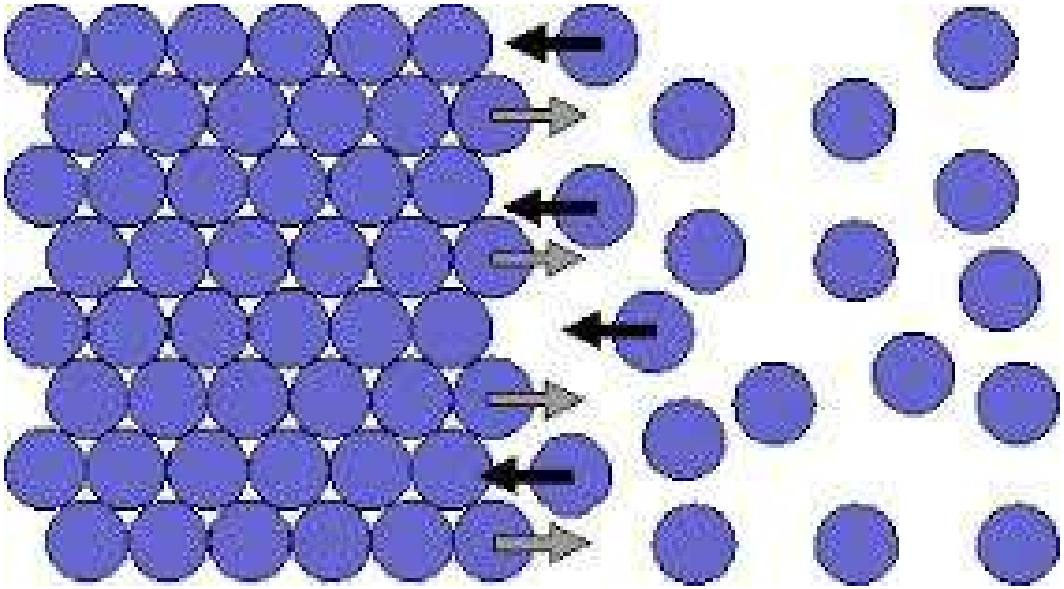
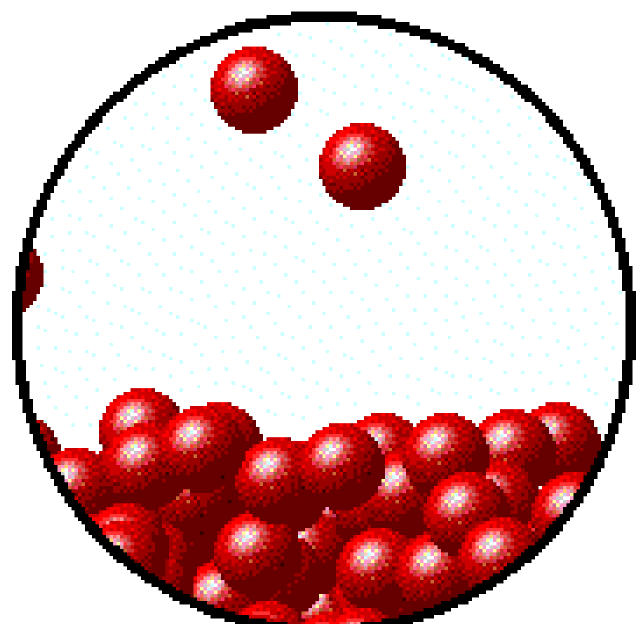
Chapter 15: Chemical Equilibrium



Jennie L. Borders

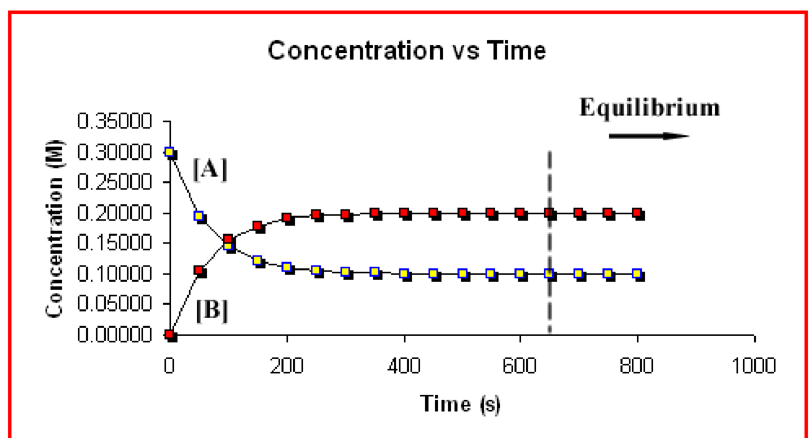
Section 15.1 – The Concept of Equilibrium

- At equilibrium, two opposing processes are occurring at the same rate.
- Ex: vapor pressure of a liquid in a closed container.



Chemical Equilibrium

- In chemical equilibrium, the rate at which the products are formed from reactants equals the rate at which the reactants are formed from products.
- As a result, concentrations cease to change, making the reaction appear to be stopped.



