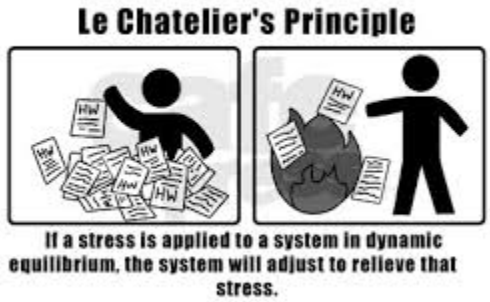
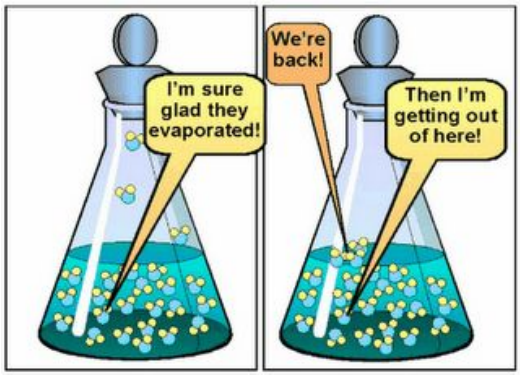
AP Learning Objectives:

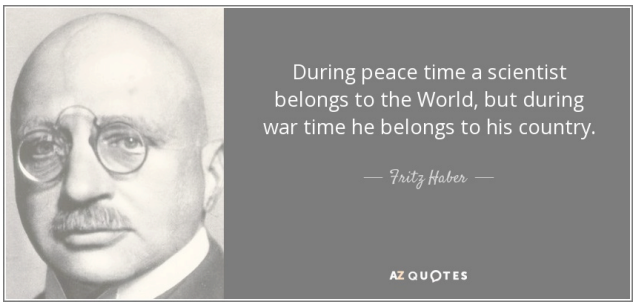
- Explain the relationship between the occurrence of a reversible chemical or physical process, and the establishment of equilibrium, to experimental observations (7.1)
- Explain the relationship between the direction in which a reversible reaction proceeds and the relative rates of the forward and reverse reactions.(7.2)
- Represent the reaction quotient Qc p or Q , for a reversible reaction, and the corresponding equilibrium expressions Kc = Qc or K p = Qp . (7.3)
- Calculate Kc or Kp based on experimental observations of concentrations or pressures at equilibrium. (7.4)
- Explain the relationship between very large or very small values of K and the relative concentrations of chemical species at equilibrium (7.5)
- Represent a multistep process with an overall equilibrium expression, using the constituent K expressions for each individual reaction(7.6)
- Identify the concentrations or partial pressures of chemical species at equilibrium based on the initial conditions and the equilibrium constant.(7.7)
- Represent a system undergoing a reversible reaction with a particulate model. (7.8)
- Identify the response of a system at equilibrium to an external stress, using Le Châtelier's principle.(7.9)
- Explain the relationships between Q, K, and the direction in which a reversible reaction will proceed to reach equilibrium. (7.10)
- Calculate the solubility of a salt based on the value of Ksp for the salt.(7.11)
- Identify the solubility of a salt, and/or the value of Ksp for the salt, based on the concentration of a common ion already present in solution.(7.12)
- Identify the qualitative effect of changes in pH on the solubility of a salt.(7.13)
- Explain the relationship between the solubility of a salt and changes in the enthalpy and entropy that occur in the dissolution process. (7.14)











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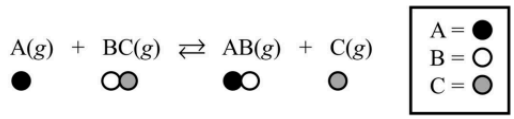
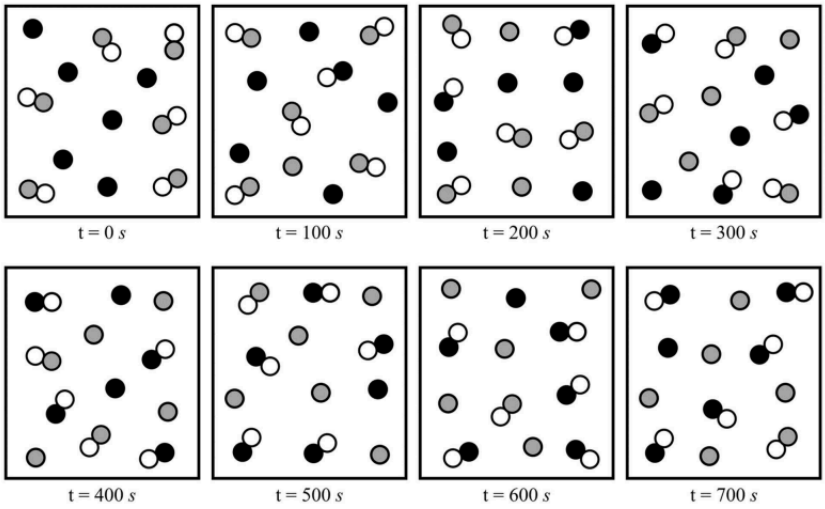
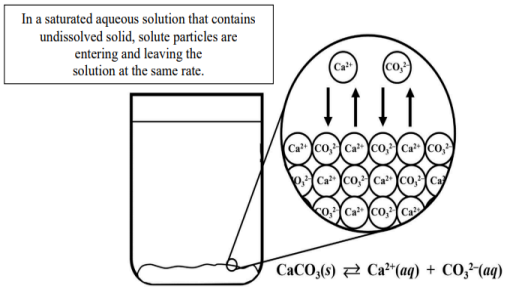
Equilibrium Review

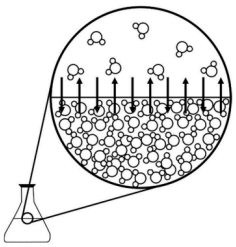


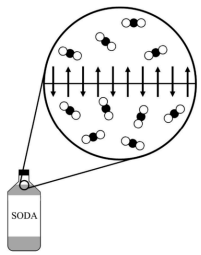


1. Consider the chemical equation represented above. Below it, a series of particle diagrams represent the reaction mixture over time as the reaction proceeds. Label the diagrams above by counting the number of each substance in the reaction mixture at each time interval.
2. At which point was equilibrium achieved? Justify your answer.

3. On each diagram below, identify why each represents an equilibrium system. The first is done for you.







4. On the same diagrams, explain observations you may see when these representations are at equilibrium.

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5. Consider the decomposition reaction below. The partial pressures of each gas are monitored over time and the data is graphed below. $A_2X_4(g) \leftrightarrow 2AX_2(g)$

