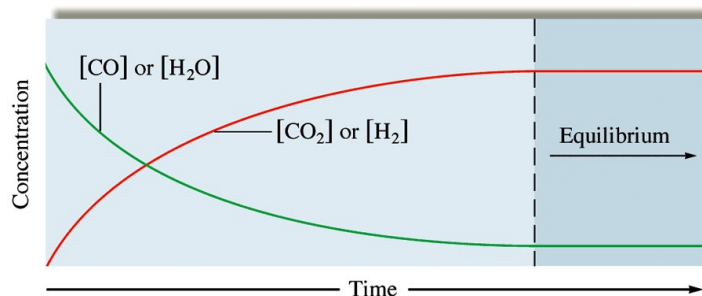


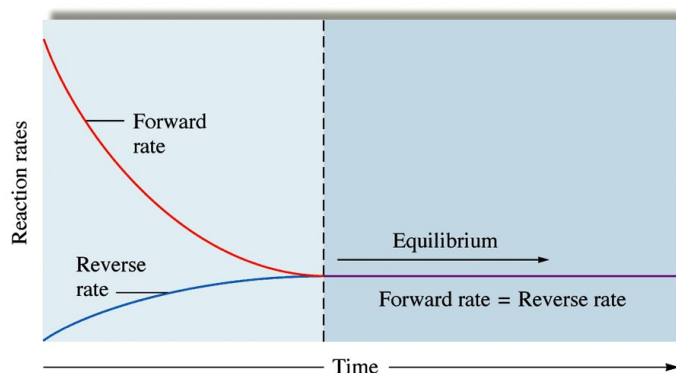
Chapter 13 Outline – Chemical Equilibrium

The Equilibrium Condition

- In stoichiometry we assumed that reactions went to completion. Most reactions do go to completion but there are many that stop far short of completion.
- Chemical equilibrium** is that state where **the concentrations of all reactants and products remain constant with time.**
- Since no changes occur in the concentrations of reactants and products in a reaction at equilibrium, it may appear everything has stopped.
- Equilibrium is not static; it is highly dynamic and frantic on the molecular level. The reaction continues to proceed in both directions but the rate of the forward reaction is equal to the rate of the reverse reaction.**
- The figure below is a profile of the progress of a reaction: $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$. Note that once equilibrium is reached, the concentrations of the products and reactants do not change and neither becomes zero.



- The other graphic below represents the rates of the forward and reverse reaction for the same reaction



The Equilibrium Constant

- From their observations of many chemical reactions, two Norwegian Chemists, Cato Maximilian Guldberg (1836-1902) and Peter Waage (1833-1900) proposed in 1864 **the law of mass action.**
- $j\text{A} + k\text{B} \rightleftharpoons l\text{C} + m\text{D}$ would be represented as:

$$K_c = \frac{[\text{C}]^l [\text{D}]^m}{[\text{A}]^j [\text{B}]^k}$$

- Example: Write the mass action expression for the following equation: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Answer:
$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

- You try: Write the equilibrium expression for the following: $4\text{NH}_3(\text{g}) + 7\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

- The value of the equilibrium constant at a given temperature can be calculated if you know the equilibrium concentrations of the reaction components.
- Equilibrium constants are customarily given without units. K is unitless because the values of concentration or partial pressure that we substitute into the equilibrium constant expression are ratios of the concentration or pressure to a reference concentration (exactly 1M) or a reference pressure (exactly 1 atm).
- Example: For the following equation: $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$. At a particular temperature, a scientist determined the concentration of HI to be 1.30M, H_2 to be 0.30M & I_2 to be 0.30M.