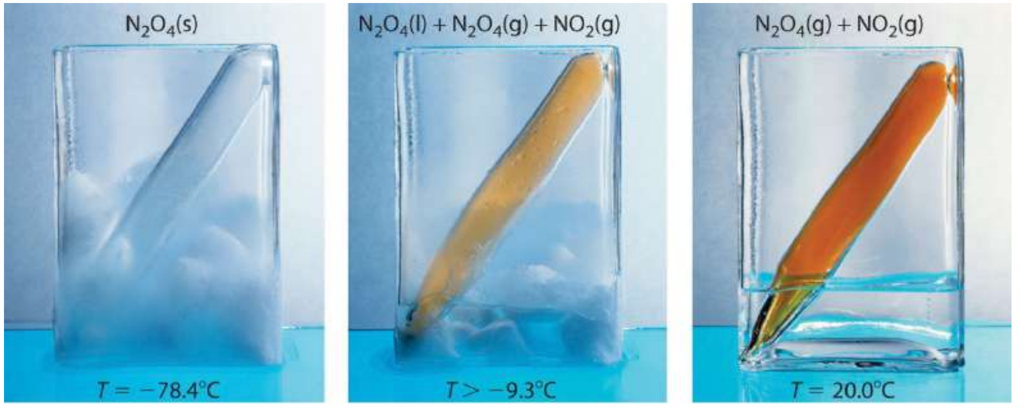
Reversible Reactions

- Equilibrium mixture occur in reversible reactions.