   Use the words increasing, decreasing, or remaining the same:

   a. During the first 30 seconds of the reaction,

      i. the partial pressure of the reactant is _____

      ii. the partial pressure of the product is _____

      iii. the rate of the forward reaction is _____

      iv. the rate of the reverse reaction is _____

   b. During the last 30 seconds of the reaction,

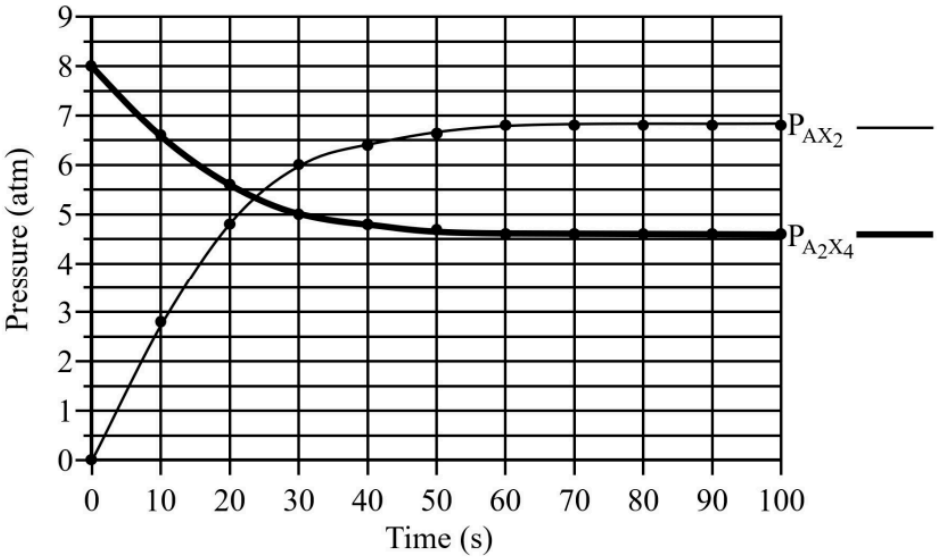
      i. the partial pressure of the reactant is _____

      ii. the partial pressure of the product is _____

      iii. the rate of the forward reaction is _____

      iv. the rate of the reverse reaction is _____

   c. At what point did the reaction hit an equilibrium? Justify your answer.



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LeChatelier Rules:

1. If a substance (or heat) is ADDED shift AWAY from that substance (or heat)
2. If a substance (or heat) is TAKEN shift TOWARDS that substance (or heat)
3. If pressure is added, there is less volume/room for moles. Shift towards the side with less moles.
4. If pressure is relieved, there is more room. Shift towards the side with more moles.
5. Catalysts speed up the forward AND reverse reaction. Therefore equilibrium is unchanged.
6. At equilibrium RATES are equal. Not amount!

6. Circle which **direction** the equilibrium will shift towards to relieve the stress and cite the rule used:

$2NH_{3(g)}$ $N_{2(g)} + 3H_{2(g)} + heat$

					Rule #
a.	Ammonia is added	**left**	**right**	**no effect**	_____
b.	Nitrogen is added	**left**	**right**	**no effect**	_____
c.	Hydrogen is added	**left**	**right**	**no effect**	_____
d.	Heat is added	**left**	**right**	**no effect**	_____
e.	Ammonia is removed	**left**	**right**	**no effect**	_____
f.	Nitrogen is removed	**left**	**right**	**no effect**	_____
g.	Hydrogen is removed	**left**	**right**	**no effect**	_____
h.	Heat is removed	**left**	**right**	**no effect**	_____
i.	Pressure is increased	**left**	**right**	**no effect**	_____
j.	Pressure is decreased	**left**	**right**	**no effect**	_____
k.	A catalyst is added	**left**	**right**	**no effect**	_____

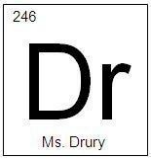
7. Circle what will happen to the **Nitrogen** to relieve the stress:

$N_{2(g)} + 3H_{2(g)} + heat$ $2NH_{3(g)}$

a.	Ammonia is removed	**increase**	**decrease**	**remain the same**
b.	Heat is added	**increase**	**decrease**	**remain the same**
c.	Pressure is increased	**increase**	**decrease**	**remain the same**
d.	Heat is removed	**increase**	**decrease**	**remain the same**
e.	Ammonia is added	**increase**	**decrease**	**remain the same**
f.	Hydrogen is removed	**increase**	**decrease**	**remain the same**
g.	Hydrogen is added	**increase**	**decrease**	**remain the same**

8. Indicate how each of the following changes affects the amount of each gas in the system below, for which $\Delta H_{reaction}$ = +9.9 kcal. **$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$**

a) addition of CO_2	___		___	___
b) addition of H_2O	___	___		___
c) increase in temperature	___	___	___	___
d) decrease in the volume of the container	___	___	___	___



Equilibrium Expressions

For the following three reactions,

a) write the K_{eq} expression in terms of concentration, K_c.

b) given the equilibrium concentrations, state whether each equilibrium is product-favored, reactant-favored, or fairly even ([products] ≈ [reactants]).

c) calculate the value of K_c.

1. $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$
   At equilibrium: $[N_2] = 1.50$ M
   $[H_2] = 2.00$ M
   $[NH_3] = 0.010$M

2. $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$
   At equilibrium: $[HF] = 0.55$ M
   $[H^+] = 0.0010$ M
   $[F^-] = 0.0010$ M

3. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$
   At equilibrium: $[Fe^{3+}] = 0.55$ M
   $[SCN^-] = 0.0010$ M
   $[FeSCN^{2+}] = 0.0010$M

Summarize: Fill in the blanks with product-favored, reactant-favored, or approximately equal.

K_c	state of equilibrium
$K_c >> 1$	
$K_c << 1$	
$K_c \approx 1$	

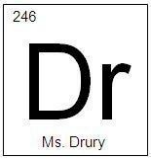
Important Note:
Since the concentrations of solids and liquids are constant, they are **not** incorporated into the equilibrium constant, K_{eq}. That means, just leave them out of the K_c or K_p expression. Only include (g) and (aq)!

5. Write equilibrium expressions for each of the following reactions:
   a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

   b) $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$

   c) $5CO(g) + I_2O_5(s) \rightleftharpoons I_2(g) + 5CO_2(g)$

   d) $Ca(HCO_3)_2(aq) \rightleftharpoons CaCO_3(s) + H_2O(l) + CO_2(g)$



6. Rate the reactions in order of their increasing tendency to proceed toward completion:
   (a) $4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$ $K_p = 1 \times 10^{228}$ atm
   (b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_p = 5 \times 10^{-31}$
   (c) $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$ $K_p = 1 \times 10^{-13}$
   (d) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ $K_p = 4.7 \times 10^{-4}$ atm

7. a. Write the K_c expression for $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$

   At equilibrium: $[SO_2] = 1.50$ M $[O_2] = 1.25$ M $[SO_3] = 3.50$ M

   b. Calculate the value of K_c:

   c. If we **reverse** the equation, it is: $2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$
   Write the K_c expression for this equation and calculate the new value of K_c:

   d. How does the expression and the value of K_c in 7c compare with those in 7b?

   e. If we now **multiply all of the coefficients by ½:** $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}\ O_2(g)$
   Write the K_c expression for this equation and calculate the new value of K_c:

   f. How does the expression and the value of K_c in 7e compare with those in 7b?

   g. What would happen to the K_c expression and its value if we **doubled** the coefficients?

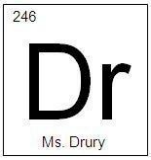
8. Summarize:

Equation	K_c expression & Value
doubled	
reversed	
halved	
combined reactions	

9. Consider an equilibrium that occurs in two steps:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq)$$
$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq)$$

   (a) Write the overall reaction.
   (b) How do the K_c's for the two steps (K_{c1} & K_{c2}) relate to the K_c of the overall reaction (K_c)?