- Calculate the equilibrium constant at this temperature.
- Calculate the equilibrium constant for the reverse reaction.
- Calculate the equilibrium constant for the following reaction $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{I}_2(\text{g}) \rightleftharpoons \text{HI}(\text{g})$

$$\frac{[\text{H}_2] \times [\text{I}_2]}{[\text{HI}]^2} \longrightarrow \frac{[0.30] \times [0.30]}{[1.30]^2} \longrightarrow K_c = 0.053$$

The reverse reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

- $$\frac{[\text{HI}]^2}{[\text{H}_2] \times [\text{I}_2]} = \frac{[1.30]^2}{[0.30] \times [0.30]} \quad K'_c = 19 \text{ (rounded from 18.77)}$$

The equilibrium constant for a reverse reaction can be found by taking the reciprocal of the equilibrium constant for the forward reaction. Using the values from above: $K'_{\text{reverse}} = 1 / K_{\text{forward}}$

$$\begin{aligned} K'_{\text{reverse}} &= 1 / K_{\text{forward}} \\ K'_{\text{reverse}} &= 1 / 0.053 \\ K'_{\text{reverse}} &= 19 \end{aligned}$$

- $$\frac{[\text{HI}]}{[\text{H}_2]^{1/2} \times [\text{I}_2]^{1/2}} = \frac{[1.30]}{[0.30]^{1/2} \times [0.30]^{1/2}} \quad K''_c = 4.3$$

Since $\left(\frac{[\text{HI}]^2}{[\text{H}_2] \times [\text{I}_2]} \right)^{1/2} = \frac{[\text{HI}]}{[\text{H}_2]^{1/2} \times [\text{I}_2]^{1/2}}$ Thus: $K''_c = \sqrt{K'_c}$

- A set of equilibrium concentrations is called an **equilibrium position**. There can be many equilibrium positions for a reaction at a certain temperature, but only one equilibrium constant for a particular system at a particular temperature.
 - I think you need to try one. The following concentrations were observed for the Haber Process at 127 °C. $[\text{NH}_3] = 3.1 \times 10^{-2} \text{ mol/L}$, $[\text{N}_2] = 8.5 \times 10^{-1} \text{ mol/L}$, $[\text{H}_2] = 3.1 \times 10^{-3} \text{ mol/L}$.
- Calculate the value of K at 127 °C for the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - Calculate the equilibrium constant at 127 °C for the reaction: $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
 - Calculate the equilibrium constant at 127 °C for the reaction: $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$

Equilibrium Expressions Involving Pressures

- The ideal gas law ($PV = nRT$) can be derived to include concentration (n/V or moles per Volume). This formula is: $P = CRT$.
- In terms of partial pressure, the **equilibrium partial pressures of the gases equation** can be used. For the sample equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_P = \frac{(P_{NH_3})^2}{(P_{N_2}) \times (P_{H_2})^3}$$

P represents the partial pressure of each gas.

- Example: The reaction for the formation of nitrosyl chloride: $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl$ The pressures at equilibrium were found to be: $P_{NO} = 0.60$ atm, $P_{Cl_2} = 0.40$ atm and $P_{NOCl} = 2.20$ atm Calculate the K_P for the reaction.

$$K_P = \frac{(P_{NOCl})^2}{(P_{NO})^2 \times (P_{Cl_2})}$$

$$K_P = 34$$

- You try: Calculate K_P for the following: $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$ if $P_{HF} = 775$ mm Hg, $P_{H_2} = 650$ mm Hg and $P_{F_2} = 480$ mm Hg

- The relationship between K_c and K_P is: $K_P = K_c(RT)^{\Delta n}$ Δn = the sum of the moles of gaseous product – sum of the moles of the gaseous reactants.

- Example: Calculate the K_c at $25^\circ C$ for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ K_P (from earlier example: 34)

$$K_P = K_c(RT)^{\Delta n}$$

$$K_c = K_P / (RT)^{\Delta n}$$

$$K_c = 34 / [(0.08206)(298)]^{-1}$$

$$K_c = 830$$

- You try: Calculate the equilibrium constants (K_P & K_c) at $40.0^\circ C$ for the following equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $P_{N_2} = 2.11$ atm, $P_{H_2} = 1.65$ atm and $P_{NH_3} = 3.45$ atm

Heterogeneous Equilibria

- So far we have only looked at equilibria for systems in the gas phase, where all reactants and products are gases. These are homogeneous equilibria.
- Equilibria involving more than one phase are called heterogeneous equilibria.
- If pure solids or pure liquids are involved in a chemical reaction, their concentrations are not included in the equilibrium expression for the reaction.

