7.6 Properties of the Equilibrium Constant

Essential knowledge statements from the AP Chemistry CED:

- When a reaction is reversed, *K* for the reversed equation is equal to the reciprocal of the original *K*.
- When the stoichiometric coefficients of a reaction are multiplied by a factor *N*, *K* for the modified equation is equal to the original *K* raised to the power *N*.
- When reactions are added together, the *K* of the resulting overall reaction is the product of the individual *K* values for the reactions that were added together.
- Since the expressions for *K* and *Q* have identical mathematical forms, all valid algebraic manipulations of *K* also apply to *Q*.

$$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g) \qquad K_c = 51 \text{ at } 448°C$$

1. Fill in the missing information in the table below. Write the modification that was made to the equation shown above, and calculate the new value of K_c.

Equation	Modification made to the original equation shown above	K_c
$2\,HI(g) \rightleftarrows H_2(g) + I_2(g)$		
$\frac{1}{2}\,H_2(g) + \frac{1}{2}\,I_2(g) \rightleftarrows HI(g)$		
$2\,H_2(g) + 2\,I_2(g) \rightleftarrows 4\,HI(g)$		
$HI(g) \rightleftarrows \frac{1}{2}\,H_2(g) + \frac{1}{2}\,I_2(g)$		

	Equation	K_c
#1	$FeF_2(s) \rightleftarrows Fe^{2+}(aq) + 2\,F^-(aq)$	2.4×10^{-6}
#2	$HF(aq) \rightleftarrows H^+(aq) + F^-(aq)$	6.8×10^{-4}
#3	$FeF_2(s) + 2\,H^+(aq) \rightleftarrows Fe^{2+}(aq) + 2\,HF(aq)$	?

2. Three chemical equations are listed in the table above. In the space below, show how equations #1 and #2 can be combined in a certain way in order to produce equation #3. Calculate the equilibrium constant (K_c) for equation #3.

7.7 Calculating Equilibrium Concentrations

Essential knowledge statement from the AP Chemistry CED:

- The concentrations or partial pressures of species at equilibrium can be predicted given the balanced reaction, initial concentrations, and the appropriate *K*.

$$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g) \qquad K_c = 51 \text{ at } 448°C$$

Questions #3 – #5 are related to the system represented by the equation shown above.

3. Samples of $H_2(g)$ and $I_2(g)$ were added to a previously evacuated reaction vessel. The initial values for the concentrations of $H_2(g)$ and $I_2(g)$ were each equal to 2.00 *M*. The reaction was allowed to proceed at 448ºC until the system reached equilibrium. Calculate the concentrations of all three gases in the reaction vessel at equilibrium.

4. A sample of $HI(g)$ was added to a previously evacuated reaction vessel, with an initial concentration of 6.00 *M* for $HI(g)$. The reaction was allowed to proceed at 448ºC until the system reached equilibrium. Calculate the concentrations of all three gases in the reaction vessel at equilibrium.

$$H_2(g) + I_2(g) \rightleftarrows 2\ HI(g) \qquad K_c = 51 \text{ at } 448°C$$

5. Samples of $H_2(g)$, $I_2(g)$, and $HI(g)$ were added to a previously evacuated rigid reaction vessel at 448°C, with initial concentrations of the following.

$$[H_2] = 2.00\ M \qquad [I_2] = 2.00\ M \qquad [HI] = 6.00\ M$$

(a) In which direction, toward the left (reactants) or toward the right (products), should the reaction proceed in order to achieve equilibrium? Justify your answer by comparing the value of the reaction quotient (Q_c) with the value of the equilibrium constant (K_c) at 448°C.

(b) The reaction was allowed to proceed at 448ºC until the system reached equilibrium. Calculate the concentrations of all three gases in the reaction vessel at equilibrium.

$$C(s) + CO_2(g) \rightleftarrows 2\ CO(g)$$

6. Solid carbon and carbon dioxide gas at 1160 K were placed in a rigid previously evacuated 2.00 L container, and a chemical reaction occurred, producing carbon monoxide gas as represented by the equation shown above. As the reaction proceeded, the total pressure in the container was monitored. Solid carbon remained in the container at all times. Results are recorded in the table below.