Mass Action Expression Practice

1. Consider the following equilibrium, for which K=0.112 at 700C,

   $SO_2(g) + ½\ O_2(g) \leftrightarrow SO_3(g)$

   What is the value of K for the following reactions:

   a. $SO_3(g) \leftrightarrow SO_2(g) + ½\ O_2(g)$

   b. $2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$

   c. $2SO_3(g) \leftrightarrow 2SO_2(g) + O_2(g)$

2. Consider the following equilibrium, for which $K=1.1x10^{-2}$ at 25C,

   $HClO_2(aq) \leftrightarrow H^+ + ClO_2^-$

   What is the value of K for the following reactions:

   a. $2HClO_2(aq) \leftrightarrow 2H^+ + 2ClO_2^-$

   b. $½\ HClO_2(aq) \leftrightarrow ½\ H^+ + ½\ ClO_2^-$

   c. $3H^+ + 3ClO_2^- \leftrightarrow 3HClO_2(aq)$

3. Consider the following equilibria at STP,

   $HF(aq) \leftrightarrow H^+ + F^-$ $\quad K_1 = 2.0x10^{-3}$

   $H_2C_2O_4(aq) \leftrightarrow 2H^+ + C_2O_4^{-2}$ $\quad K_2 = 1.0x10^{-4}$

   What is the value of K for the following reaction:

   $2HF(aq) + C_2O_4^{-2} \leftrightarrow 2F^- + H_2C_2O_4(aq)$

4. Consider the following equilibria at STP,

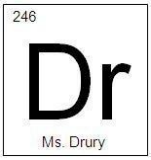
   $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$ $\quad K_1 = 2.5x10^{-8}$

   $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ $\quad K_2 = 4.1x10^{2}$

   What is the value of K for the following reaction:

   $2NH_3(g) + 3I_2(g) \leftrightarrow 6HI(g) + N_2(g)$

5. In each question above, identify the reaction that most drives towards completion.



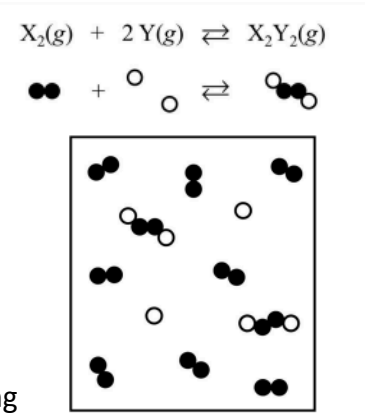
Equilibrium Practice

1. The reaction $PCl_{3(g)} + Cl_{2(g)} \leftrightarrow PCl_{5(g)}$ comes to equilibrium at 498K and the concentrations are 10.0M, 9.0M and 12.0M respectively. Calculate the equilibrium constant.

2. For the Haber process, an equilibrium mixture at 600K contained 0.31M N_2, 0.50M H_2, and 0.14M NH_3. Calculate Kc. $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$

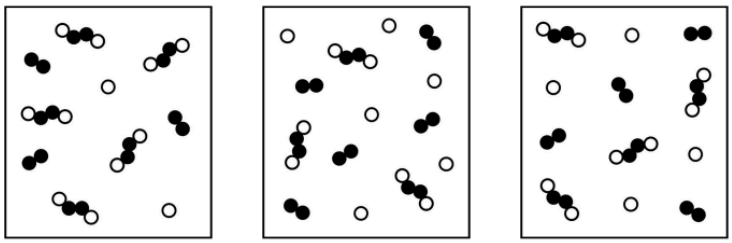
3. For the gaseous reaction: $2NO + Cl_2 \leftrightarrow 2NOCl$, the pressures at equilibrium are 1.2 atm, 0.30 atm, and 0.05 atm respectively. Calculate Kp at 100K.

4. The equilibrium constant for the reaction $CO + H_2O(l) \leftrightarrow CO_2 + H_2$ is K=4.0 at a given T. At equilibrium, the mixture contains 0.80mol CO, 0.35mol water and 2.2mol CO_2. How many moles of H_2 are present in 1.00L?



5. Use the key and images provided:
   a. Write the Kc for the reaction shown.
   b. The diagram shows a reaction mixture after equilibrium is achieved at 500K. Assume each particle represents one mole of the substance and the reaction vessel is 1.00L. Calculate the value of the Kc.

   c. The three diagrams below represent the mixture at various times during the reaction. calculate the Q (similar to K but may not be equilibrium yet) of each diagram and determine if the reaction is at equilibrium.



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Equilibrium Quotient

1. What is the equilibrium quotient of a mixture which contains 0.41atm SO_2, 0.16atm O_2, and 0.57atm SO_3? Which way will the reaction $2SO_2 + O_2 \leftrightarrow 2SO_3$ shift to reach an equilibrium where K=3.40?

2. The Kc for the reaction: $2NO \leftrightarrow N_2 + O_2$, all species in the gas phase, is 0.0024. In a 1L flask, 0.024mol NO, 2.0mol N_2 and 2.6mol O_2 exist. Is the system at equilibrium? If not, how would the reaction shift?

3. Consider the equilibrium: $2\ SO_2(g) + O_2(g) \leftrightarrow 2\ SO_3(g)$ $K_c = 4.36\ \underline{M}^{-1}$
   a. Calculate the Q in which concentrations are $[SO_2]$=2.00M, $[O_2]$=1.50M and $[SO_3]$= 1.25M.

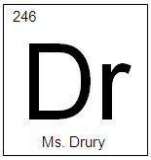
   b. Does this mixture shift toward the reactants or products to reach equilibrium?

4. $PbCl_{2\ (s)}$ ⍰⍰ $Pb^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$
   Experimentally, the amount of Pb^{2+} and Cl^- does not depend on the amount of $PbCl_2$. Why?

$$H_2(g) + I_2(g) \leftrightarrow 2\ HI(g)\ Kc = 51 \text{ at } 448°C$$

5. For each set of experimental conditions listed in the table below, use the data to calculate the value of the reaction quotient (Qc). Compare Kc with Qc and choose one of the following consequences.
   - The system is already at equilibrium.
   - The system should proceed toward the products (from left to right) until equilibrium is achieved.
   - The system should proceed toward the reactants (from right to left) until equilibrium is achieved

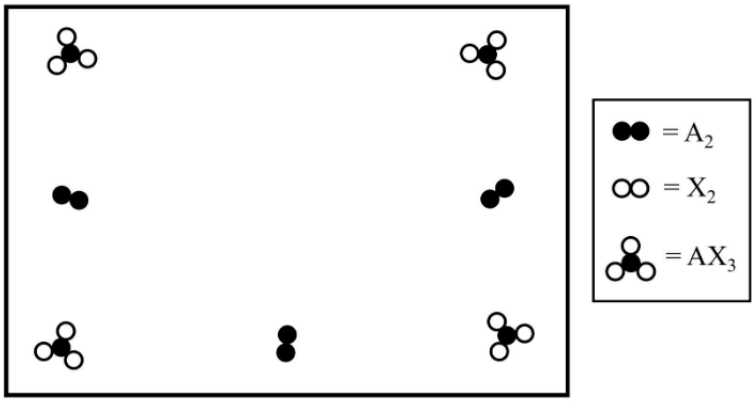
$[H_2]$	$[I_2]$	[HI]	Q	K vs Q	Consequence
0.35M	0.45M	3.0M			
4.6M	1.4M	4.2M			
0.90M	0.81M	6.1M			



$A_2(g) + 3\ X_2(g) \leftarrow\!\rightarrow 2\ AX_3(g)$ Kc = 0.667 at 300 K

6. Substance $A_2(g)$ reacts with substance $X_2(g)$ according to the equation shown above.
   a. Write the expression for the equilibrium constant (Kc) for the reaction.

   b. The particulate diagram shown below is incomplete. Draw in the correct number of molecules of X_2 so that the diagram shows a representative sample of the gas mixture at equilibrium at 300 K (Kc = 0.667). Each molecule in the particulate diagram represents one mole of that substance in a 1.00 L container.



   c. In a certain experiment, a reaction vessel contains a mixture of $A_2(g)$, $X_2(g)$, and $AX_3(g)$ at 300 K with the following concentrations.