- Consider the following heterogeneous equilibria: $2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$

$$\text{Thus: } K_c = [H_2]^2[O_2] \text{ and } K_P = (P_{H_2})^2(P_{O_2})$$

Water is not included because it is a pure liquid.

- You try: Write the expression for K_c and K_P for the following process: Solid phosphorus pentachloride decomposes to form liquid phosphorus trichloride and chlorine gas.

Application of the Equilibrium Constant

- The tendency for a reaction to occur is indicated by the magnitude of the equilibrium constant. A value of K larger than 1 means that at equilibrium the reaction will consist of mostly products – the equilibrium lies to the right. A very small K value, one less than one, means that most of the system will be in the form of the reactants.
- The size of the K and the time required to reach equilibrium are not directly related. The time required to achieve equilibrium depends on reaction rate, which is determined by the size of the activation energy.
- When the reactants and products are mixed, it is useful to know whether the mixture is at equilibrium, or if not, the direction in which the system must shift to reach equilibrium. To determine the shift, the **reaction quotient, Q** , is used. The reaction quotient is obtained by applying the law of mass action using initial concentrations instead of equilibrium concentrations.
- To determine the direction a system will shift, compare the Q & K values for a reaction.
 - **If $Q = K$, the reaction is already at equilibrium.**
 - **If $Q > K$, the system shifts to the left and more reactants are formed until equilibrium is reached.**
 - **If $Q < K$, the system shifts to the right and more products are formed until equilibrium is reached.**
- Be sure to make proper relationships between Q_c and K_c and Q_p and K_p . Initial pressure relates to equilibrium pressure as initial concentration relates to equilibrium concentration.
- For example: For the synthesis of ammonia at 500°C , the equilibrium constant is 6.0×10^{-2} . Determine the direction in which the system will shift to reach equilibrium in the following case: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$. $[\text{N}_2]_0 = 1.0 \times 10^{-5} \text{ M}$, $[\text{H}_2]_0 = 2.0 \times 10^{-3} \text{ M}$, $[\text{NH}_3]_0 = 1.0 \times 10^{-3} \text{ M}$.

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$Q = 1.3 \times 10^7$$

Since $Q > K$ the reaction shifts to the left and ammonia decomposes to form nitrogen gas and hydrogen gas.

- You try: For the synthesis of ammonia at 500°C , the equilibrium constant is 6.0×10^{-2} . Determine the direction in which the system will shift to reach equilibrium in the following case: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$. $[\text{N}_2]_0 = 5.0 \text{ M}$, $[\text{H}_2]_0 = 1.0 \times 10^{-2} \text{ M}$, $[\text{NH}_3]_0 = 1.0 \times 10^{-4} \text{ M}$.
- Calculating equilibrium pressure. Example: O_2 can be converted into ozone, O_3 . If oxygen is placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.250$. At equilibrium, the pressure of O_2 is found to be 2.25 atm. Calculate the equilibrium pressure of $\text{O}_3(\text{g})$.
$$3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$$
$$K_p = \frac{(P_{\text{O}_3})^2}{(P_{\text{O}_2})^3}$$
$$0.250 = \frac{(P_{\text{O}_3})^2}{(2.25)^3}$$
$$P_{\text{O}_3} = \sqrt{2.847656}$$
$$P_{\text{O}_3} = 1.69 \text{ atm}$$
- You try: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$. Calculate the pressure of nitrogen dioxide if the $K_p = 0.133$ and the pressure of N_2O_4 is 2.48 atm.

- Example: At a certain temperature a 1.00 L flask initially contained 0.298 mol $\text{PCl}_3(\text{g})$ and 8.70×10^{-3} mol PCl_5 . After the system had reached equilibrium, 2.00×10^{-3} mol of $\text{Cl}_2(\text{g})$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ Calculate the equilibrium concentrations of all species and the value of K_c .

