \times 10^{-4}] = 1.8 \times 10^{-11} \gg 1.1 \times 10^{-12} \text{ so yes, ppt}$$

3. Will a ppt of BaCO_3 ($K_{sp} = 2.6 \times 10^{-9}$) form if 50 mL of $4 \times 10^{-5} \text{ M Ba}^{+2}$ is mixed with 50 mL of $8 \times 10^{-5} \text{ M CO}_3^{-2}$?

$$Q = [(50/100)4 \times 10^{-5}][(50/100)8 \times 10^{-5}] = 8 \times 10^{-10} \ll 2.6 \times 10^{-9} \text{ so no ppt}$$

4. Will a ppt of PbBr_2 ($K_{sp} = 6.6 \times 10^{-6}$) form if 150 mL of $2 \times 10^{-2} \text{ M Pb}(\text{NO}_3)_2$ is mixed with 50 mL of $3 \times 10^{-2} \text{ M AlBr}_3$?

$$Q = [(150/200)2 \times 10^{-2}][(50/200)(3) 3 \times 10^{-2}] = 7.6 \times 10^{-6} \gg 6.6 \times 10^{-6} \text{ so yes, ppt}$$

5. What concentration of $[\text{OH}^{-1}]$ will cause a ppt of $\text{Fe}(\text{OH})_2$ ($K_{sp} = 4.9 \times 10^{-17}$) of a $2 \times 10^{-5} \text{ M Fe}^{+2}$ solution?

$$4.9 \times 10^{-17} = (2 \times 10^{-5})(\text{OH}^{-1})^2 \quad [\text{OH}^{-1}] = 1.56 \times 10^{-6} \text{ M}$$

6. What concentration of $[\text{C}_2\text{O}_4^{-2}]$ will cause a ppt of $\text{Ag}_2\text{C}_2\text{O}_4$ ($K_{sp} = 5.4 \times 10^{-12}$) of a $4 \times 10^{-4} \text{ M Ag}^{+1}$ solution?

$$5.4 \times 10^{-12} = (4 \times 10^{-4})^2 (\text{C}_2\text{O}_4^{-2}) \quad [\text{C}_2\text{O}_4^{-2}] = 3.4 \times 10^{-5} \text{ M}$$

7. What mass of $\text{Ni}(\text{NO}_3)_2 \cdot 7 \text{H}_2\text{O}$ (s) will cause a ppt of NiCO_3 ($K_{sp} = 1.4 \times 10^{-7}$) in a 2 L solution of $3.5 \times 10^{-4} \text{ M CO}_3^{-2}$?

$$1.4 \times 10^{-7} = [\text{Ni}^{+2}](3.5 \times 10^{-4}) \quad [\text{Ni}^{+2}] = 4 \times 10^{-4} \text{ M}$$

Molar mass of $\text{Ni}(\text{NO}_3)_2 \cdot 7 \text{H}_2\text{O} = 308.7 \text{ g/mole}$

$$[\text{Ni}^{+2}] = 4 \times 10^{-4} \text{ moles/L} * 2 \text{ L} * 308.7 \text{ g/mole} = 0.247 \text{ grams Ni}(\text{NO}_3)_2 \cdot 7 \text{H}_2\text{O}$$

8. What mass of $\text{Pb}(\text{NO}_3)_2$ will cause a ppt of PbCl_2 ($K_{sp} = 1.7 \times 10^{-5}$) in 100 mL of a $2.4 \times 10^{-2} \text{ M}$ solution of AlCl_3 ?

Since there are 3 Cl^{-1} ions for every AlCl_3 then $[\text{Cl}^{-1}] = 7.2 \times 10^{-2} \text{ M}$ so:

$$1.7 \times 10^{-5} = [\text{Pb}^{+2}](0.072)^2 \quad [\text{Pb}^{+2}] = 3.28 \times 10^{-3} \text{ M}$$

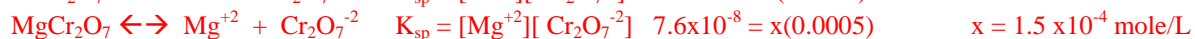
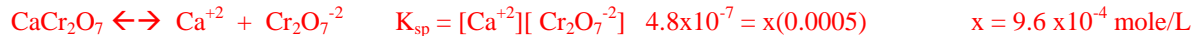
Molar mass of $\text{Pb}(\text{NO}_3)_2$ is 331.2 g/mole

$$\text{Thus: } 3.28 \times 10^{-3} \text{ moles/L} * 1 \text{ L/100 mL} * 100 \text{ mL} * 331.2 \text{ g/mole} = 0.109 \text{ grams Pb}(\text{NO}_3)_2$$