$$N_2O_{4(g)} \leftarrow\rightarrow 2NO_{2(g)}$$

→is considered the "forward" reaction

← is considered the "reverse" reaction



Reversible Reactions

$N_2O_{4(g)} \leftarrow\rightarrow 2NO_{2(g)}$

Forward Reaction: Rate = $k_f[N_2O_4]$

Reverse Reaction: Rate = $k_r[NO_2]^2$

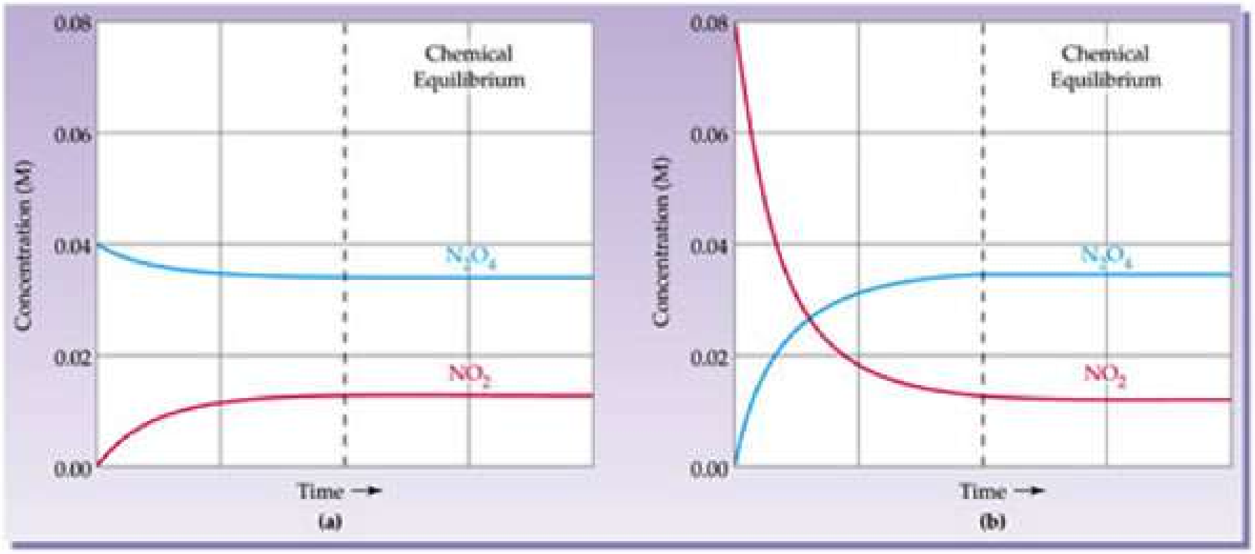
The rates are equal so…

$$K_f[N_2O_4] = k_r[NO_2]^2$$

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_r} = \text{constant}$$

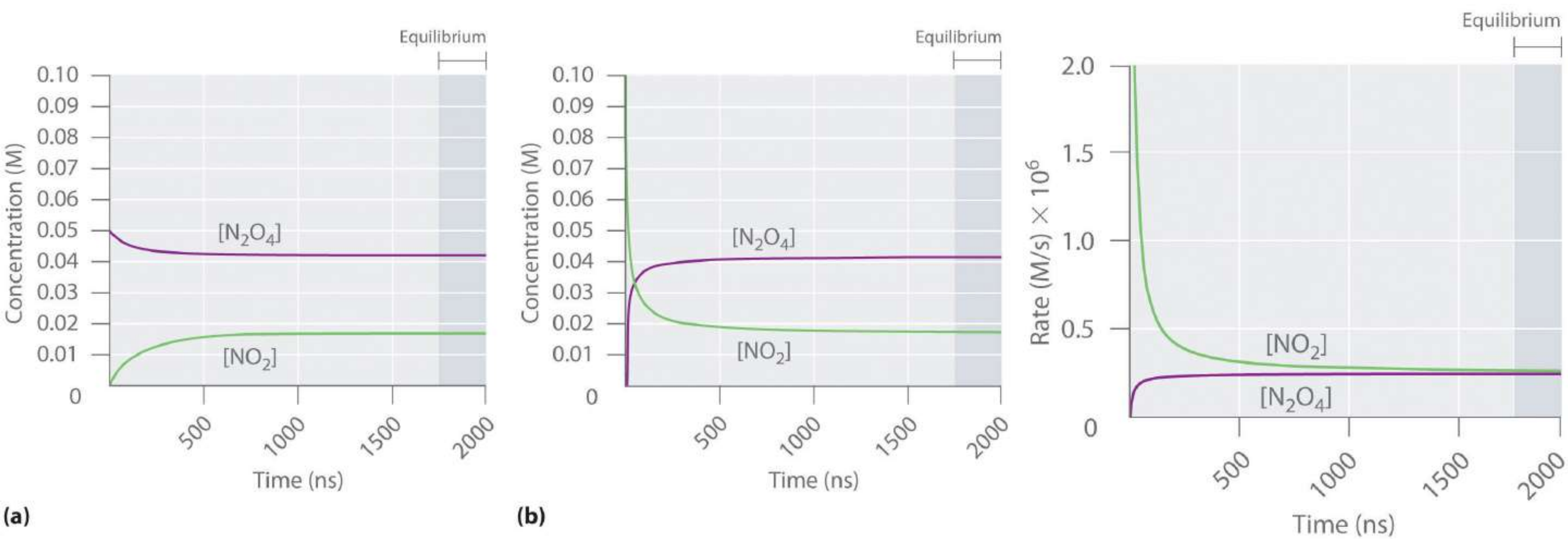
Equilibrium

- It doesn't make any difference whether we start with the reactants, products, or some mixture of the two. At equilibrium, the ratio equals a specific value at a certain temperature.



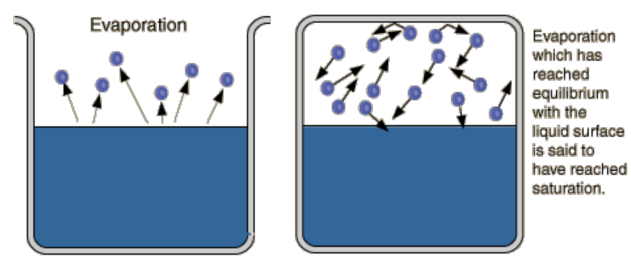
Equilibrium

- At equilibrium the concentrations of the reactants and products do not change and the rates of each process are equal.



3 Important Equilibrium Concepts

1. At equilibrium, the concentrations of reactants are products no longer change.
2. For equilibrium to occur, neither reactants nor products can escape from the system.
3. At equilibrium a particular ratio of concentration terms equal a constant.



Section 15.2 – The Equilibrium Constant

- The constant formed by the ratio of the concentration of products to reactants is called the equilibrium constant, K_c.

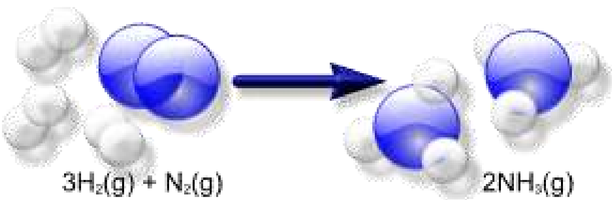
$$aA + bB \rightarrow dD + eE$$

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

- The c in K_c means that the values are concentrations with the units of molarity.

Equilibrium Expression

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$



$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

- Unlike the rate law, the equilibrium expression can be written from the balanced equation.
- The value K_c depends only on temperature, not on the initial amounts of products and reactants.

Sample Exercise 15.1

- Write the equilibrium expression for K_c for the following reactions:

a. $2O_3 \leftrightarrow 3O_2$

b. $2NO + Cl_2 \leftrightarrow 2NOCl$

c. $Ag^+ + 2NH_3 \leftrightarrow Ag(NH_3)_2^+$

Practice Exercise

- Write the equilibrium-constant expression, K_c, for

a. $H_2 + I_2 \leftrightarrow 2HI$

b. $Cd^{2+} + 4Br^- \leftrightarrow CdBr_4^{2-}$

K_c

- When using the K_c expression, equilibrium concentrations must be used.
- K_c has no units.
- K_c does not change as initial concentrations change.

TABLE 15.1 Initial and Equilibrium Concentrations (M) of N_2O_4 and NO_2 in the Gas Phase at 100°C

Experiment	Initial N_2O_4 Concentration (M)	Initial NO_2 Concentration (M)	Equilibrium N_2O_4 Concentration (M)	Equilibrium NO_2 Concentration (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

K_p

- K_c has concentrations in terms of molarity.
- K_p has partial pressures in terms of atmospheres.

$$aA + bB \leftarrow\rightarrow dD + eE$$

$$K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$$

K_c vs. K_p

- You can convert between K_c and K_p by using the following equation:

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

- Δn = moles of gaseous product – moles of gaseous reactants.

Sample Exercise 15.2

- In the synthesis of ammonia from nitrogen and hydrogen,

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

K_c = 9.60 at 300^{o}C. Calculate K_p for this reaction at this temperature.