   $[A_2] = 0.75$ M $[X_2] = 1.25$ M $[AX_3] = 1.50$ M

   Do you predict that the number of moles of $A_2(g)$ will decrease, increase, or remain the same as this system approaches equilibrium at 300 K? Justify your answer by comparing the value of the reaction quotient Q with the value of the equilibrium constant K.

Summary

Q vs. K	Ratio	Inequality Symbol Used	Consequence
Q is equal to K	$\frac{\text{products}}{\text{reactants}}$	K= Q	no shift
Q is less than K	$\frac{\text{products}}{\text{reactants}}$	K>Q	reactants convert to products until equilibrium is achieved
Q is more than K	$\frac{\text{products}}{\text{reactants}}$	K<Q	products convert to reactants until equilibrium is achieved

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Ice Box Questions

1) 1.0 mol Sulfur dioxide and 1.00 mol of oxygen are sealed in a 1.00 L rigid container at 1000K. When equilibrium is established, 0.925 mol of sulfur trioxide is formed. Calculate Keq for this reaction.

2) Suppose a tank initially contains H_2S at a pressure of 10.0 atm and at a temperature of 800 K. When the reaction has come to equilibrium, the partial pressure of S_2 vapor is 0.020 atm. Calculate K_p.

$$2\ H_2S(g) \leftrightarrow 2\ H_2(g) + S_2(g)$$

3) A sample of hydrogen fluoride is synthesized when 3.000 mol hydrogen and 3.000 mol fluorine are mixed in a 3.000-L flask. The value of K_c at the temperature of the reaction is 1.15×10^2. Calculate the equilibrium concentrations of all species

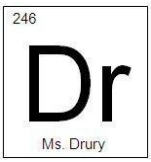
$$H_2(g) + F_2(g) \leftrightarrow 2HF(g)$$

4) A sample of $COCl_2$ is allowed to decompose. The value of K_c for the equilibrium is 2.2×10^{-10} at 100 °C. If the initial concentration of $COCl_2$ is 0.095M, what will be the equilibrium concentrations for each?

$$COCl_2\ (g) \leftrightarrow CO\ (g) + Cl_2\ (g)$$

5) You have 1.00 M CH_3COOH. Calculate the equilibrium concentrations of CH_3COOH, H^+, CH_3COO^-. $K_a=1.8\times10^{-5}$

$$CH_3COOH(aq) \leftrightarrow CH_3COO^-(aq) + H^+(aq)$$



6) If 0.160mol NO_2 and 0.40mol N_2O_4 are placed in a 20.0L container and the reaction $2NO_2 \leftrightarrow N_2O_4$ is allowed to come to equilibrium at 352.5K, at equilibrium $[NO_2] = 0.0150M$. What is the equilibrium concentration of N_2O_4? Calculate Kc for the reaction.

7) When heated, H_2S gas is decomposed: $2H_2S \leftrightarrow 2H_2 + S_2$. A 3.40g sample of H_2S is in a 1.25L container which is sealed and heated to 483K. At equilibrium 0.0372 mol S_2 are present.

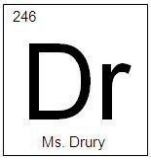
a. Write the expression for Kc.

b. Calculate the equilibrium concentration in mol/L at 483K for H_2 and H_2S.

c. Calculate the value of Kc at 483K.

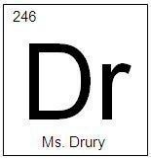
d. For the reaction $H_2 + ½\ S_2 \leftrightarrow H_2S$ at 483K, what is Kc?

e. Which reaction is most favorable? $2H_2S \leftrightarrow 2H_2 + S_2$ or $H_2 + ½\ S_2 \leftrightarrow H_2S$. Justify your answer.



Summary of Le Châtelier's Principle (Assume Constant Temperature Unless Specified)

Stress Imposed on the Equilibrium System	Q vs. K	How the Equilibrium System Responds to the Stress	Will K change?
A catalyst is added to speed up the reaction.	$Q = K$	No shift occurs. The system will reach equilibrium at a faster rate.	No.
Additional reactant is added (not including solids or pure liquids).	$Q < K$	System shifts toward the right (products).	No.
Additional product is added (not including solids or pure liquids).	$Q > K$	System shifts toward the left (reactants).	No.
Some of the reactant is removed (not including solids or pure liquids).	$Q > K$	System shifts toward the left (reactants).	No.
Some of the product is removed (not including solids or pure liquids).	$Q < K$	System shifts toward the right (products).	No.
Additional solid is added, or some of the solid is removed.	$Q = K$	No shift occurs. The concentrations and partial pressures of all species are unchanged.	No.
An aqueous system is diluted with water.	results may vary	The concentrations of all aqueous species decrease. System shifts toward the side of the equation that has a higher number of moles of aqueous particles.	No.
In a gaseous equilibrium system, the volume of the reaction vessel is decreased.	results may vary	The partial pressures of all gaseous species increase. System shifts toward the side of the equation that has a lower number of moles of gaseous particles.	No.
In a gaseous equilibrium system, the volume of the reaction vessel is increased.	results may vary	The partial pressures of all gaseous species decrease. System shifts toward the side of the equation that has a higher number of moles of gaseous particles.	No.
An inert gas (such as He) is added to a gaseous equilibrium system.	$Q = K$	No shift occurs. The partial pressures of all reacting gaseous species are unchanged.	No.
The temperature of the system is increased.	**N/A**	**An endothermic reaction shifts toward the right (products).**	***K* increases.**
	N/A	**An exothermic reaction shifts toward the left (reactants).**	***K* decreases.**
The temperature of the system is decreased.	**N/A**	**An endothermic reaction shifts toward the left (reactants).**	***K* decreases.**
	N/A	**An exothermic reaction shifts toward the right (products).**	***K* increases.**



LeChatelier Practice

$2\ SO_3(g) \leftrightarrow 2\ SO_2(g) + O_2(g)$

1. Sulfur trioxide gas decomposes at high temperature to produce sulfur dioxide gas and oxygen gas according to the equation above. A sample of $SO_3(g)$ was added to a previously evacuated rigid reaction vessel. The reaction represented by the equation above was allowed to proceed until it reached equilibrium at 1000 K. The partial pressures were determined to be the following.

   $SO_3 = 3.43$ atm $SO_2 = 2.00$ atm $O_2 = 1.00$ atm

   a. Write the equilibrium constant expression (Kp) for the reaction.