Time (hours)	Total Pressure of Gases in Container at 1160 K (atm)
0	5.00
2.0	6.26
4.0	7.09
6.0	7.75
8.0	8.37
10.0	8.37

(a) At what time during this experiment was equilibrium achieved? Justify your answer.

6. (continued)

$$C(s) + CO_2(g) \rightleftarrows 2\,CO(g)$$

(b) Calculate the number of moles of $CO_2(g)$ initially placed in the container. Assume that the volume of solid carbon in the container is negligible.

(c) For the reaction mixture at equilibrium at 1160 K, the partial pressure of $CO_2(g)$ is equal to 1.63 atm. Calculate the partial pressure of $CO(g)$ in the container at equilibrium.

(d) Write the expression for the equilibrium constant, K_p, for this reaction, and calculate the value of K_p at 1160 K.

(e) A second trial of this experiment is carried out at 1160 K, with the same initial amount of $C(s)$ and $CO_2(g)$. A solid catalyst is placed in the reaction vessel. Do you predict that the total pressure of the gas mixture at equilibrium will be less than, greater than, or equal to the total pressure at equilibrium in Trial 1 in the absence of a catalyst? Justify your prediction. Assume that the volume of the solid catalyst is negligible.

(f) In another experiment involving the same reaction, a rigid 2.00 L container initially contained 10.0 g $C(s)$ and a mixture of $CO(g)$ and $CO_2(g)$. The initial values for the partial pressures of $CO_2(g)$ and $CO(g)$ were each equal to 3.00 atm. The system is allowed to reach equilibrium at 1160 K. Solid carbon remained in the container at all times. Do you predict that the partial pressure of $CO_2(g)$ at equilibrium is less than or greater than 3.00 atm? Justify your answer by comparing the value of the reaction quotient (Q_p) with the value of the equilibrium constant (K_p) at 1160 K.

6. (continued)

(g) When the system described in part (f) has reached equilibrium at 1160 K, the total pressure of gases in the container is equal to 7.61 atm. Calculate the partial pressure of $CO_2(g)$ and $CO(g)$ in the container at equilibrium.

7.8 Representations of Equilibrium

Essential knowledge statement from the AP Chemistry CED:

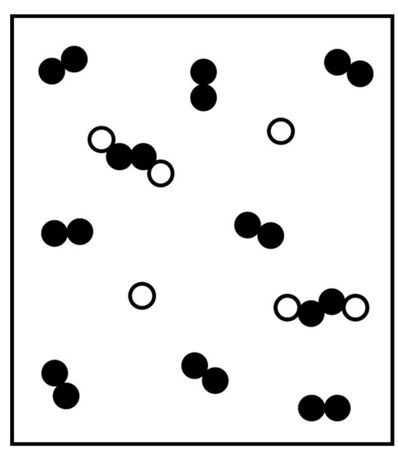
- Particulate representations can be used to describe the relative numbers of reactant and product particles present prior to and at equilibrium, and the value of the equilibrium constant.

$$X_2(g) + 2\,Y(g) \rightleftarrows X_2Y_2(g)$$

7. Substance $X_2(g)$ reacts with $Y(g)$ according to the equation above. A particulate representation of the reaction is also shown above.

(a) Write the equilibrium constant expression (K_c) for the reaction represented by the equation above. ______________________________

(b) The particulate diagram shown at right represents the reaction mixture after equilibrium has been achieved at 500 K. Assume that each particle in the diagram represents 1 mole, and that volume of the reaction vessel is 1.00 L. Use the information from this diagram to calculate the value of the equilibrium constant (K_c) for this reaction at 500 K.