Practice Exercise

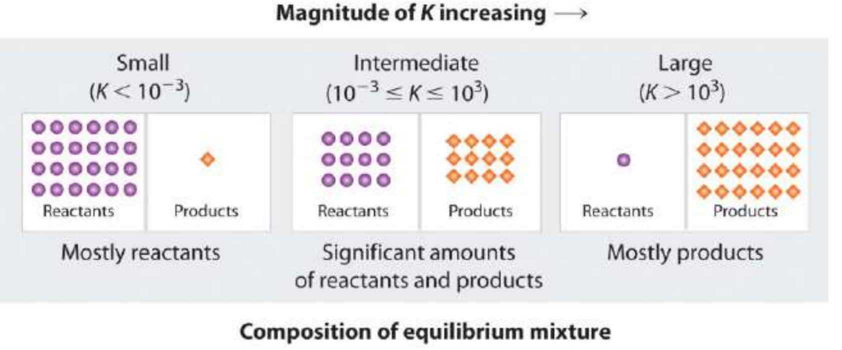
- For the equilibrium

$$2SO_{3(g)} \leftrightarrow 2SO_{2(g)} + O_{2(g)}$$

K_c is 4.08×10^{-3} at 1000K. Calculate the value for K_p.

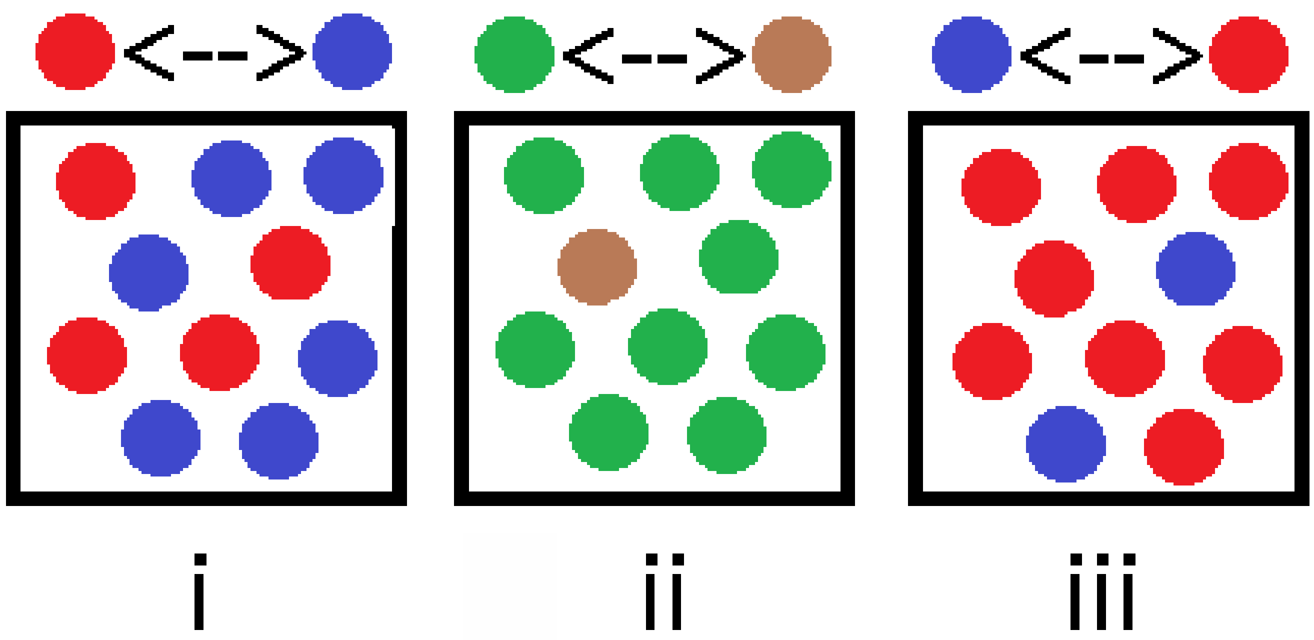
Section 15.3 – Interpreting and Working with Equilibrium Constants

- If K > 1: Equilibrium lies to the right; products predominate.
- If K < 1: Equilibrium lies to the left; reactants predominate.
- Remember the opposing reaction rates are equal at equilibrium, not the actual concentrations.



Sample Exercise 15.3

- The following diagrams represent 3 different systems at equilibrium, all in the same size containers.



Sample Exercise 15.3 con't

a. Without doing any calculations, rank the 3 systems in order of increasing equilibrium constant, K_c.

b. If the volume of the containers is 1.0L and each sphere represents 0.10 mol, calculate K_c for each system.

Practice Exercise

- For the reaction,

$$H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$$

K_p = 794 at 298K and K_p = 54 at 700K. Is the formation of HI favored more at the higher or lower temperature?

Reverse Reactions

- The equilibrium-constant expression for a reaction written in one direction is the reciprocal of the one for the reaction written in the reverse direction.

$N_2O_4 \leftrightarrow 2NO_2 \qquad K_c = \dfrac{[NO_2]^2}{[N_2O_4]} = 0.212$

$2NO_2 \leftrightarrow N_2O_4 \qquad K_c = \dfrac{[N_2O_4]}{[NO_2]^2} = 4.72$

$1/0.212 = 4.72$

Sample Exercise 15.4

- The equilibrium constant for the following reaction is 1 x 10^{-30} at 25^{o}C:

$$N_2 + O_2 \leftarrow\rightarrow 2NO$$

Using this information, write the equilibrium constant expression and calculate the equilibrium constant for the following reaction:

$$2NO \leftarrow\rightarrow N_2 + O_2$$

Practice Exercise

- For the following reaction,

$$N_2 + 3H_2 \leftarrow\rightarrow 2NH_3$$

$K_p = 4.34 \times 10^{-3}$ at 300^oC. What is the value of K_p for the reverse reaction?

Hess' Law

- When adding reactions to give a new overall reaction:

1. The equilibrium constant of a reverse reaction is the inverse of the forward reaction.
2. The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power equal to that number.