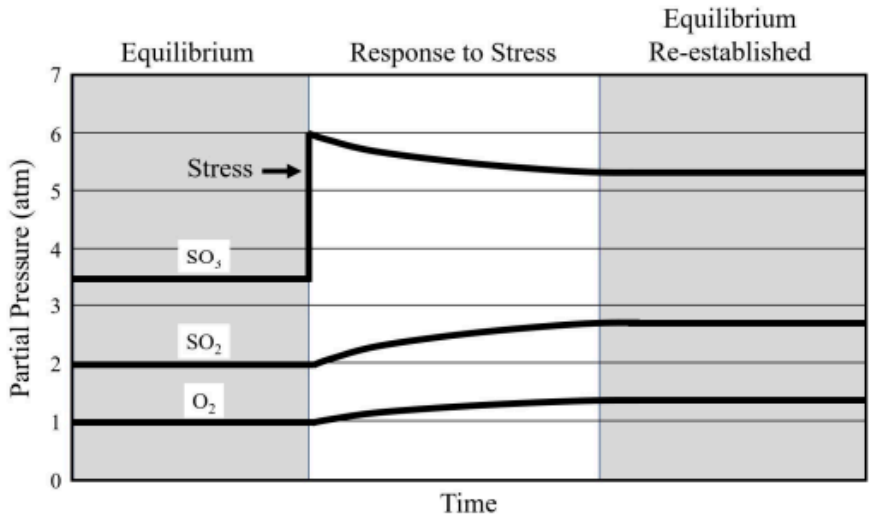
   b. Calculate the value of Kp at 1000 K.

   c. Additional $SO_3(g)$ is added to the reaction vessel at 1000 K until the partial pressure of $SO_3(g)$ is 6.00 atm. Calculate the value of Qp at the moment that additional $SO_3(g)$ is added.

   d. The addition of $SO_3(g)$ to the reaction vessel caused a disturbance in the equilibrium system that had already been established. As the system re-establishes equilibrium at 1000 K, which of the following statements should be true?

      The partial pressure of $SO_2(g)$ will decrease until Qp = Kp.
      The partial pressure of $SO_2(g)$ will increase until Qp = Kp.

   e. When equilibrium is reestablished at 1000 K, the partial pressure of $O_2(g)$ in the reaction vessel is 1.3 atm. Calculate the partial pressures of $SO_3(g)$ and $SO_2(g)$ when equilibrium is reestablished and the K value to compare to the initial K value.



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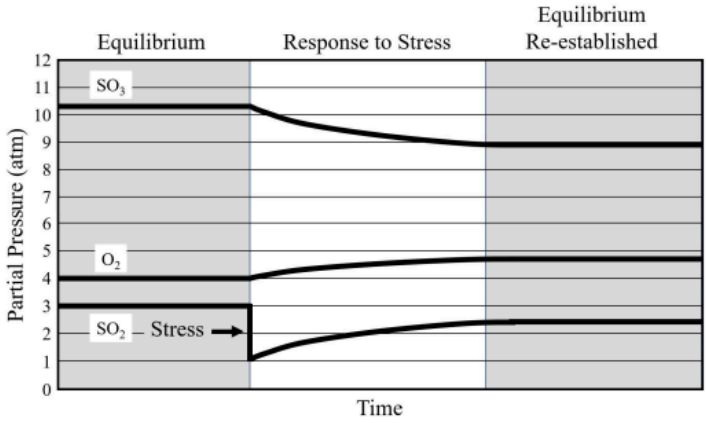
$2\ SO_3(g) \leftrightarrow 2\ SO_2(g) + O_2(g)$ Kp = 0.340 at 1000 K

2. A reaction vessel contains a mixture of $SO_3(g)$, $SO_2(g)$, and $O_2(g)$ at 1000 K with the following values of partial pressure. SO_3 = 10.29 atm SO_2 = 3.00 atm O_2 = 4.00 atm
   a. Is this system at equilibrium? Justify your answer with a calculation.

   b. Some of the $SO_2(g)$ is removed from the reaction vessel at 1000 K, reducing the partial pressure of $SO_2(g)$ to a value of 1.00 atm. Calculate the value of Qp at the moment that the $SO_2(g)$ is removed.

   c. The removal of $SO_2(g)$ from the reaction vessel caused a disturbance in the equilibrium system that had already been established. As the system re-establishes equilibrium at 1000 K, which of the following statements should be true?
   The partial pressure of $O_2(g)$ will decrease until Qp = Kp.
   The partial pressure of $O_2(g)$ will increase until Qp = Kp.

   d. When equilibrium is reestablished at 1000 K, the partial pressure of $O_2(g)$ in the reaction vessel is 4.70 atm. Calculate the partial pressures of $SO_3(g)$ and $SO_2(g)$ when equilibrium is reestablished and the K value to compare to the initial K value.



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AP Practice LeChatelier

1. For the system $2\ SO_2(g) + O_2(g) \leftrightarrow 2\ SO_3(g)$, ΔH is negative for the production of SO_3. Assume that one has an equilibrium mixture of these substances. Predict the effect of each of the following changes on the value of the equilibrium constant and on the number of moles of SO_3 present in the mixture at equilibrium. Briefly account for each of your predictions. (Assume that in each case all other factors remain constant.)

(a) Decreasing the volume of the system.

(b) Adding oxygen to the equilibrium mixture.

(c) Raising the temperature of the system.

$NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$ ΔH = +42.1 kilocalories

2. Suppose the substances in the reaction above are at equilibrium at 600K in volume V and at pressure P. State whether the partial pressure of $NH_3(g)$ will have increased, decreased, or remained the same when equilibrium is reestablished after each of the following disturbances of the original system. Some solid NH_4Cl remains in the flask at all times. Justify each answer with a one-or-two sentence explanation.

(a) A small quantity of NH_4Cl is added.

(b) The temperature of the system is increased.

(c) The volume of the system is increased.

(d) A quantity of gaseous HCl is added.

(e) A quantity of gaseous NH_3 is added.

$NH_4HS(s) \leftrightarrow NH_3(g) + H_2S(g)$ ΔH^o = +93 kilojoules

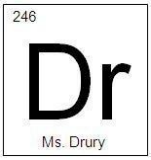
3. The equilibrium above is established by placing solid NH_4HS in an evacuated container at 25ºC. At equilibrium, some solid NH_4HS remains in the container. Predict and explain each of the following.

(a) The effect on the equilibrium partial pressure of NH_3 gas when additional solid NH_4HS is introduced

(b) The effect on the equilibrium partial pressure of NH_3 gas when additional solid H_2S is introduced

(c) The effect on the mass of solid NH_4HS present when the volume of the container is decreased

(d) The effect on the mass of solid NH_4HS present when the temperature is increased.



AP Equilibrium

1. Sulfuryl chloride, SO_2Cl_2, is a highly reactive gaseous compound. When heated, it decomposes as follows: $SO_2Cl_{2(g)} \leftarrow\rightarrow SO_2(g) + Cl_2(g)$. This decomposition is endothermic. A sample of 3.509 grams of SO_2Cl_2 is placed in an evacuated 1.00 liter bulb and the temperature is raised to 375K.

   (a) What would be the pressure in atmospheres in the bulb if no dissociation of the $SO_2Cl_{2(g)}$ occurred?

   (b) When the system has come to equilibrium at 375K, the total pressure in the bulb is found to be 1.43 atmospheres. Calculate the partial pressures of SO_2, Cl_2, and SO_2Cl_2 at equilibrium at 375K.

   (c) Give the expression for the equilibrium constant (either K_p or K_c) for the decomposition of $SO_2Cl_{2(g)}$ at 375K. Calculate the value of the equilibrium constant you have given, and specify its units.

   (d) If the temperature were raised to 500K, what effect would this have on the equilibrium constant?

2. At elevated temperatures, $SbCl_5$ gas decomposes into $SbCl_3$ gas and Cl_2 gas as shown by the following equation: $SbCl_5(g) \leftrightarrow SbCl_3(g) + Cl_2(g)$

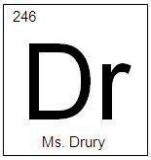
   (a) An 89.7 gram sample of $SbCl_5$ (molecular weight 299.0) is placed in an evacuated 15.0 liter container at 182ºC.

      i) What is the concentration in M of $SbCl_5$ in the container before any decomposition occurs?

      ii) What is the pressure in atmospheres of $SbCl_5$ in the container before any decomposition occurs?