Separations by K_{sp}

1. A solution is made so that $[Ca^{+2}] = 0.00050$ and $[Mg^{+2}] = 0.00050$ as well. If $Cr_2O_7^{-2}$ is added, answer the following questions. Know that $K_{sp} CaCr_2O_7 = 4.8 \times 10^{-7}$ and $K_{sp} MgCr_2O_7 = 7.6 \times 10^{-8}$

a. Which will ppt 1st? At what $[Cr_2O_7^{-2}]$ will it begin to ppt?

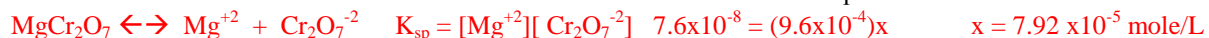


$MgCr_2O_7$ ppts 1st

b. What is the maximum $[Cr_2O_7^{-2}]$ that can be made to ppt almost all of one and none of the other?

$$9.6 \times 10^{-4} \text{ moles/L}$$

c. What is the concentration of the less soluble ion under the conditions specified in "b"?

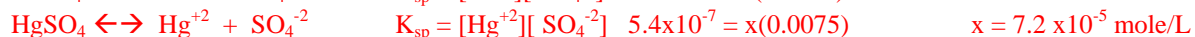
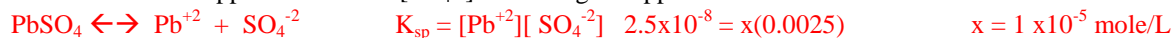


d. What % of the less soluble ion remains in solution under the conditions specified in "b"?

$$(7.92 \times 10^{-5} / 0.0005) * 100\% = 15.8\%$$

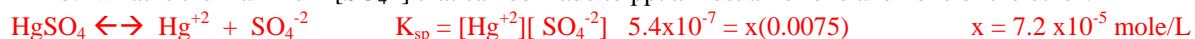
2. A solution is made so that $[Pb^{+2}] = 0.00250$ and $[Hg^{+2}] = 0.0075$. If SO_4^{-2} is added, answer the following questions. Know that $K_{sp} PbSO_4 = 2.5 \times 10^{-8}$ and $K_{sp} HgSO_4 = 5.4 \times 10^{-7}$

a. Which will ppt 1st? At what $[SO_4^{-2}]$ will it begin to ppt?



$PbSO_4$ ppts 1st

b. What is the maximum $[SO_4^{-2}]$ that can be made to ppt almost all of one and none of the other?



c. What is the concentration of the less soluble ion under the conditions specified in "b"?

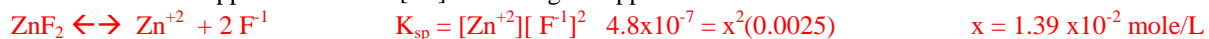


d. What % of the less soluble ion remains in solution under the conditions specified in "b"?

$$(3.5 \times 10^{-4} / 0.0025) * 100\% = 13.9\%$$

3. A solution is made so that $[Zn^{+2}] = 0.00250$ and $[Ag^{+1}] = 0.057$. If F^{-1} is added, answer the following questions. Know that $K_{sp} ZnF_2 = 4.8 \times 10^{-7}$ and $K_{sp} AgF = 7.6 \times 10^{-8}$

a. Which will ppt 1st? At what $[F^{-1}]$ will it begin to ppt?



AgF ppts 1st

b. What is the maximum $[F^{-1}]$ that can be made to ppt almost all of one and none of the other?

$$1.39 \times 10^{-2} \text{ mole/L}$$

c. What is the concentration of the less soluble ion under the conditions specified in "b"?