Determine the initial concentration of each substance.

$$\text{Cl}_2 = 0$$

$$\text{PCl}_3 = 0.298 \text{ mol} / 1.00 \text{ L} = 0.298 \text{ M}$$

$$\text{PCl}_5 = 8.70 \times 10^{-3} \text{ mol} / 1.00 \text{ L} = 8.70 \times 10^{-3} \text{ M}$$

Since there was no original chlorine and at equilibrium there was 2.00×10^{-3} mol, we can assume that the PCl_5 decreased by 2.00×10^{-3} moles and PCl_3 increased by 2.00×10^{-3} moles. Use this fact to determine the concentration at equilibrium

$$\text{First convert moles to M. } 2.00 \times 10^{-3} \text{ moles} / 1.00 \text{ L} = 2.00 \times 10^{-3} \text{ M}$$

$$\text{Cl}_2 = 0 + 2.00 \times 10^{-3} = 2.00 \times 10^{-3} \text{ M}$$

$$\text{PCl}_3 = 0.298 \text{ M} + 2.00 \times 10^{-3} = 0.300 \text{ M}$$

$$\text{PCl}_5 = 8.70 \times 10^{-3} \text{ M} - 2.00 \times 10^{-3} = 6.70 \times 10^{-3} \text{ M}$$

Plug it in to the mass action expression to find K_c .

$$K_c = (2.00 \times 10^{-3})(0.300) / 6.70 \times 10^{-3}$$

$$K_c = 8.96 \times 10^{-2}$$

- Your turn: A 1.00 L flask was filled with 2.00 mol gaseous SO_2 and 2.00 mol gaseous NO_2 are heated. After equilibrium was reached, it was found that 1.30 mol gaseous NO was present. Assume that the reaction: $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$ occurs under these conditions. Calculate the value of the equilibrium constant, K , for this reaction.

- Calculating Equilibrium Concentrations Using ICE. Example: Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 2.00 mol of each component is mixed in a 1.000 L flask.

Find Molarity of each substance: $2.00/1.000 = 2.00 \text{ M}$

Since $K_c > 1$ the reaction will shift to the right and the value of x is significant enough to include in the subtraction and addition.. Products will increase by a value of x and reactants will decrease by a value of x .

Reaction	CO	H ₂ O	CO ₂	H ₂
Initial	2.00 M	2.00 M	2.00 M	2.00 M
Change	-x	-x	+x	+x
Equilibrium	2.00 - x	2.00 - x	2.00 + x	2.00 + x
Answer	1.23	1.23	2.77	2.77

$$\frac{5.10}{1} = \frac{[2.00 + x][2.00 + x]}{[2.00 - x][2.00 - x]} \rightarrow \frac{5.10}{1} = \frac{[2.00 + x]^2}{[2.00 - x]^2} \rightarrow \frac{\sqrt{5.10}}{1} = \frac{[2.00 + x]}{[2.00 - x]} \rightarrow$$

$$\frac{2.26}{1} = \frac{[2.00 + x]}{[2.00 - x]} \rightarrow 4.52 - 2.26x = 2.00 + x \rightarrow 2.52 = 3.26x \rightarrow x = 0.773$$

Insert into ICE Chart.

- You try: Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature. In a particular experiment 4.000 moles of each reactant was added to a 1.750 L flask. Calculate the concentration of all species.

Note that most systems we deal with have small equilibrium constants. If the equilibrium constant is small, mathematical simplifications can be made. See below. Worked in class. Please copy.

Example: Gaseous NOCl decomposes to form the gases NO & Cl₂. At 35°C the equilibrium constant is 1.6×10^{-5} . In an experiment in which 1.0 mol NOCl is placed in a 2.0 L flask, what are the equilibrium concentrations?