   (b) If the $SbCl_5$ is 29.2 percent decomposed when equilibrium is established at 182ºC, calculate the value for either equilibrium constant K_p or K_c, for this decomposition reaction. Indicate whether you are calculating K_p or K_c.

   (c) In order to produce some $SbCl_5$, a 1.00 mole sample of $SbCl_3$ is first placed in an empty 2.00 liter container maintained at a temperature different from 182ºC. At this temperature, K_c, equals 0.117. How many moles of Cl_2 must be added to this container to reduce the number of moles of $SbCl_3$ to 0.700 mole at equilibrium?



$2\ NaHCO_3(s) \leftrightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$

3. Solid sodium hydrogen carbonate, $NaHCO_3$, decomposes on heating according to the equation above.

(a) A sample of 100. grams of solid $NaHCO_3$ was placed in a previously evacuated rigid 5.00-liter container and heated to 160ºC. Some of the original solid remained and the total pressure in the container was 7.76 atmospheres when equilibrium was reached. Calculate the number of moles of $H_2O(g)$ present at equilibrium.

(b) How many grams of the original solid remain in the container under the conditions described in (a)?

(c) Write the equilibrium expression for the equilibrium constant, K_P, and calculate its value for the reaction under the conditions in (a).

(d) If 110. grams of solid $NaHCO_3$ had been placed in the 5.00-liter container and heated to 160ºC, what would the total pressure have been at equilibrium? Explain

$CO_2(g) + H_2(g) \leftrightarrow H_2O(g) + CO(g)$

4. When $H_2(g)$ is mixed with $CO_2(g)$ at 2,000 K, equilibrium is achieved according to the equation above. In one experiment, the following equilibrium concentrations were measured.

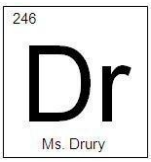
$[H_2] = 0.20$ mol/L $\quad [CO_2] = 0.30$ mol/L $\quad [H_2O] = [CO] = 0.55$ mol/L

(a) What is the mole fraction of $CO(g)$ in the equilibrium mixture?

(b) Using the equilibrium concentrations given above, calculate the value of K_c, the equilibrium constant for the reaction.

(c) When the system is cooled from 2,000 K to a lower temperature, 30.0 percent of the $CO(g)$ is converted back to $CO_2(g)$. Calculate the value of K_c at this lower temperature.

(d) In a different experiment, 0.50 mole of $H_2(g)$ is mixed with 0.50 mole of $CO_2(g)$ in a 3.0-liter reaction vessel at 2,000 K. Calculate the equilibrium concentration, in moles per liter, of $CO(g)$ at this temperature.



AP Chemistry: Equilibrium Multiple Choice Part 1 show work or explanation.

1. In which of the following systems would the number of moles of the substances present at equilibrium NOT be shifted by a change in the volume of the system at constant temperature?

(A) $CO_{(g)} + NO_{(g)} \rightleftarrows CO_{2(g)} + 1/2\ N_{2(g)}$ (B) $N_{2(g)} + 3\ H_{2(g)} \rightleftarrows 2\ NH_{3(g)}$

(C) $N_{2(g)} + 2\ O_{2(g)} \rightleftarrows 2\ NO_{2(g)}$ (D) $N_2O_{4(g)} \rightleftarrows 2\ NO_{2(g)}$

(E) $NO_{(g)} + O_{3(g)} \rightleftarrows NO_{2(g)} + O_{2(g)}$

2. $PCl_{3(g)} + Cl_{2(g)} \rightleftarrows PCl_{5(g)}$ + energy

Some PCl_3 and Cl_2 are mixed in a container at 200 °C and the system reaches equilibrium according to the equation above. Which of the following causes an increase in the number of moles of PCl_5 present at equilibrium?

I. Decreasing the volume of the container

II. Raising the temperature

III. Adding a mole of He gas at constant volume

(A) I only (B) II only (C) I and III only (D) II and III only (E) I, II, and III

3. $4\ HCl_{(g)} + O_{2(g)} \rightleftarrows 2\ Cl_{2(g)} + 2\ H_2O_{(g)}$

Equal numbers of moles of HCl and O_2 in a closed system are allowed to reach equilibrium as represented by the equation above. Which of the following must be true at equilibrium?

I. [HCl] must be less than $[Cl_2]$.

II. $[O_2]$ must be greater than [HCl].

III. $[Cl_2]$ must equal $[H_2O]$.

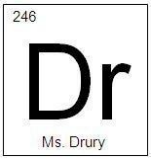
(A) I only (B) II only (C) I and III only (D) II and III only (E) I, II, and III

4. $2\ SO_{2(g)} + O_{2(g)} \rightleftarrows 2\ SO_{3(g)}$

When 0.40 moles of SO_2 and 0.60 moles of O_2 are placed in an evacuated 1.00-liter flask, the reaction represented above occurs. After the reactants and the product reach equilibrium and the initial temperature is restored, the flask is found to contain 0.30 moles of SO_3. Based on these results, the expression for the equilibrium constant, K_c, of the reaction is…

(A) $(0.30)^2 / [(0.45)(0.10)^2]$ (B) $(0.30)^2 / [(0.60)(0.40)^2]$ (C) $(2 \times 0.30) / [(0.45)(2 \times 0.10)]$

(D) $(0.30) / [(0.45)(0.10)]$ (E) $(0.30) / [(0.60)(0.40)]$



5. $2NO_{(g)} + O_{2(g)} \rightleftarrows 2\ NO_{2(g)}$; $\Delta H < 0$

Which of the following changes alone would cause a decrease in the value of K_{eq} for the reaction represented above?

(A) Decreasing the temperature (B) Increasing the temperature

(C) Decreasing the volume of the reaction vessel (D) Increasing the volume of the reaction vessel

(E) Adding a catalyst

$$2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g)$$

6. After the equilibrium represented above is established, some pure $O_2(g)$ is injected into the reaction vessel at constant temperature. After equilibrium is reestablished, which of the following has a lower value compared to its value at the original equilibrium?

(A) K_{eq} for the reaction

(B) The total pressure in the reaction vessel

(C) The amount of $SO_3(g)$ in the reaction vessel

(D) The amount of $O_2(g)$ in the reaction vessel

(E) The amount of $SO_2(g)$ in the reaction vessel

7. $H_{2(g)} + Br_{2(g)} \rightleftarrows 2HBr_{(g)}$

At a certain temperature, the value of the equilibrium constant, K, for the reaction represented above is 2.0×10^5. What is the value of K for the reverse reaction at the same temperature?

(A) -2.0×10^{-5} (B) 5.0×10^{-6} (C) 2.0×10^{-5} (D) 5.0×10^{-5} (E) 5.0×10^{-4}

8. $CuO_{(s)} + H_{2(g)} \rightleftarrows Cu_{(s)} + H_2O_{(g)}$; $\Delta H = -2.0$ kilojoules

When the substances in the equation above are at equilibrium at pressure P and temperature T, the equilibrium can be shifted to favor the products by…

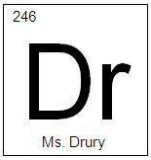
(A) increasing the pressure by means of a moving piston at constant T.