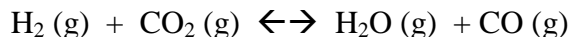


d. What % of the less soluble ion remains in solution under the conditions specified in "b"?

$$(5.47 \times 10^{-6} / 0.057) * 100\% = 0.0096\%$$

Combination Problems

1. For the reaction at 2000 K



For an experiment, the equilibrium values of each substance are as follows:

$$[\text{H}_2] = 0.20 \text{ M}$$

$$[\text{CO}_2] = 0.30 \text{ M}$$

$$[\text{H}_2\text{O}] = [\text{CO}] = 0.55 \text{ M}$$

a. What is the mole fraction of CO in the equilibrium mixture?

$$X_{\text{CO}} = (0.55)/(0.20+0.30+0.55+0.55) = 0.355$$

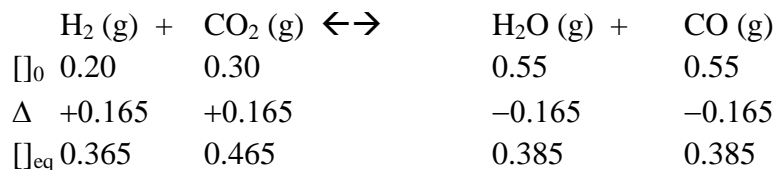
b. Calculate the value of K_c , the equilibrium constant for the reaction above.

$$K_c = (0.55)^2/(0.20)(0.30) = 5.042$$

c. Determine K_p in terms of K_c for this system. $K_p = K_c$ because $\Delta n_{\text{gas}} = 0$

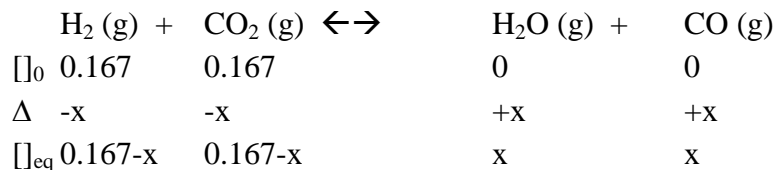
d. When the system is cooled from 2000 K to a lower temperature, 30% of the CO is converted back to CO_2 . Calculate the value of K_c at this lower temperature.

Since 30% of CO is converted: $0.55 \times 0.30 = 0.165$ changes for each



$$K_c = (0.385)^2/(0.365)(0.465) = 0.873$$

e. In a different experiment, 0.50 mole of H_2 is mixed with 0.50 mole of CO_2 in a 3.0 L reaction vessel at 2000 K. Calculate the equilibrium concentration, in M, of CO at this temperature.



$$5.042 = x^2 / (0.167-x)^2 \qquad 2.245 = x / (0.167-x) \qquad x = [\text{CO}] = 0.1156$$

2. For the reaction:



It is observed that greater amounts of PCl_3 and Cl_2 are produced as the temperature is increased.

a) What is the sign of ΔS° for the reaction? Explain.

ΔS should be positive. You are going from one mole of gas on the left to 2 moles on the right. This shows an increase in disorder and a positive entropy change

b) What change, if any, will occur in ΔG° for the reaction as the temperature is increased?

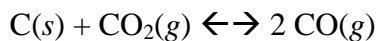
Explain. Since ΔS is positive, ΔG should decrease as temperature is increased. This is due to the equation $\Delta G = \Delta H - T\Delta S$. Since T is in K and therefore positive, you will be subtracting a positive value from ΔG .

c) If He gas is added to the original mixture at constant volume and temperature, what will happen to the partial pressure of Cl_2 ? Explain. Dalton's law of partial pressures says that the total pressure is equal to the sum of the individual pressures. Adding more He gas will increase the total pressure but not change the pressure the Cl_2 exerts.

d) If the volume of the reaction mixture is decreased at constant temperature to half the original volume, what will happen to the number of moles of Cl_2 in the reaction vessel? Explain.

By decreasing the volume, you are increasing the pressures of each of the above species. Since there are unequal amounts of gas on the reactant and product sides of the equation above, the system will try to reduce the pressure increase it experienced. It can do this by going to the left side which will reduce the number of moles of Cl_2

3. For the reaction:



Solid carbon and carbon dioxide gas at 1,160 K were placed in a rigid 2.00 L container, and the reaction represented above occurred. As the reaction proceeded, the total pressure in the container was monitored. When equilibrium was reached, there was still some C(s) remaining in the container. Results are recorded in the table below.

Time (hours)	Total Pressure of gases (atm)
0.0	5.00
2.0	6.26
4.0	7.09
6.0	7.75
8.0	8.37
10.0	8.37

(a) Write the expression for the equilibrium constant, K_p , for the reaction.

$$K_p = P_{\text{CO}}^2 / P_{\text{CO}_2}$$

(b) Calculate the number of moles of $\text{CO}_2(g)$ initially placed in the container. (Assume that the volume of the solid carbon is negligible.)

$$n = PV/RT = (5 \text{ atm})(2 \text{ L}) / (0.0821)(1160 \text{ K}) = 0.105 \text{ moles}$$

(c) For the reaction mixture at equilibrium at 1,160 K, the partial pressure of the $\text{CO}_2(g)$ is 1.63 atm.

