

# ***GENERAL CHEMISTRY***

## ***Chapter 6*** **Chemical Equilibrium**

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# Introduction

- Some chemical reactions simply run in one direction until at least one of the reactants are used up.



- These reactions are said to be irreversible, one-way reaction, complete reaction.
- One-way arrow is used in the equation

# Reversible reaction

- Consider colorless frozen  $\text{N}_2\text{O}_4$ . At room temperature, it decomposes to brown  $\text{NO}_2$ :



- After some time, the color stops changing  $\rightarrow$  stop
- Analyze the mixture, found a mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ .
- The opposite direction should take place at the same time
- These reaction are reversible, two-way reaction, incomplete reaction, equilibrium reaction
- Double arrows are used

# The Concept of Equilibrium

- **Chemical equilibrium** is the point at which the concentrations of all species are constant.
- “stop” (overall)
- Chemical equilibrium occurs when the reverse direction proceed at equal rates as the forward reaction.

# Collision Model: Understanding Equilibrium

- **Using the collision model:**
  - At the beginning of the reaction, there is no  $\text{NO}_2$  so the reverse reaction ( $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ ) does not occur.
    - Only the production of  $\text{NO}_2$  will occur.
  - As the amount of  $\text{NO}_2$  builds up, there is a chance that two  $\text{NO}_2$  molecules will collide to form  $\text{N}_2\text{O}_4$ .
    - Thus, the forward chemical reaction has an opposing reaction that will increase with the increase in product formation.

# Dynamic Equilibrium

- After some time: rate of forward = rate of reverse
- The point at which the rate of decomposition:



equals the rate of dimerization:



is dynamic equilibrium.

- The equilibrium is dynamic because the reaction has not stopped: the opposing rates are equal.

# Expressing Equilibrium Reactions

- At equilibrium, as much  $\text{N}_2\text{O}_4$  reacts to form  $\text{NO}_2$  as  $\text{NO}_2$  reacts to re-form  $\text{N}_2\text{O}_4$ :



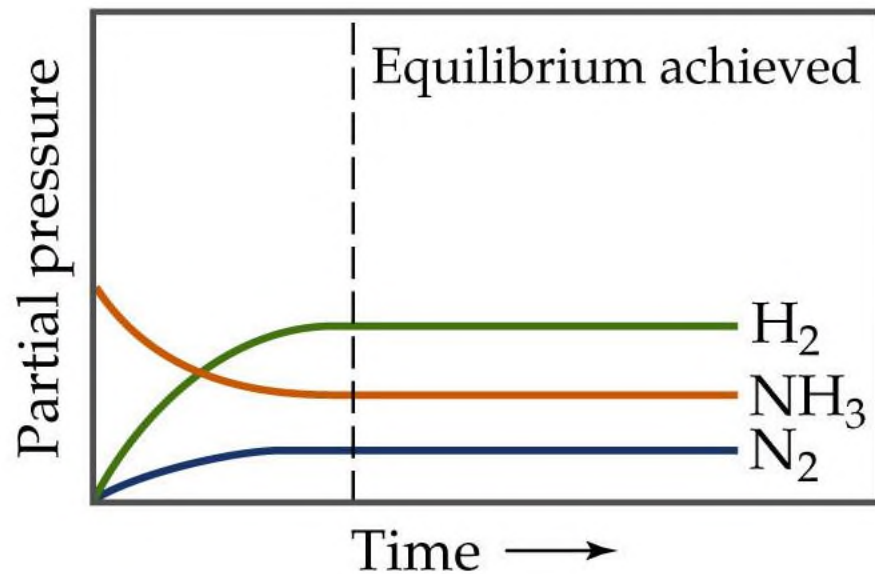
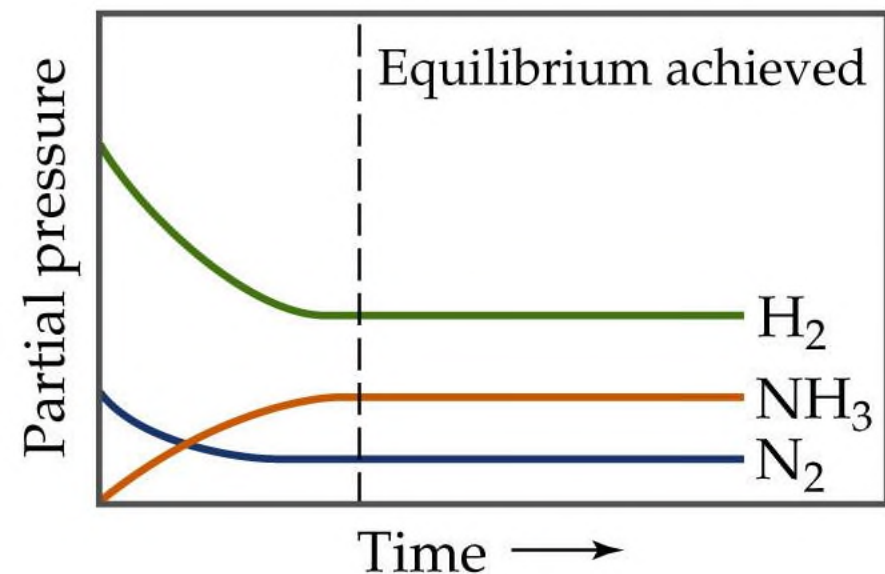
- The double arrow implies the process is dynamic.
- Consider