(B) increasing the pressure by adding an inert gas such as nitrogen.

(C) decreasing the temperature.

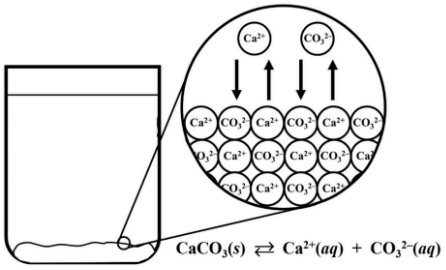
(D) allowing some gases to escape at constant P and T.

(E) adding a catalyst.



Ksp and (Molar) Solubility

Ksp is known as the solubility product constant. It is constructed and calculated the same as Kc but specifically for "insoluble" salts. The concentrations, measured in M, used to calculate the Ksp are also known as "Molar Solubility" whereas "Solubility" is measured in g/L.



1. Write the Ksp for the reaction above.

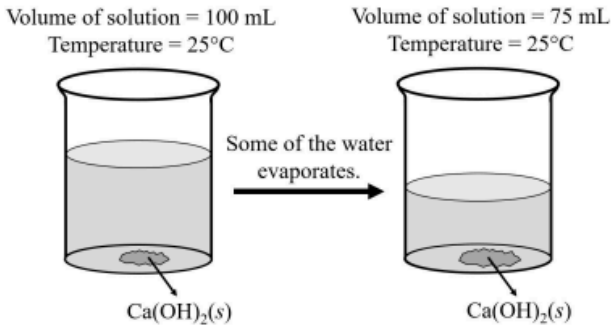
2. Explain the equilibrium system represented in terms of concentration of reactants and products and the rates of the forward and reverse reactions.

3. If the solubility of $CaCO_3$ is 0.015g/L at 298K, calculate the Molar Solubility.

4. Calculate the Ksp of $CaCO_3$.

5. Compare the solubility of $CaCO_3$ to $Ca(OH)_2$ (Ksp=$5.0x10^{-6}$).

A beaker contains 100 mL of a saturated solution of $Ca(OH)_2(aq)$ at 25°C with a small amount of undissolved $Ca(OH)_2(s)$ present at the bottom of the beaker. The beaker is warmed gently, and some of the water evaporates so that the volume of the solution decreases to 75 mL. The beaker is allowed to sit at room temperature until the temperature returns to 25°C.



6. Is the value of $[Ca^{2+}]$ in the 75 mL sample of solution (on the right in the diagram above) less than, greater than, or equal to the value of $[Ca^{2+}]$ in the 100 mL sample of solution (on the left in the diagram above)? Justify your answer.

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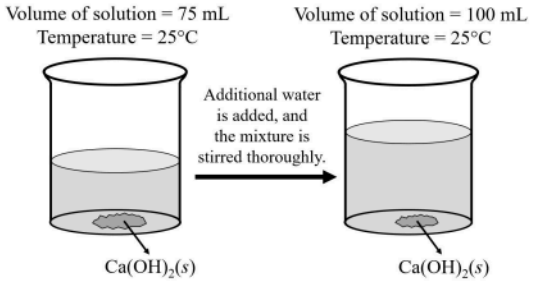
A beaker contains 75 mL of a saturated solution of $Ca(OH)_2(aq)$ at 25°C with a small amount of undissolved $Ca(OH)_2(s)$ at the bottom. Water is added to the beaker, and the mixture is stirred thoroughly. The volume of the solution increases to 100 mL. A small amount of undissolved $Ca(OH)_2(s)$ is present at the bottom of the beaker.



7. Is the value of $[Ca^{2+}]$ in the 100 mL sample of solution (on the right in the diagram above) less than, greater than, or equal to the value of $[Ca^{2+}]$ in the 75 mL sample of solution (on the left in the diagram above)? Justify your answer.

Additional Examples: Write the Equilibrium expression for each question and then solve:

1. If the molar solubility of CaF_2 is 1.24×10^{-3} M, calculate the Ksp.

2. The Ksp for LaF_3 is 2×10^{-19}.
   a. What is the molar solubility of LaF_3 in M?

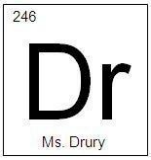
   b. What is the solubility in g/L?

3. The Ksp for $Cr(OH)_3$ is 1.6×10^{-30}. Calculate the molar solubility of $Cr(OH)_3$ and the ion concentrations.

4. The Ksp for Calcium Phosphate is 2.0×10^{-29}. Calculate the molar solubility and ion concentrations.

5. A 1.00L solution is saturated at 25 C with Lead (II) Iodide containing 0.54g of PbI_2. Calculate the Ksp.

6. Soluble barium compounds are poisonous; however, barium sulfate is routinely ingested as a suspended solid to improve the contrast in x-ray images. Calculate the concentration of dissolved barium per liter of water in equilibrium with solid barium sulfate. The Ksp is 1.1×10^{-10}.

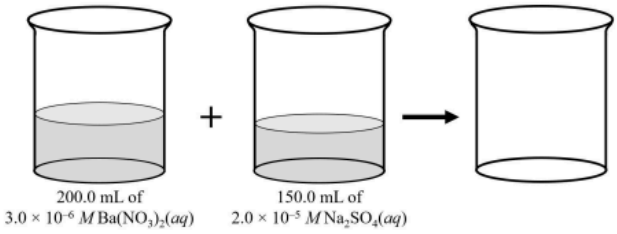


Compound	CaF_2	SrF_2	BaF_2
Ksp at 25C	3.9×10^{-11}	4.3×10^{-9}	1.8×10^{-7}

7. Saturated solutions of each compound listed in the table above were prepared at 25°C. Use the information in the table above to answer the following questions.
   a. Which compound has the smallest value for molar solubility in water at 25°C? Justify your answer.

   b. Calculate the value of $[F^-]$ (in mol/L) in a saturated solution of the compound that you selected in part (a).

8. A student adds an excess amount of $Na_2SO_4(aq)$ to a solution of $Ba(NO_3)_2(aq)$, resulting in the formation of a precipitate.
   a. Write the net ionic equation for the reaction that occurred in this experiment.



   b. In a separate experiment, a 200.0 mL sample of 3.0×10^{-6} M $Ba(NO_3)_2(aq)$ is added to a 150.0 mL sample of 2.0×10^{-5} M $Na_2SO_4(aq)$. The mixture is stirred to ensure that it is thoroughly mixed. Calculate the number of moles of $Ba^{2+}(aq)$ present in 200.0 mL of 3.0×10^{-6} M $Ba(NO_3)_2(aq)$.

   c. Calculate the number of moles of $SO_4^{2-}(aq)$ present in 150.0 mL of 2.0×10^{-5} M $Na_2SO_4(aq)$.

   d. The volume of the mixture formed in this experiment is 350.0 mL. Calculate the initial concentrations of $Ba^{2+}(aq)$ and $SO_4^{2-}(aq)$ in the mixture at the moment that the two solutions are combined, but before any chemical reaction occurs.

   e. Use your answers to part (d) to calculate the value of the reaction quotient (Qsp) for $BaSO_4$.

   f. The value of Ksp for $BaSO_4$ is 1.1×10^{-10}. Will a precipitate of $BaSO_4(s)$ be formed in this experiment? Justify your answer by comparing Qsp with Ksp.