Hess' Law

3. The equilibrium constant for a net reaction made up of 2 or more steps is the product of the equilibrium constants for the individual steps.

Sample Exercise 15.5

- Given the following information,

$HF \leftrightarrow H^+ + F^-$ $K_c = 6.8 \times 10^{-4}$

$H_2C_2O_4 \leftrightarrow 2H^+ + C_2O_4^{2-}$ $K_c = 3.8 \times 10^{-6}$

Determine the value of K_c for the reaction

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

Practice Exercise

- Given that at 700K

$$H_2 + I_2 \leftrightarrow 2HI \quad K_p = 54.0$$

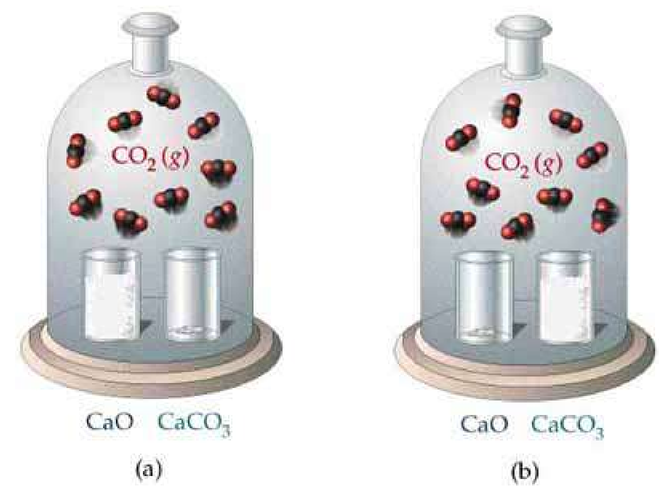
$$N_2 + 3H_2 \leftrightarrow 2NH_3 \quad K_p = 1.04 \times 10^{-4}$$

Determine the value of K_p for the reaction

$$2NH_3 + 3I_2 \leftrightarrow 6HI + N_2$$

Section 15.4 – Heterogeneous Equilibria

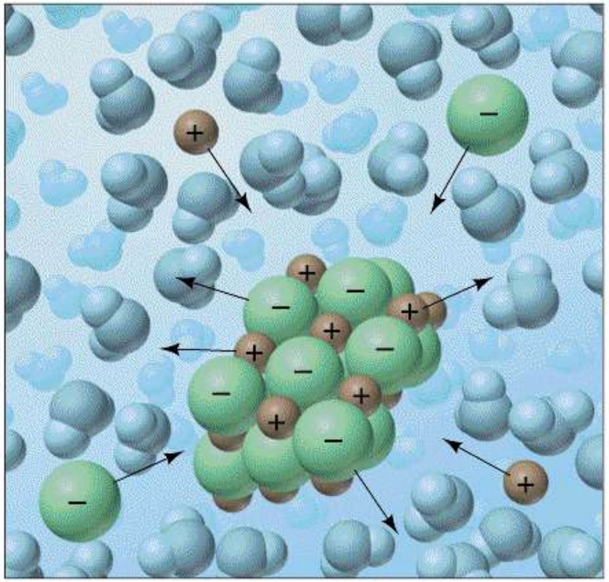
- Homogeneous equilibrium occurs when all substances are the same phase.
- Heterogeneous equilibrium occurs when all substances are in different phases.
- When pure solids or liquids are in an equilibrium mixture, they are not included in the equilibrium expression because the concentration cannot change.



Equilibrium Expression

$$PbCl_{2(s)} \leftrightarrow Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

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



Sample Exercise 15.6

- Write the equilibrium-constant expression for K_c for each of the following reactions:

a. $CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(l)}$

b. $SnO_{2(s)} + 2CO_{(g)} \leftrightarrow Sn_{(s)} + 2CO_{2(g)}$

Practice Exercise

- Write the following equilibrium-constant expressions:

a. K_c - $Cr_{(s)} + 3Ag^{+}_{(aq)} \leftarrow\rightarrow Cr^{3+}_{(aq)} + 3Ag_{(s)}$

b. K_p – $3Fe_{(s)} + 4H_2O_{(g)} \leftarrow\rightarrow Fe_3O_{4(s)} + 4H_{2(g)}$

Sample Exercise 15.7

- Each of the following mixtures was placed in a closed container and allowed to stand. Which is capable of attaining the equilibrium $CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$:

a. Pure $CaCO_3$

b. CaO and a CO_2 pressure greater than the value for K_p

c. Some $CaCO_3$ and a CO_2 pressure greater than the value of K_p

d. $CaCO_3$ and CaO

Practice Exercise

- When added to $Fe_3O_{4(s)}$ in a closed container, which one of the following substances – $H_{2(g)}$, $H_2O_{(g)}$, $O_{2(g)}$ – will allow equilibrium to be established in the reaction

$$3Fe_{(s)} + 4H_2O_{(g)} \leftarrow\rightarrow Fe_3O_{4(s)} + 4H_{2(g)}$$

Section 15.5 – Calculating Equilibrium Constants

- Remember when using an equilibrium equation, you must use equilibrium concentrations or partial pressures.