Le Chatelier's Principle

Le Chatelier's Principle was devised by French Chemist Henri Le Chatelier (1850-1936). **It states that when a system is at equilibrium and it is subjected to a stress, it will shift its equilibrium point to relieve the stress.** The way a system responds to certain stresses is outlined below:



I. Addition or Removal of Reactant or Product

- If a reactant is added, the reaction shifts to the right & increases the concentration of the products.
- If a product is added, the reaction shifts to the left & increases the concentration of the reactants.
- If a reactant is removed, the reaction shifts to the left & decreases the concentration of the products.
- If a product is removed, the reaction shifts to the right & decreases the concentration of the reactants.

The equilibrium value(K) remains the same whenever a reactant or product is added or removed from the system.

II. Temperature Changes

- In an endothermic reaction, an increase in temperature shifts right and increases the concentration of the products.
- In an exothermic reaction, an increase in temperature shifts left and increases the concentration of the reactants.
- In an endothermic reaction, a decrease in temperature shifts left and decreases the concentration of the products.
- In an exothermic reaction, a decrease in temperature shifts right and decreases the concentration of the reactants.

Since an increase in the concentration of the reactants means a decrease in the concentration of the products, and vice versa, changes in temperature do affect equilibrium. Because the equilibrium value is a measure of the concentration of the products divided by the concentration of the reactants, an increase in the concentration of the products means an increase in the equilibrium value(K) and an increase in the concentration of the reactants means a decrease in the equilibrium value(K).

III. Volume/Pressure Changes

Changes in volume or pressure only affect gaseous substances.

- An increase in pressure (decrease in volume) will shift the equilibrium to where there are fewer moles of gas and increase the concentrations of the molecules on that side of the equation.
- A decrease in pressure (increase in volume) will shift the equilibrium to where there are more moles of a gas and increase the concentrations of the molecules on that side of the equation.
- **Even though a change in pressure or volume may cause a shift right or left. There is a change in the equilibrium position due to the work done on the system but the equilibrium constant does not change. It is a constant at a certain temperature.**
- **The addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants.**

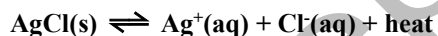
IV. Catalysts

Catalysts only speed up a reaction and do not affect the concentration of the reactants or products or the equilibrium value.

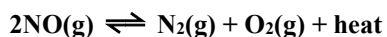
Complete the following charts by writing LEFT, RIGHT or NONE for the equilibrium shift and INCREASES, DECREASES or STAYS THE SAME for the concentrations of the reactants, products and equilibrium value(K).



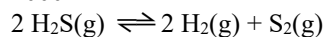
Stress	Equilibrium Shift	[N ₂]	[H ₂]	[NH ₃]	K
1. Add N ₂		-----			
2. Add H ₂			-----		
3. Add NH ₃				-----	
4. Remove N ₂		-----			
5. Remove H ₂			-----		
6. Remove NH ₃				-----	
7. Increase Temperature					
8. Decrease Temperature					
9. Increase Pressure					
10. Decrease Pressure					
11. Add a catalyst					
12. Decrease Volume					



Stress	Equilibrium Shift	Mass AgCl	[Ag ⁺]	[Cl ⁻]	K
13. Add AgCl(s)					
14. Add AgNO ₃			-----		
15. Add HCl				-----	
16. Increase Temperature					
17. Decrease Temperature					
18. Increase Pressure					
19. Decrease Pressure					
20. Increase Volume					

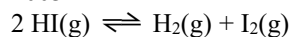


Stress	Equilibrium Shift	[NO]	[N ₂]	[O ₂]	K
21. Remove NO		-----			
22. Remove N ₂			-----		
23. Remove O ₂				-----	
24. Decrease Temperature					
25. Increase Temperature					
26. Decrease Pressure					
27. Increase Pressure					
28. Add Ar gas					
29. Decrease Volume					

2000 - #1

When heated, hydrogen sulfide gas decomposes according to the equation above. A 3.40 g sample of $\text{H}_2\text{S}(\text{g})$ is introduced into an evacuated rigid 1.25 L container. The sealed container is heated to 483 K, and 3.72×10^{-2} mol of $\text{S}_2(\text{g})$ is present at equilibrium.