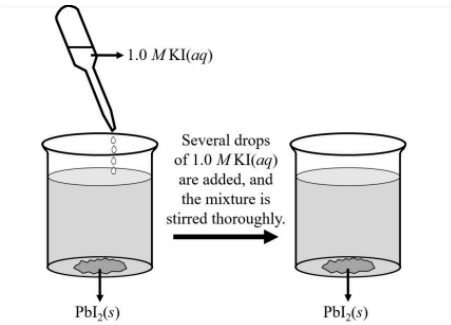
9. A solution of NaF is added dropwise to a solution that is 0.0144M Ba^{2+}. At what concentration will BaF_2 precipitate? Ignore changes in volume. Ksp = $1.7x10^{-7}$.

10. A solution of Barium chromate is prepared by dissolving $6.3x10^{-3}$ g of this yellow solid in 1.00L of hot water. Will solid barium chromate precipitate upon cooling according to the Ksp? If so, how much will precipitate? Ksp=$2.1x10^{-10}$.

11. Summarize:

	saturated, unsaturated, supersaturated?	precipitate, dissolve more, equilibrium?
Q=Ksp		
Q>Ksp		
Q<Ksp		

12. A saturated solution is prepared in a beaker by adding excess $PbI_2(s)$ to distilled water. A small amount of undissolved $PbI_2(s)$ remained at the bottom of the beaker. Then several drops of 1.0 M KI(aq) are added to the saturated solution in the beaker. The contents of the beaker are stirred thoroughly. Assume that the change in volume is negligible.



   a. Do you predict that the mass of $PbI_2(s)$ present in the beaker should decrease, increase, or remain the same as a result of the addition of KI(aq)? Justify your answer in terms of the common-ion effect and Le Châtelier's principle.

   b. Do you predict that the concentration of $Pb^{2+}(aq)$ in the solution should decrease, increase, or remain the same as a result of the addition of KI(aq)? Justify your answer in terms of the common-ion effect and Le Châtelier's principle.

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Ksp and pH

The following information describes relationships between $[H^+]$, $[OH^-]$, and pH. Calculations involving pH will be featured in Unit 8 (Acids and Bases). When an acid is added to water, $[H^+]$ increases, and the pH decreases. When a base is added to water, $[OH^-]$ increases, and the pH increases.

$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ OH^-(aq)$ $\quad K_{sp} = 5.6 \times 10^{-12}$

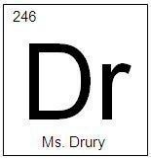
1. The dissolution of $Mg(OH)_2(s)$ in water is represented by the equation above. A saturated solution is prepared in a beaker by adding excess $Mg(OH)_2(s)$ to distilled water. A small amount of undissolved $Mg(OH)_2(s)$ remained at the bottom of the beaker.
    a. Several drops of concentrated NaOH(aq) are added to a saturated solution of $Mg(OH)_2(aq)$, and the mixture is stirred thoroughly. Assume that the change in volume is negligible. The addition of NaOH(aq) causes the concentration of $Mg^{2+}(aq)$ in the solution to decrease. Explain this result in terms of Le Châtelier's principle.

    b. Several drops of concentrated $HNO_3(aq)$ are added to a saturated solution of $Mg(OH)_2(aq)$, and the mixture is stirred thoroughly. Assume that the change in volume is negligible. The addition of $HNO_3(aq)$ causes the mass of $Mg(OH)_2(s)$ present in the mixture to decrease. Explain this result in terms of Le Châtelier's principle.

$Ni(OH)_2(s) \rightleftarrows Ni^{2+}(aq) + 2\ OH^-(aq)$ $\quad K_{sp} = 5.5 \times 10^{-16}$

2. The dissolution of $Ni(OH)_2(s)$ in water is represented by the equation above.
    a. How will a change in pH decrease the solubility of $Ni(OH)_2$ in an aqueous solution? Justify your answer in terms of Le Châtelier's principle.

    b. How will a change in pH increase the solubility of $Ni(OH)_2$ in an aqueous solution? Justify your answer in terms of Le Châtelier's principle.



AP Solubility FRQ

1. At 25ºC the solubility product constant, K_{sp}, for strontium sulfate, $SrSO_4$, is 7.6×10^{-7}. The solubility product constant for strontium fluoride, SrF_2, is 7.9×10^{-10}.

(a) What is the molar solubility of $SrSO_4$ in pure water at 25ºC?

(b) What is the molar solubility of SrF_2 in pure water at 25ºC?

(c) An aqueous solution of $Sr(NO_3)_2$ is added slowly to 1.0 litre of a well-stirred solution containing 0.020 mole F^- and 0.10 mole SO_4^{2-} at 25ºC. (You may assume that the added $Sr(NO_3)_2$ solution does not materially affect the total volume of the system.)

i. Which salt precipitates first?

ii. What is the concentration of strontium ion, Sr^{2+}, in the solution when the first precipitate begins to form?

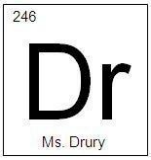
2.

$H_2S + H_2O \leftrightarrow H_3O^+ + HS^-$	$K_1 =$	1.0×10^{-7}
$HS^- + H_2O \leftrightarrow H_3O^+ + S^{2-}$	$K_2 =$	1.3×10^{-13}
$H_2S + 2\ H_2O \leftrightarrow 2\ H_3O^+ + S^{2-}$	$K =$	1.3×10^{-20}
$Ag_2S(s) \leftrightarrow 2\ Ag^+ + S^{2-}$	$K_{sp}=$	5.5×10^{-51}

(a) Calculate the concentration of H_3O^+ of a solution which is 0.10 molar in H_2S.

(b) Calculate the concentration of the sulfide ion, S^{2-}, in a solution that is 0.10 molar in H_2S and 0.40 molar in H_3O^+.

(c) Calculate the maximum concentration of silver ion, Ag^+, that can exist in a solution that is 1.5×10^{-17} molar in sulfide ion, S^{2-}.



AP Chemistry: Equilibrium Multiple Choice Part 2 Show work.

1. $HgO_{(s)} + 4\ I^- + H_2O \rightleftarrows HgI_4^{2-} + 2\ OH^-$; $\Delta H < 0$

Consider the equilibrium above. Which of the following changes will increase the concentration of HgI_4^{2-}?

(A) Increasing the concentration of OH^- (B) Adding 6 M HNO_3

(C) Increasing the mass of HgO present (D) Increasing the temperature (E) Adding a catalyst

2. The solubility of CuI is 2×10^{-6} molar. What is the solubility product constant, K_{sp}, for CuI?

(A) 1.4×10^{-3} (B) 2×10^{-6} (C) 4×10^{-12} (D) 2×10^{-12} (E) 8×10^{-18}

3. $HCO_3^-(aq) + OH^-(aq) \rightleftarrows H_2O(l) + CO_3^{2-}(aq)$ $\Delta H° = -41.4kJ$

When the reaction represented by the equation above is at equilibrium at 1 atm and 25°C, the ratio $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ can be increased by doing which of the following?

(A) Decreasing the temperature (B) Adding acid

(C) Adding a catalyst (D) Diluting the solution with distilled water

(E) Bubbling neon gas through the solution

4. In a saturated solution of $Zn(OH)_2$ at 25°C , the value of $[OH^-]$ is 2.0×10^{-6}M. What is the value of the solubility-product constant, K_{sp}, for $Zn(OH)_2$ at 25°C ?

(A) 4.0×10^{-18} (B) 8.0×10^{-18} (C) 1.6×10^{-17} (D) 4.0×10^{-12} (E) 2.0×10^{-6}