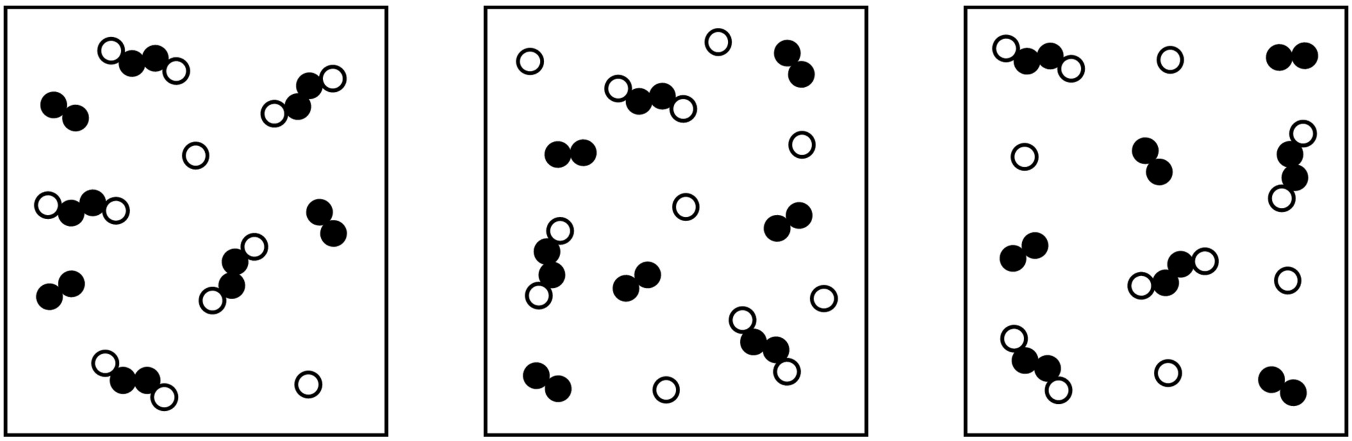


7. (continued)

$$X_2(g) + 2\,Y(g) \rightleftarrows X_2Y_2(g)$$

(c) The three diagrams below are particulate representations of the reaction mixture at various points in time.

- Calculate the value of the reaction quotient (Q_c) for each diagram.
- Based on the comparison of Q_c and K_c, determine if the reaction mixture represented in the diagram is at equilibrium.
- If the system is not at equilibrium, determine the direction, toward the right (products) or toward the left (reactants), that the reaction should proceed in order to reach equilibrium.



7.9 Introduction to Le Châtelier's Principle

Essential knowledge statements from the AP Chemistry CED:

- Le Châtelier's principle can be used to predict the response of a system to stresses such as addition or removal of a chemical species, change in temperature, change in volume/pressure of a gas-phase system, or dilution of a reaction system.
- Le Châtelier's principle can be used to predict the effect that a stress will have on experimentally measurable properties such as pH, temperature, and color of a solution.

7.10 Reaction Quotient and Le Châtelier's Principle

Essential knowledge statements from the AP Chemistry CED:

- A disturbance to a system at equilibrium causes *Q* to differ from *K*, thereby taking the system out of equilibrium. The system responds by bringing *Q* back into agreement with *K*, thereby establishing a new equilibrium state.
- Some stresses, such as changes in concentration, cause a change in *Q* only. A change in temperature causes a change in *K*. In either case, the concentrations or partial pressures of species redistribute to bring *Q* and *K* back into equality.

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

8. 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.

$P_{SO_3} = 3.43$ atm $\qquad P_{SO_2} = 2.00$ atm $\qquad P_{O_2} = 1.00$ atm

(a) Write the equilibrium constant expression (K_p) for the reaction and calculate the value of K_p at 1000 K.