- (a) Write the expression for the equilibrium constant, K_c , for the decomposition reaction represented above.
- (b) Calculate the equilibrium concentration, in mol L^{-1} , of the following gases in the container at 483 K.
- $\text{H}_2(\text{g})$
 - $\text{H}_2\text{S}(\text{g})$
- (c) Calculate the value of the equilibrium constant, K_c , for the decomposition reaction at 483 K.
- (d) Calculate the partial pressure of $\text{S}_2(\text{g})$ in the container at equilibrium at 483 K.
- (e) For the reaction $\text{H}_2(\text{g}) + \frac{1}{2}\text{S}_2(\text{g}) \rightleftharpoons \text{H}_2\text{S}(\text{g})$ at 483 K, calculate the value of the equilibrium constant, K_c .

2003B - #1

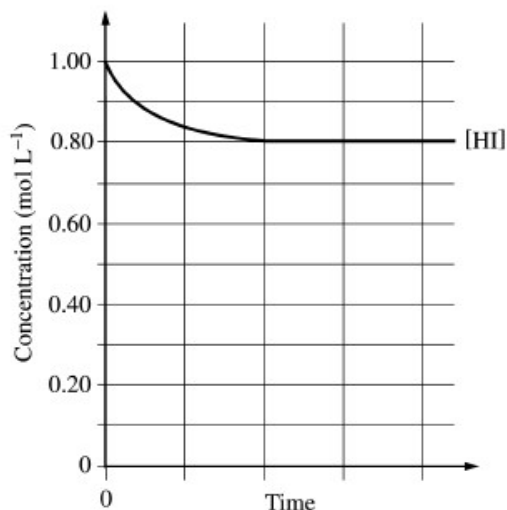
After a 1.0 mole sample of $\text{HI}(\text{g})$ is placed into an evacuated 1.0 L container at 700. K, the reaction represented above occurs. The concentration of $\text{HI}(\text{g})$ as a function of time is shown below.

- (a) Write the expression for the equilibrium constant, K_c , for the reaction.
- (b) What is $[\text{HI}]$ at equilibrium?
- (c) Determine the equilibrium concentrations of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$.
- (d) On the graph above, make a sketch that shows how the concentration of $\text{H}_2(\text{g})$ changes as a function of time.
- (e) Calculate the value of the following equilibrium constants at 700. K.

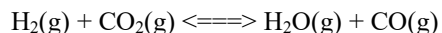
(i) K_c

(ii) K_p

- (f) At 1,000 K, the value of K_c for the reaction is 2.6×10^{-2} . In an experiment, 0.75 mole of $\text{HI}(\text{g})$, 0.10 mole of $\text{H}_2(\text{g})$, and 0.50 mole of $\text{I}_2(\text{g})$ are placed in a 1.0 L container and allowed to reach equilibrium at 1,000 K. Determine whether the equilibrium concentration of $\text{HI}(\text{g})$ will be greater than, equal to, or less than the initial concentration of $\text{HI}(\text{g})$. Justify your answer.



1995 - #1



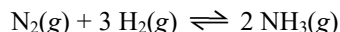
When $\text{H}_2(\text{g})$ is mixed with $\text{CO}_2(\text{g})$ at 2,000 K, equilibrium is achieved according to the equation above.

In one experiment, the following equilibrium concentrations were measured.

$$[\text{H}_2] = 0.20 \text{ mol/L}, [\text{CO}_2] = 0.30 \text{ mol/L}, [\text{H}_2\text{O}] = [\text{CO}] = 0.55 \text{ mol/L}$$

- What is the mole fraction of $\text{CO}(\text{g})$ in the equilibrium mixture?
- Using the equilibrium concentrations given above, calculate the value of K_c , the equilibrium constant for the reaction.
- Determine K_p , in terms of K_c for this system.
- When the system is cooled from 2,000 K to a lower temperature, 30.0 percent of the $\text{CO}(\text{g})$ is converted back to $\text{CO}_2(\text{g})$. Calculate the value of K_c at this lower temperature.
- In a different experiment, 0.50 mole of $\text{H}_2(\text{g})$ is mixed with 0.50 mole of $\text{CO}_2(\text{g})$ in a 3.0-liter reaction vessel at 2,000 K. Calculate the equilibrium concentration, in moles per liter, of $\text{CO}(\text{g})$ at this temperature.