Forward reaction:  $\text{A} \rightarrow \text{B}$  Rate =  $k_f[\text{A}]$

Reverse reaction:  $\text{B} \rightarrow \text{A}$  Rate =  $k_r[\text{B}]$

- At equilibrium  $k_f[\text{A}] = k_r[\text{B}]$ , which implies  $\text{A} \rightleftharpoons \text{B}$
- The mixture at equilibrium is called an equilibrium mixture.
- $[\text{B}]/[\text{A}] = k_f/k_r = \text{const}$  at a given temperature

# The Equilibrium Constant



- No matter the starting composition of reactants and products, the same ratio of concentrations is achieved at equilibrium.



# Defining the Equilibrium Constant

- For a general reaction in the gas phase



the equilibrium constant expression is

$$K_{eq} = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where  $K_{eq}$  is the equilibrium constant.

# Defining the Equilibrium Constant

- For a general reaction



the **equilibrium constant** expression is

$$K_{eq} = \frac{\prod [\text{products}]^{c,d}}{\prod [\text{reactants}]^{a,b}}$$

where  $K_{eq}$  is the equilibrium constant.

Species i: (1) gas: partial pressure  $p_i$

(2) solution: molarity (molar conc.)  $C_i$

(3) pure solid, pure liquid, solvent: skip

# Defining the Equilibrium Constant

- If the rxn has only gas or gas+pure solid/liquid/solvent

$$K_{eq} = \frac{P_C^c P_D^d}{P_A^a P_B^b} = K_P$$

- Gas also has the concentration (mol/L)

$$p_i V = n_i RT \qquad p_i = C_i RT$$

$$K_C = \frac{C_C^c C_D^d}{C_A^a C_B^b}$$

$$K_P = K_C (RT)^{\Delta n_{gas}}$$

$$\Delta n_{gas} = (c + d) - (a + b) \Big|_{gas}$$

# Defining the Equilibrium Constant

- There are two equilibrium constant
- $K_{eq}=K_P$  : primary (use in thermodynamic relation)
- $K_C$  : constant, but secondary
- $R=0.082 \text{ atm.L/mol.K}$

$$K_C = K_P (RT)^{-\Delta n_{gas}}$$

# Defining the Equilibrium Constant

- If the rxn has only solution or solution+solid/liquid/solvent

$$K_{eq} = \frac{C_C^c C_D^d}{C_A^a C_B^b} = K_C$$

No  $K_P$

- If the rxn has both gas+solution:  
only  $K_{eq}$  (no  $K_P$ , no  $K_C$ )

# The Equilibrium Constant

- For a general reaction



the equilibrium constant expression for everything in solution is

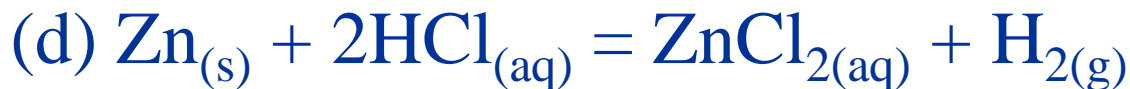
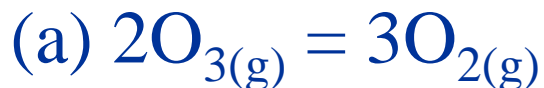
$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where  $K_{eq}$  is the equilibrium constant, A, B, C, and D are the reactants and products, and a, b, c, and d are the stoichiometric coefficients.

# Class Practice Problem:

## Writing Equilibrium Expressions (2)

- Write the equilibrium constant expression  $K_{eq}$ ,  $K_P$  and  $K_C$  (if any) and the relation between  $K_P$  and  $K_C$  (if any) of the following reactions:



# Properties of the Equilibrium Constant

- $K_{eq}$  is based on the amount of reactants and products **at equilibrium**.
- We generally omit the units of the equilibrium constant.
- Note that the equilibrium constant expression has products over reactants.
  - $K > 1$  implies products are favored, and  $K_{eq}$  lies to the right.
  - $K < 1$  implies reactants are favored, and  $K_{eq}$  lies to the left.
- The same equilibrium is established not matter how the reaction is begun.