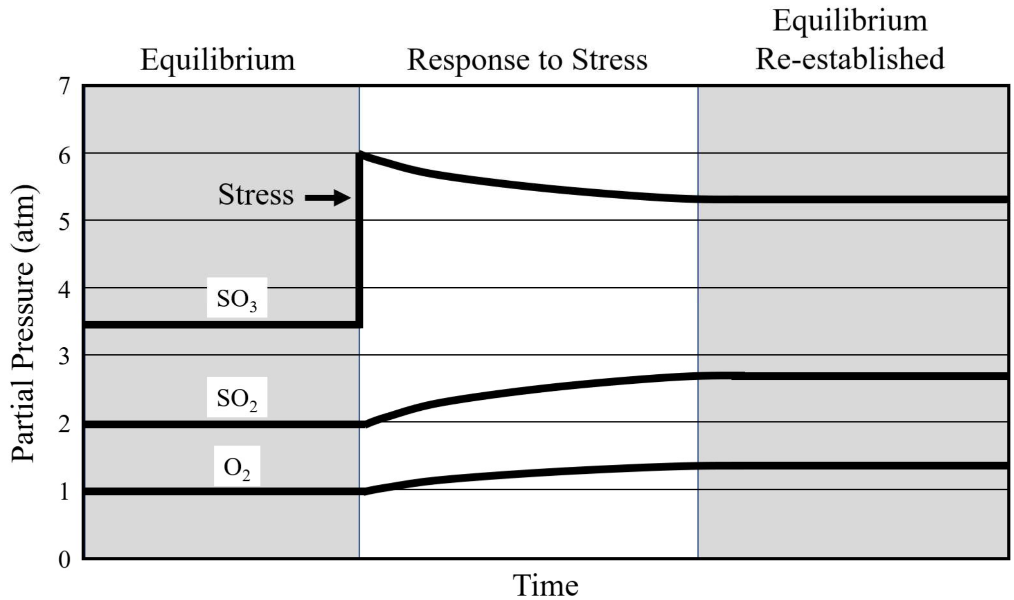
(b) Additional $SO_3(g)$ is added to the reaction vessel at 1000 K until the partial pressure of $SO_3(g)$ is 6.00 atm. Calculate the value of Q_p at the moment that additional $SO_3(g)$ is added.

(c) 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 $Q_p = K_p$.

_______ The partial pressure of $SO_2(g)$ will increase until $Q_p = K_p$.

(d) When equilibrium is re-established at 1000 K, the partial pressure of $O_2(g)$ in the reaction vessel is 1.34 atm. Calculate the partial pressures of $SO_3(g)$ and $SO_2(g)$ when equilibrium is re-established.



Le Châtelier's Principle is stated as follows.

> *If a system at equilibrium is disturbed by a stress, the reaction will proceed in a certain way so as to counteract the effect of the disturbance.*

Stresses that can occur to disturb an equilibrium system include the following.

- the addition or removal of certain substances
- a change in the volume of the reaction vessel (for a gaseous system)
- the addition or removal of water (for an aqueous system)
- a change in temperature

If the temperature remains constant, the value of the equilibrium constant *K* remains constant.

$$2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g) \qquad K_p = 0.340 \text{ at } 1000\text{ K}$$

9. 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.

$$P_{SO_3} = 9.70\text{ atm} \qquad P_{SO_2} = 4.00\text{ atm} \qquad P_{O_2} = 2.00\text{ atm}$$

(a) Is this system at equilibrium? Justify your answer with a calculation.

9. (continued)

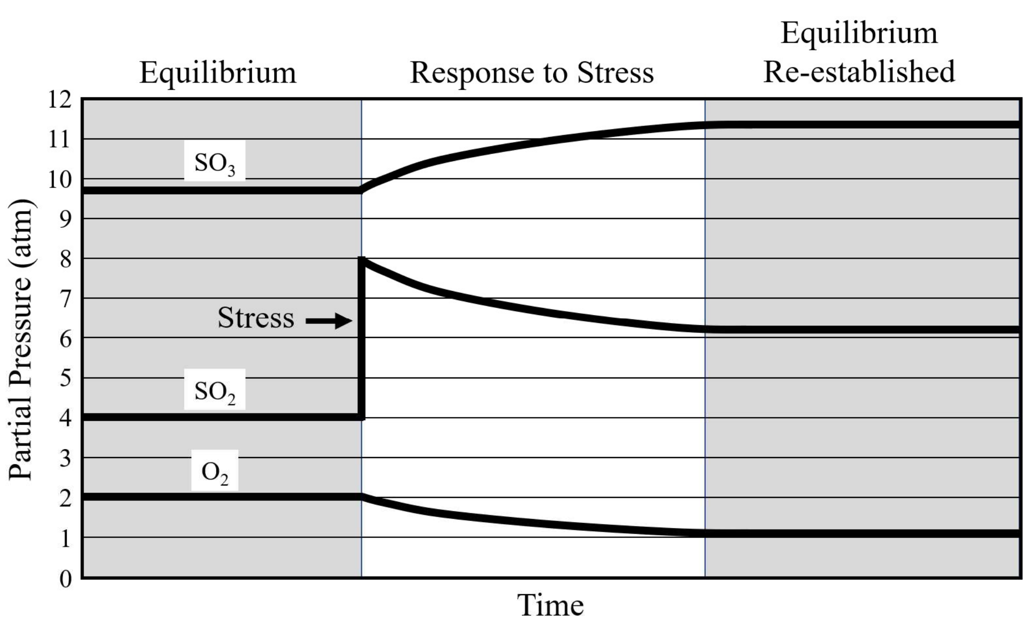
(b) Additional $SO_2(g)$ is added to the reaction vessel at 1000 K until the partial pressure of $SO_2(g)$ is 8.00 atm. Calculate the value of Q_p at the moment that additional $SO_2(g)$ is added.