Calculate:

(i) the partial pressure of $\text{CO}(g)$, and

$$\text{CO}_2: 5 \text{ atm} - 1.63 \text{ atm} = 3.37 \text{ atm CO}_2 \text{ reacted} * (2 \text{ mole CO} / 1 \text{ mole CO}_2) = 6.74 \text{ atm CO}$$

(ii) the value of the equilibrium constant, K_p .

$$K_p = P_{\text{CO}}^2 / P_{\text{CO}_2} = (6.74)^2 / 1.63 = 27.87$$

(d) If a suitable solid catalyst were placed in the reaction vessel, would the final total pressure of the gases at equilibrium be greater than, less than, or equal to the final total pressure of the gases at equilibrium without the catalyst? Justify your answer. (Assume that the volume of the solid catalyst is negligible.)

Nothing would change. It would just get to equilibrium faster.

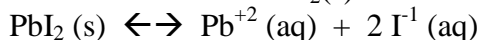
(e) In another experiment involving the same reaction, a rigid 2.00 L container initially contains 10.0 g of C(s), plus $\text{CO}(g)$ and $\text{CO}_2(g)$, each at a partial pressure of 2.00 atm at 1,160 K. Predict whether the partial pressure of $\text{CO}_2(g)$ will increase, decrease, or remain the same as this system approaches equilibrium. Justify your prediction with a calculation.

$$Q = (2)^2 / 2 = 2 \quad Q \lll K_p \quad \text{so reaction will go to the right}$$

This will cause the partial pressure of CO_2 to decrease

4. Answer the following questions:

- a. A saturated solution is prepared by adding excess $\text{PbI}_2(\text{s})$ to distilled water to form 1.0 L of solution at 25°C . The concentration of $\text{Pb}^{+2}(\text{aq})$ in the saturated solution is found to be $1.3 \times 10^{-3} \text{ M}$. The chemical equation for the dissolution of $\text{PbI}_2(\text{s})$ in water is shown below:



i) Write the equilibrium-constant expression for the equation.

$$K_{\text{sp}} = [\text{Pb}^{+2}][\text{I}^{-1}]^2$$

ii) Calculate the molar concentration of $\text{I}^{-1}(\text{aq})$ in the solution.

$$[\text{Pb}^{+2}] = 1.3 \times 10^{-3} \text{ M} * (2 \text{ moles } \text{I}^{-1} / 1 \text{ mole } \text{Pb}^{+2}) = 2.6 \times 10^{-3} \text{ M}$$

iii) Calculate the value of the equilibrium constant, K_{sp} .

$$K_{\text{sp}} = (1.3 \times 10^{-3})(2.6 \times 10^{-3})^2 = 8.79 \times 10^{-9}$$

- b. A saturated solution is prepared by $\text{PbI}_2(\text{s})$ to distilled water to form 2.0 L of solution at 25°C . What are the molar concentrations of $\text{Pb}^{+2}(\text{aq})$ and $\text{I}^{-1}(\text{aq})$ in the solution? Justify your answer.

The concentrations should be the same as above; $[\text{Pb}^{+2}] = 1.3 \times 10^{-3}$ and $[\text{I}^{-1}] = 2.6 \times 10^{-3}$. Changing the volume does not change the concentration if the solution is still saturated.

- c. Solid NaI is added to a saturated solution of PbI_2 at 25°C . Assuming that the volume of the solution does not change, does the molar concentration of $\text{Pb}^{+2}(\text{aq})$ in the solution increase, decrease, or stay the same? Justify your answer.