In the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

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

[A] = concentration of A in $moldm^{-3}$

a = number of moles of A

Sample Exercise 15.8

- A mixture of hydrogen and nitrogen in a reaction vessel is allowed to reach equilibrium at 472°C. The equilibrium mixture of gases was analyzed and found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. Calculate the equilibrium constant K_p for the reaction

$$N_2 + 3H_2 \leftarrow\rightarrow 2NH_3$$

Practice Exercise

- An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25°C: $[HC_2H_3O_2]$ = 1.65×10^{-2}M; $[H^+] = 5.44 \times 10^{-4}$M; and $[C_2H_3O_2^-] = 5.44 \times 10^{-4}$M. Calculate the equilibrium constant K_c for the following reaction:

$$HC_2H_3O_2 \leftrightarrow H^+ + C_2H_3O_2^-$$

Equilibrium Problems

- Sometimes you are not given all of the equilibrium concentrations.
- You must use the information given to calculate the equilibrium concentrations in an ICE (initial, change, equilibrium) chart.

	B	+ H_2O	$\rightleftarrows$ BH^+	+ OH^-
I	moles B	--------	0	0
C	-0.3 mol	--------	+0.3 mol	+0.3 mol
E	moles B – 0.3	--------	0.3 mol	0.3 mol

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Sample Exercise 15.9

- A closed system initially contains 1.000×10^{-3}M H_2 and 2.000×10^{-3}M I_2 at 448^{o}C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3}M. Calculate K_c at 448^{o}C for the reaction

$$H_2 + I_2 \leftrightarrow 2HI$$

Practice Exercise

- Sulfur trioxide decomposes at high temperature in a sealed container:

$$2SO_3 \leftrightarrow 2SO_2 + O_2$$

Initially, the vessel is charged at 1000K with SO_3 at a partial pressure of 0.500atm. At equilibrium the SO_3 partial pressure is 0.200 atm. Calculate the value of K_p at 1000K.

Section 15.6 – Applications of Equilibrium Constants

- Equilibrium concentrations are used to calculate the equilibrium constant K_c.
- Initial concentrations are used to calculate the reaction quotient Q.
- The expression for Q is identical to K, but initial concentrations (or partial pressures) are used.

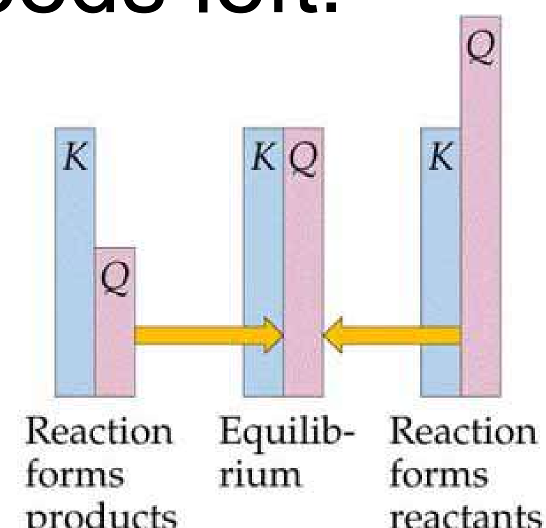
$$aA + bB \rightleftharpoons cC + dD \qquad (1)$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (2a) \qquad K_{eq} = \frac{[C]_{eq}^c[D]_{eq}^d}{[A]_{eq}^a[B]_{eq}^b} \qquad (2b)$$

Direction of Reaction

- The value of Q tells us which way the reaction will proceed to reach equilibrium:

1. Q = K; Reaction is at equilibrium.
2. Q>K: The concentration of products is too large, so reaction proceeds left.
3. Q<K: The concentration of reactants is too large, so reaction proceeds right.



Sample Exercise 15.10

- At 448°C the equilibrium constant K_c for the reaction

$$H_2 + I_2 \leftrightarrow 2HI$$

Is 50.5. Predict in which direction the reaction will proceed to reach equilibrium at 448°C if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol H_2, and 3.0×10^{-2} mol of I_2 in a 2.00L container.

Practice Exercise

- At 1000K the value of K_p for the reaction

$$2SO_3 \leftrightarrow 2SO_2 + O_2$$

is 0.338. Calculate the value for Q_p, and predict the direction in which the reaction will proceed toward equilibrium if the initial partial pressures are $P_{SO3} = 0.16$ atm; $P_{SO2} = 0.41$ atm; $P_{O2} = 2.5$ atm.

Equilibrium Problems with Unknowns

- Sometimes certain equilibrium concentrations are unknown.
- If we know the value for K, then we can solve for the unknown concentration.

Sample Exercise 15.11

- For the Haber process

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

$K_p = 1.45 \times 10^{-5}$ at 500°C. In an equilibrium mixture of the three gases at 500°C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

Practice Exercise

- At 500K the reaction

$$PCl_5 \leftrightarrow PCl_3 + Cl_2$$

has $K_p = 0.497$. In an equilibrium mixture at 500K, the partial pressure of PCl_5 is 0.860 atm and that of PCl_3 is 0.350 atm. What is the partial pressure of Cl_2 in the equilibrium mixture?

Harder Equilibrium Problems

- Sometimes you have to calculate the equilibrium concentrations.
- When this happens we have to plug X's in the ice chart.

	B +	H_2O ⇄	BH^+ +	OH^-
I	[B]	--------	0	0
C	-x	--------	+x	+x
E	[B] - x	--------	x	x

Harder Equilibrium Problems

- I hope that you remember the quadratic equation:

$$X = \frac{-b +/- (b^2 - 4ac)^{1/2}}{2a}$$

- Only one answer will be possible.