(c) The addition of $SO_2(g)$ 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 $O_2(g)$ will decrease until $Q_p = K_p$.

_______ The partial pressure of $O_2(g)$ will increase until $Q_p = K_p$.

(d) When equilibrium is re-established at 1000 K, the partial pressure of $O_2(g)$ in the reaction vessel is 1.13 atm. Calculate the partial pressures of $SO_3(g)$ and $SO_2(g)$ when equilibrium is re-established.



$$2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g) \qquad K_p = 0.340 \text{ at } 1000\text{ K}$$

10. 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.

$$P_{SO_3} = 10.29 \text{ atm} \qquad P_{SO_2} = 3.00 \text{ atm} \qquad P_{O_2} = 4.00 \text{ atm}$$

(a) Is this system at equilibrium?
Justify your answer with a calculation. ______________________________

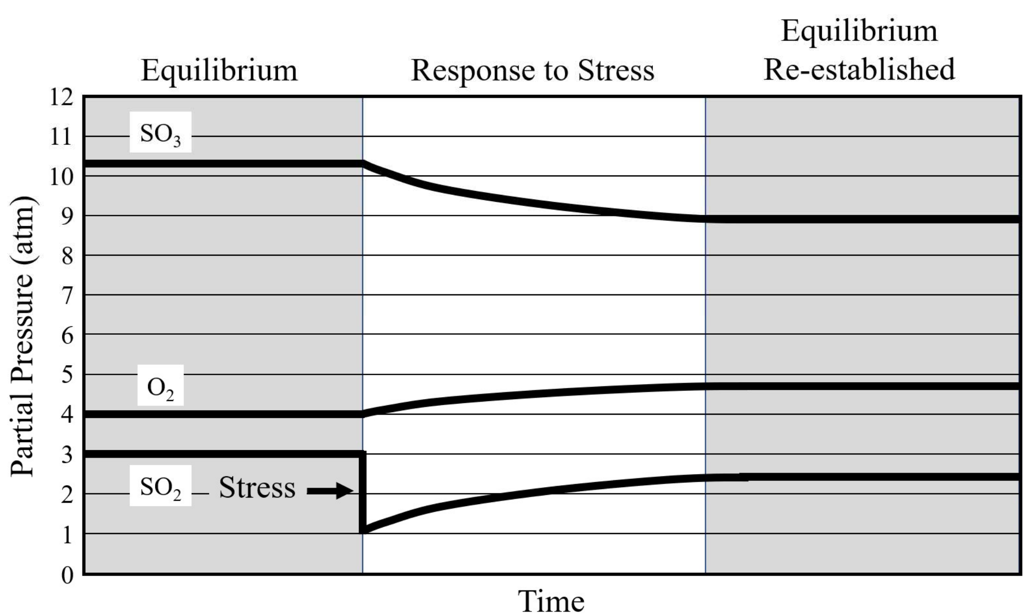
(b) Some of the $SO_2(g)$ is removed from the reaction vessel at 1000 K, reducing the partial pressure of $SO_2(g)$ to a value of 1.00 atm. Calculate the value of Q_p at the moment that the $SO_2(g)$ is removed. ______________________________

(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 $Q_p = K_p$.