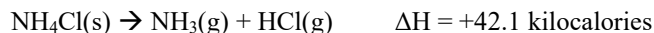
2004B - #1



For the reaction represented above, the value of the equilibrium constant, K_p , is 3.1×10^{-4} at 700. K.

- Write the expression for the equilibrium constant, K_p , for the reaction.
- Assume that the initial partial pressures of the gases are as follows:
 $p_{\text{N}_2} = 0.411 \text{ atm}$, $p_{\text{H}_2} = 0.903 \text{ atm}$, and $p_{\text{NH}_3} = 0.224 \text{ atm}$.
 - Calculate the value of the reaction quotient, Q , at these initial conditions.
 - Predict the direction in which the reaction will proceed at 700. K if the initial partial pressures are those given above. Justify your answer.
- Calculate the value of the equilibrium constant, K_c , given that the value of K_p for the reaction at 700. K is 3.1×10^{-4} .
- The value of K_p for the reaction represented below is 8.3×10^{-3} at 700. K.
$$\text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{NH}_4\text{HS}(\text{g})$$
Calculate the value of K_p at 700. K for each of the reactions represented below.
 - $$\text{NH}_4\text{HS}(\text{g}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$$
 - $$2 \text{H}_2\text{S}(\text{g}) + \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_4\text{HS}(\text{g})$$

1980 - #6



Suppose the substances in the reaction above are at equilibrium at 600 K in volume V and at pressure P. State whether the partial pressure of $\text{NH}_3(g)$ 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 small quantity of NH_4Cl is added.
- The temperature of the system is increased.
- The volume of the system is increased.
- A quantity of gaseous HCl is added.
- A quantity of gaseous NH_3 is added.

2009 - #5 a,b & d

Reaction	Equation	ΔH_{298}°
X	$\text{C}(s) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g)$	+131 kJ mol ⁻¹
Y	$\text{CO}_2(g) + \text{H}_2(g) \rightarrow \text{CO}(g) + \text{H}_2\text{O}(g)$	+41 kJ mol ⁻¹

Answer the following questions using the information related to reactions X, and Y in the table above.

- For reaction X, write the expression for the equilibrium constant, K_p .
- For reaction X, will the equilibrium constant, K_p , increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.
- For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.

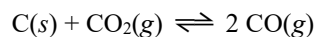
1981 - #1

Ammonia hydrogen sulfide is a crystalline solid that decomposes as follows:



- Some solid NH_4HS is placed in an evacuated vessel at 25°C. After equilibrium is attained, the total pressure inside the vessel is found to be 0.659 atmosphere. Some solid NH_4HS remains in the vessel at equilibrium. For this decomposition, write the expression for K_p and calculate its numerical value at 25°C.
- Some extra NH_3 gas is injected into the vessel containing the sample described in part (a). When equilibrium is reestablished at 25°C, the partial pressure of NH_3 is twice the partial pressure of H_2S . Calculate the numerical value of the partial pressure of NH_3 and the partial pressure of H_2S in the vessel after the NH_3 has been added and equilibrium has been reestablished.
- In a different experiment, NH_3 gas and H_2S gas are introduced into an empty 1.00-liter vessel at 25°C. The initial partial pressure of each gas is 0.500 atmosphere. Calculate the number of moles of solid NH_4HS that is present when equilibrium is established.

2008 - #1



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 in Container at 1,160 K (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.
- (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.)
- (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
- the partial pressure of $\text{CO}(g)$, and
 - the value of the equilibrium constant, K_p .
- (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.)
- 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.
- (e) 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.