Sample Exercise 15.12

- A 1.000L flask is filled with 1.000 mol of H_2 and 2.000 mol of I_2 at 448°C. The value of the equilibrium constant K_c for the reaction

$$H_2 + I_2 \leftrightarrow 2HI$$

at 448°C is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI in moles per liter?

Practice Exercise

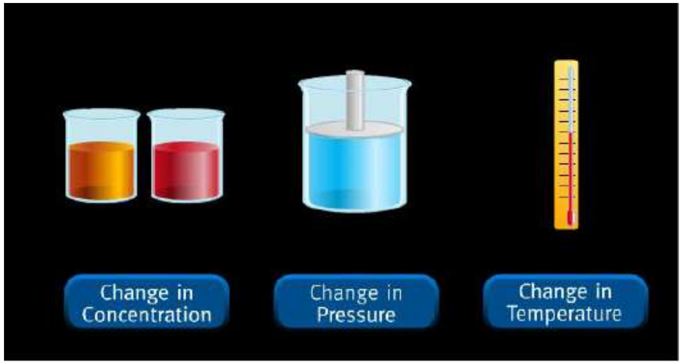
- For the equilibrium

$$PCl_5 \leftrightarrow PCl_3 + Cl_2$$

the equilibrium constant K_p has the value 0.497 at 500K. A gas cylinder at 500K is charged with PCl_5 at an initial pressure of 1.66 atm. What are the equilibrium pressures of PCl_5, PCl_3, and Cl_2 at this temperature?

Section 15.7 – Le Chatelier's Principle

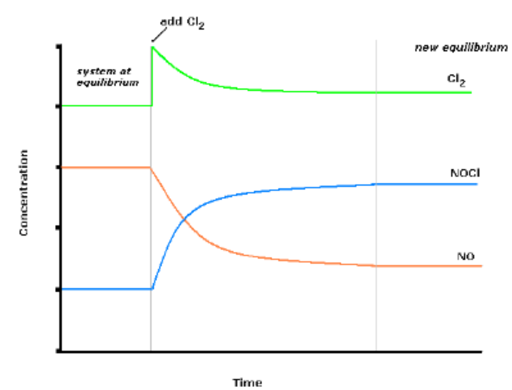
- Le Chatelier's Principle states that if a system at equilibrium is disturbed, then the system will shift to counteract the disturbance.
- Disturbances include change in concentration, change in pressure, change in temperature, and addition of a catalyst.



Concentration

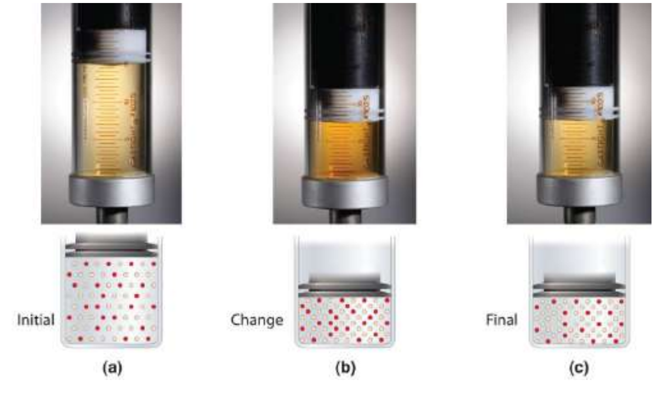
- If the concentration of a reactant or product is increased, then the equilibrium shifts to consume the excess substance.
- If the concentration of a reactant or product is decreases, then the equilibrium shifts to make more of the substance.

$2NO + Cl_2 \leftarrow\rightarrow 2NOCl$



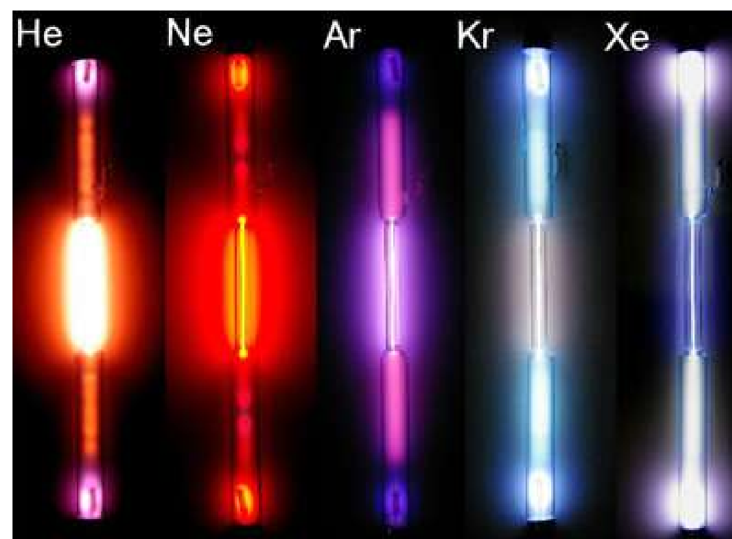
Pressure/Volume

- If the volume decreases/pressure increases, then the equilibrium shifts to the side with the lowest number of moles of gases.
- If the volume increases/pressure decreases, then the equilibrium shifts to the side with the highest number of moles of gases.