_______ The partial pressure of $O_2(g)$ will increase until $Q_p = K_p$.

(d) When equilibrium is re-established 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 re-established.



$$N_2O_4(g) \rightleftarrows 2\ NO_2(g) \qquad K_p = 0.21 \text{ at } 373 \text{ K}$$

11. A reaction vessel with a volume of 2.00 L contains a mixture of $N_2O_4(g)$ and $NO_2(g)$ at 373 K with the following values of partial pressure.

$$P_{N_2O_4} = 4.77 \text{ atm} \qquad P_{NO_2} = 1.00 \text{ atm}$$

(a) Is this system at equilibrium?
Justify your answer with a calculation. ______________________________

(b) The volume of the reaction vessel is decreased from 2.00 L to 1.00 L while the temperature is held constant at 373 K. At the moment the volume is decreased to 1.00 L, what is the partial pressure of each gas?

$P_{N_2O_4}$ = __________ atm $\qquad$ P_{NO_2} = __________ atm

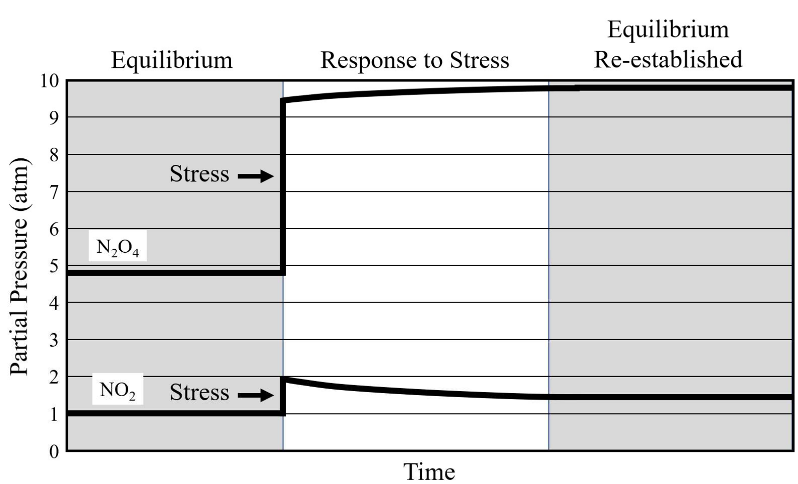
(c) Based on your answer to part (b),
calculate the value of Q_p for this system: ______________________________

(d) The change in the volume of the reaction vessel caused a disturbance in the equilibrium system that had already been established. As the system re-establishes equilibrium at 373 K, which of the following statements should be true?

_______ The partial pressure of $NO_2(g)$ will decrease until $Q_p = K_p$.

_______ The partial pressure of $NO_2(g)$ will increase until $Q_p = K_p$.

(e) When equilibrium is re-established at 373 K, the partial pressure of $N_2O_4(g)$ in the reaction vessel is 9.82 atm. Calculate the partial pressure of $NO_2(g)$ when equilibrium is re-established.



$$N_2O_4(g) \rightleftarrows 2\ NO_2(g) \qquad K_p = 0.21 \text{ at } 373 \text{ K}$$

12. A reaction vessel with a volume of 1.00 L contains a mixture of $N_2O_4(g)$ and $NO_2(g)$ at 373 K with the following values of partial pressure.

$$P_{N_2O_4} = 19.02 \text{ atm} \qquad P_{NO_2} = 2.00 \text{ atm}$$

(a) Is this system at equilibrium?
Justify your answer with a calculation. ______________________________

(b) The volume of the reaction vessel is increased from 1.00 L to 2.00 L while the temperature is held constant at 373 K. At the moment the volume is increased to 2.00 L, what is the partial pressure of each gas?