By adding NaI , you are adding $[\text{I}^{-1}]$ and thus, by LeChatelier's Principle, the reaction should go to the left and form a precipitate. To do this, you must use up some of the Pb^{+2} so thus $[\text{Pb}^{+2}]$ should decrease

5. The value of K_{sp} for the salt BaCrO_4 is 1.2×10^{-10} . When a 500. mL sample of $8.2 \times 10^{-6} \text{ M}$ $\text{Ba}(\text{NO}_3)_2$ is added to 500. mL of $8.2 \times 10^{-6} \text{ M}$ Na_2CrO_4 , no precipitate is observed.

i) Assuming the volumes are additive, calculate the molar concentrations of $\text{Ba}^{+2}(\text{aq})$ and $\text{CrO}_4^{-2}(\text{aq})$ in the 1.00 L of solution.

$$[\text{Ba}^{+2}] = 8.2 \times 10^{-6} \text{ M } \text{Ba}(\text{NO}_3)_2 * (500/1000) = 4.1 \times 10^{-6} \text{ M}$$

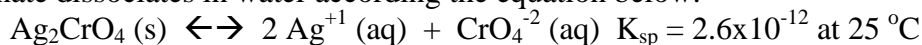
$$[\text{CrO}_4^{-2}] = 8.2 \times 10^{-6} \text{ M } \text{Na}_2\text{CrO}_4 * (500/1000) = 4.1 \times 10^{-6} \text{ M}$$

ii) Use the molar concentrations of $\text{Ba}^{+2}(\text{aq})$ and $\text{CrO}_4^{-2}(\text{aq})$ ions as determined above to show why a precipitate does not form. You must include a calculation as part of your answer.

$$Q = [\text{Ba}^{+2}][\text{CrO}_4^{-2}] = (4.1 \times 10^{-6})(4.1 \times 10^{-6}) = 1.681 \times 10^{-11}$$

$$Q < K_{\text{sp}} \quad 1.681 \times 10^{-11} < 1.2 \times 10^{-10} \quad \text{so no ppt forms}$$

6. Silver chromate dissociates in water according to the equation below:



- a) Write the equilibrium-constant expression for the dissolving of $\text{Ag}_2\text{CrO}_4 (\text{s})$

$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

- b) Calculate the concentration, in M, of $\text{Ag}^+ (\text{aq})$ in a saturated solution of Ag_2CrO_4 at 25°C

$$2.6 \times 10^{-12} = 4x^3 \quad x = 8.66 \times 10^{-5} \text{ M} \quad \text{Since there are 2 } \text{Ag}^+ \text{ ions present, } [\text{Ag}^+] = 1.732 \times 10^{-4}$$

- c) Calculate the maximum mass, in grams, of Ag_2CrO_4 that can dissolve in 100. mL of water at 25°C .

$$x = 8.6 \times 10^{-5} \text{ moles/L} * (0.10 \text{ L}) * (331.8 \text{ g/mole}) = 0.002853 \text{ g}$$

- d) A 0.100 mol sample of solid AgNO_3 is added to a 1.00 L saturated solution of Ag_2CrO_4 .

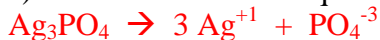
Assuming no volume change, does $[\text{CrO}_4^{2-}]$ increase, decrease, or stay the same? Justify.

Since AgNO_3 will dissolve and make more Ag^+ ions, the reaction will go left due to Le Chatelier's principle. This will cause CrO_4^{2-} to react and ppt so $[\text{CrO}_4^{2-}]$ will decrease.

7. In a saturated solution of Ag_3PO_4 at 25°C , the concentration of $\text{Ag}^+ (\text{aq})$ is $5.3 \times 10^{-5} \text{ M}$. The equilibrium constant expression for the dissolving of $\text{Ag}_3\text{PO}_4 (\text{s})$ in water is shown below:

$$K_{\text{sp}} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}]$$

- a) Write the balanced equation for the dissolving of Ag_3PO_4 in water.



- b) Calculate the value of K_{sp} for Ag_3PO_4 at 25°C .

$[\text{Ag}^+] = 5.3 \times 10^{-5}$ but there is only 1 PO_4^{3-} for every 3 Ag^+ so:

$$5.3 \times 10^{-5} * (1 \text{ mole } \text{PO}_4^{3-} / 3 \text{ mole } \text{Ag}^+) = 1.77 \times 10^{-5} \text{ M } \text{PO}_4^{3-}$$

$$K_{\text{sp}} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}] = (5.3 \times 10^{-5})^3 (1.77 \times 10^{-5}) = 2.635 \times 10^{-18}$$

- c) A 1.00 L sample of saturated Ag_3PO_4 solution is allowed to evaporate at 25°C to a final volume of 500. mL. What is the $[\text{Ag}^+]$ in the solution? Justify your answer.

The concentration does not change in a saturated solution. As 500 mL evaporates, solid Ag_3PO_4 will ppt out at the bottom of the beaker. The solution will still be saturated, though, and therefore not change its concentration.