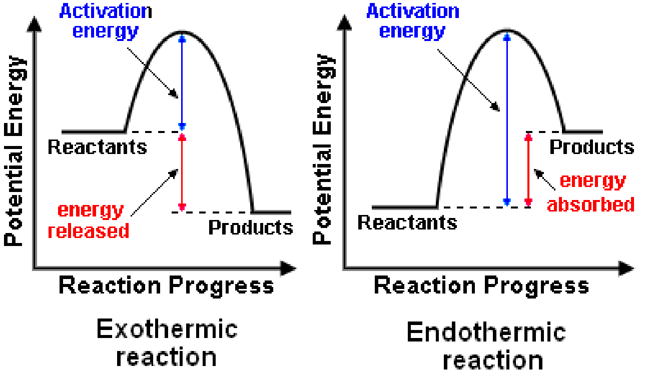
Pressure and Inert Gases

- The pressure can also be increased by adding an inert gas that is not involved in the reaction.
- Since the inert gas will not change the partial pressures of the gases, there is no shift in the equilibrium.



Temperature

- When there is a change in temperature the ΔH must be taken into account.
- If ΔH is positive, then the reaction is endothermic and heat can be considered a reactant.
- If ΔH is negative, then the reaction is exothermic and heat can be considered a product.



Temperature

- Once heat is considered a reactant or product, then we can follow the rules for change in concentration.
- If heat is added, the reaction shifts to reduce the heat.
- If heat is released, the reaction shifts to produce more heat.

Sample Exercise 15.13

- Consider the equilibrium

$$N_2O_4 \leftrightarrow 2NO_2 \quad \Delta H = 58.0kJ$$

In which direction will the equilibrium shift when

a. N_2O_4 is added

b. NO_2 is removed

c. The total pressure is increased by the addition of N_2

d. The volume is increased

e. The temperature is decreased

Practice Exercise

- For the reaction

$$PCl_5 \leftarrow\rightarrow PCl_3 + Cl_2 \quad \Delta H = 87.9kJ$$

In which direction will the equilibrium shift when

a. Cl_2 is removed

b. The temperature is decreased

c. The volume of the reaction system is increased

d. PCl_3 is added

Standard Heat of Formation

- The standard heat of formation is calculated the following way:

$$\Delta H = \Sigma(\Delta H \text{ products}) - \Sigma(\Delta H \text{ reactants})$$

Sample Exercise 15.14

a. Using the standard heat of formation data in Appendix C, determine the standard enthalpy change for the reaction

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

b. Determine how the equilibrium constant for this reaction should change with temperature.

Practice Exercise

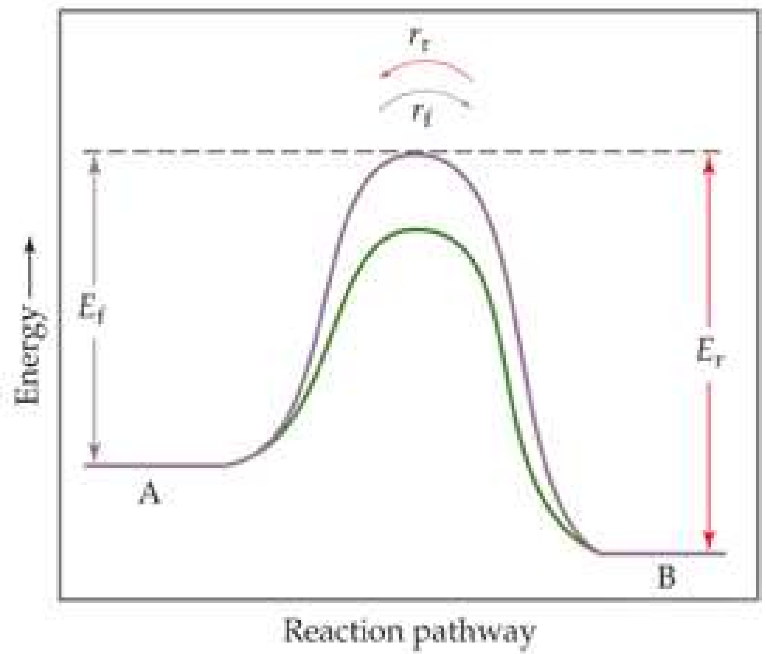
- Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction

$$2POCl_3 \leftarrow\rightarrow 2PCl_3 + O_2$$

Use the result to determine how the equilibrium constant for the reaction should change with temperature.

Catalysts

- The addition of a catalyst lowers the activation energy for a reaction.
- This activation energy is lowered for both the forward and reverse reaction.



Catalysts

- Since the activation energy for both processes is lowered by the same amount, the catalyst will increase the rate at which equilibrium is achieved, but it will not cause a shift in the equilibrium.

Sample Integrative Exercise

- At temperatures near 800^oC, steam is passed over hot coke (a form of carbon) reacts to form CO and H_2:

$$C_{(s)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + H_{2(g)}$$

The mixture of gases that results is an important industrial fuel called water gas.

Sample Integrative Exercise

a. At 800°C the equilibrium constant for the reaction is $K_p = 14.1$. What are the equilibrium partial pressures of H_2O, CO, and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H_2O in a 1.00L reaction vessel?

Sample Integrative Exercise

b. What is the minimum amount of carbon required to achieve equilibrium under these conditions?

c. What is the total pressure in the vessel at equilibrium?

Sample Integrative Exercise

d. At 25^{o}C the value of K_p for this reaction is 1.7×10^{-21}. Is the reaction exothermic or endothermic?

e. To produce the maximum amount of CO and H_2 at equilibrium, should the pressure of the system be increased or decreased?