$P_{N_2O_4}$ = __________ atm $\qquad$ P_{NO_2} = __________ atm

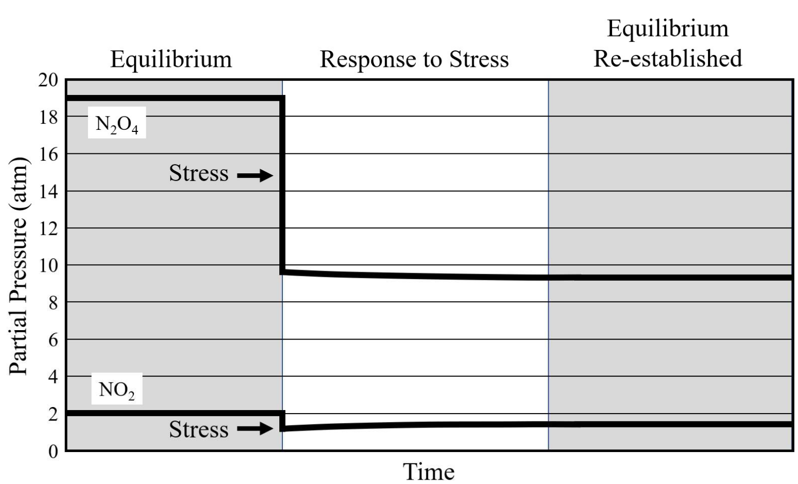
(c) Based on your answer to part (b),
calculate the value of Q_p for this system: ______________________________

(d) The change in the volume of the reaction vessel caused a disturbance in the equilibrium system that had already been established. As the system re-establishes equilibrium at 373 K, which of the following statements should be true?

_______ The partial pressure of $NO_2(g)$ will decrease until $Q_p = K_p$.

_______ The partial pressure of $NO_2(g)$ will increase until $Q_p = K_p$.

(e) When equilibrium is re-established at 373 K, the partial pressure of $N_2O_4(g)$ in the reaction vessel is 9.31 atm. Calculate the partial pressure of $NO_2(g)$ when equilibrium is re-established.



$$H_2(g) + I_2(g) \rightleftarrows 2\ HI(g) \qquad K_p = 51 \text{ at } 448°C$$

13. A reaction vessel with a volume of 2.00 L contains a mixture of $H_2(g)$, $I_2(g)$, and $HI(g)$ at 448°C with the following values of partial pressure.

$$P_{H_2} = 1.20 \text{ atm} \qquad P_{I_2} = 1.20 \text{ atm} \qquad P_{HI} = 8.57 \text{ atm}$$

(a) Is this system at equilibrium?
Justify your answer with a calculation. ____________________

(b) The volume of the reaction vessel is decreased from 2.00 L to 1.00 L while the temperature is held constant at 448°C. At the moment the volume is decreased to 1.00 L, what is the partial pressure of each gas?

P_{H_2} = __________ atm P_{I_2} = __________ atm P_{HI} = __________ atm

(c) Based on your answer to part (b),
calculate the value of Q_p for this system: ____________________

$$H_2(g) + I_2(g) \rightleftarrows 2\ HI(g) \qquad K_p = 51 \text{ at } 448°C$$

Even though the volume of the reaction vessel was decreased from 2.00 L to 1.00 L, no shift in the equilibrium system will occur. *This can be explained because there is an equal number of moles of gas on each side of this chemical equation.*

Changes in the volume of the reaction vessel can cause a disturbance in a gaseous equilibrium system when there are different numbers of moles of gas on opposite sides of the chemical equation.
The consequences of these changes are summarized in the table below. Assume that changes in the volume of the reaction vessel occur at constant temperature.

How the Volume of the Reaction Vessel is Changed (at constant temp.)	How the Gaseous Equilibrium System Responds to the Change in Volume
The volume of the reaction vessel is decreased.	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.
The volume of the reaction vessel is increased.	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.

14. If an inert, unreactive gas such as helium (He) or neon (Ne) is added to a gaseous system at equilibrium, the total pressure of the gas mixture increases. However, no shift in the equilibrium system will occur. Explain this result in terms of the reaction quotient (Q_p).

$$Co(H_2O)_6^{2+}(aq) \; + \; 4\,Cl^-(aq) \rightleftarrows CoCl_4^{2-}(aq) \; + \; 6\,H_2O(l)$$

pink   blue

15. Two different forms of the cobalt(II) ion are in equilibrium according to the equation shown above. A purple solution contains an equilibrium mixture of pink $Co(H_2O)_6^{2+}(aq)$, colorless $Cl^-(aq)$, and blue $CoCl_4^{2-}(aq)$.

 (a) Write the equilibrium-constant expression (K_c) for the reaction shown above. ______________________________

 The concentration of the aqueous ions in the purple solution is unknown. The concentration of each ion can be represented by the variables *a*, *b*, and *c* as shown below.

$$[Co(H_2O)_6^{2+}] = a \qquad [Cl^-] = b \qquad [CoCl_4^{2-}] = c$$

 (b) Write the equilibrium-constant expression (K_c) for the reaction shown above in terms of the variables *a*, *b*, and *c*. ____________________

 A 10.0 mL sample of distilled water was added to 10.0 mL of the purple solution described above. As a result of this dilution experiment, the color of the solution changed from purple to pink.

 (c) In which direction, toward the left (reactants) or toward the right (products), did the equilibrium system shift as a result of the dilution with water? ____________________

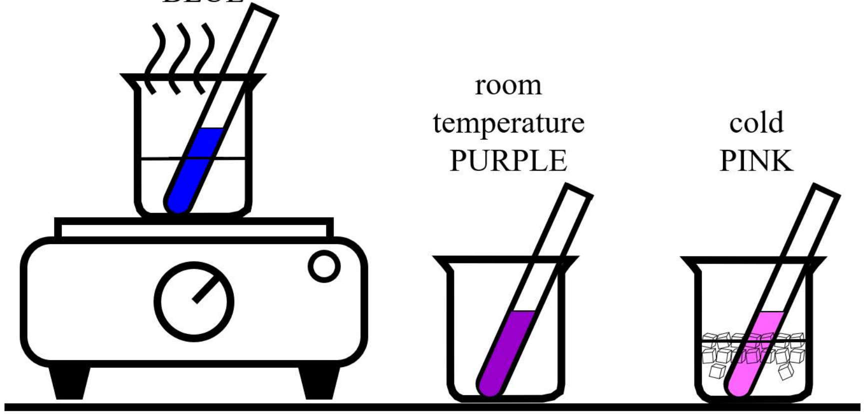
 (d) Dilution of the purple solution with water caused the concentration of all aqueous species to decrease to **half** of their original values. Use this information to write the expression for the reaction quotient (Q_c) in terms of *a*, *b*, and *c at the moment that water was added to the purple solution.* ____________________

If an aqueous equilibrium system is diluted with water, the concentrations of all aqueous species are decreased. As a result of this change, the aqueous equilibrium system shifts toward the side of the equation that has the higher number of moles of aqueous particles.

A purple solution contains an equilibrium mixture of pink $Co(H_2O)_6^{2+}(aq)$, colorless $Cl^-(aq)$, and blue $CoCl_4^{2-}(aq)$. The purple solution is added to three separate test tubes.

- One test tube is placed in a hot water bath, and the color changes from purple to blue.
- One test tube is kept at room temperature, and the color remains purple.
- One test tube is placed in an ice water bath, and the color changes from purple to pink.

Results of the experiment are shown in the diagram below.



$$Co(H_2O)_6^{2+}(aq) + 4\ Cl^-(aq) \rightleftarrows CoCl_4^{2-}(aq) + 6\ H_2O(l)$$

pink blue

16. (a) In which direction, toward the left (reactants) or toward the right (products), did the equilibrium system shift as a result of placing the test tube in the hot water bath? ______________________________

    (b) In which direction, toward the left (reactants) or toward the right (products), did the equilibrium system shift as a result of placing the test tube in the ice water bath? ______________________________

    (c) Is the reaction represented by the equation shown above classified as endothermic or exothermic? ______________________________

- If the temperature of an equilibrium system is increased, the system will shift in the direction of the endothermic process.
- If the temperature of an equilibrium system is decreased, the system will shift in the direction of the exothermic process.
- Changes in temperature cause the value of the equilibrium constant (K) to change.
- If a temperature change causes a shift toward the right (products), the value of K will increase.
- If a temperature change causes a shift toward the left (reactants), the value of K will decrease.

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.**