# Meaning of Equilibrium Constant

- $K > 1$ : reaction is product-favored; equilibrium concentrations of products are greater than equilibrium concentrations of reactants.
- $K \gg 1$ : rxn becomes complete (one-way) ( $K > 10^7$ ): at equilibrium: no reactant, only product
- $K < 1$ : reaction is reactant-favored; equilibrium concentrations of reactants are greater than equilibrium concentrations of products.
- $K \ll 1$ : rxn does not occur ( $K < 10^{-7}$ ): at equilibrium: no product, only reactant

# Forward Equilibrium Direction

- An equilibrium can be approached from any direction.
- Example:



- Has

$$K_{eq} = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = 6.46$$

# Reverse Equilibrium Direction

- In the reverse direction:



- Thus,

$$K_{eq} = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = 0.155 = \frac{1}{6.46}$$

# Squaring Equilibrium Constants

- The reaction



- has

$$K_{eq} = \frac{P_{\text{NO}_2}^4}{P_{\text{N}_2\text{O}_4}^2}$$

- which is the square of the equilibrium constant for



# Heterogeneous Equilibria

- When all reactants and products are in one phase, the equilibrium is homogeneous.
- If one or more reactants or products are in a different phase, the equilibrium is heterogeneous.
- Consider:



- experimentally, the amount of  $\text{CO}_2$  does not seem to depend on the amounts of  $\text{CaO}$  and  $\text{CaCO}_3$ . Why?

# Heterogeneous Equilibria

- The concentration of a solid or pure liquid is its density divided by molar mass.
- Neither density nor molar mass is a variable, the concentrations of solids and pure liquids are constant.
- For the decomposition of  $\text{CaCO}_3$ :

$$K_{eq} = \frac{[\text{CaO}]}{[\text{CaCO}_3]} \times [\text{CO}_2] = \text{constant} \times [\text{CO}_2]$$

- Thus, if a pure solid or a pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium expression for the reaction.

# $K_{eq}$ Problem Solving

- In one of their experiments, Harber and co-workers introduced a mixture of hydrogen and nitrogen into a reaction vessel and allowed the system to attain chemical equilibrium at 472 °C. The equilibrium mixture of gases was analyzed and found to contain 0.1207 *M* H<sub>2</sub>, 0.0402 *M* N<sub>2</sub>, and 0.00272 *M* NH<sub>3</sub>. From these data, calculate the equilibrium constant,  $K_{eq}$  ( $K_P$  and  $K_C$ ) for



# $K_{eq}$ Problem Solving

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# Calculating $K_{eq}$ Practice Problem

- Gaseous Hydrogen iodide is placed in a closed container at 425 °C, where it partially decomposes to hydrogen and iodine:  $2\text{HI (g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$ . At equilibrium, it is found that  $[\text{HI}] = 3.35 \times 10^{-3} \text{M}$ ;  $[\text{H}_2] = 4.79 \times 10^{-4} \text{M}$ ;  $[\text{I}_2] = 4.79 \times 10^{-4} \text{M}$ . What is the value of  $K_{eq}$  at this temperature.

1/ A mixture of 0.100 mole of NO, 0.050 mole of H<sub>2</sub>, and 0.050 mole of H<sub>2</sub>O is placed in a 1.00-L vessel. The following equilibrium is established:



(a) Calculate the K<sub>C</sub> for the reaction, knew at eq. there is 0.060 mol of NO.

2/ A mixture of 0.100 mole of NO, 0.050 mole of H<sub>2</sub>, and 0.050 mole of H<sub>2</sub>O is placed in a 1.00-L vessel (at 25<sup>0</sup>C). The following equilibrium is established:



• Calculate the concentration at equilibrium of all substances in this reaction at the same temperature, knew the eq. constant K<sub>C</sub> is 4.

# Calculating Equilibrium Constants

- Proceed as follows:
  - Tabulate the initial and the equilibrium concentrations (or partial pressures) that are given.
  - If an initial and equilibrium concentration is given for a species, calculate the change in concentration.
  - Use stoichiometry on the change in concentration line only to calculate the changes in concentration of all other species in the equilibrium .
  - Use initial concentrations and the changes in concentration to calculate the equilibrium concentration. These are used to evaluate the equilibrium constant.

# Calculating Equilibrium Concentrations

- The same steps used to calculate equilibrium constants are used.
- Generally, we do not have a number for the change in concentration line.
- Therefore, we need to assume that  $x$  mol/L of a species is produced (or used).
- The equilibrium concentrations are given as algebraic expressions of  $x$ .
- Solve for  $x$  from known equilibrium constant

# Class Example Problem

- Enough ammonia is dissolved in 5.00 liters of water at 25 °C to produce a solution that is 0.0124 *M* in ammonia. The solution is then allowed to come to equilibrium. Analysis of the equilibrium mixture shows that the concentration of OH<sup>-</sup> is 4.64 x 10<sup>-4</sup>*M*. Calculate K<sub>eq</sub> at 25 °C for the reaction.



# Class Example Problem Cont.

- A mixture of  $5.00 \times 10^{-3}$  mol of  $\text{H}_2$  and  $1.00 \times 10^{-2}$  mol of  $\text{I}_2$  is placed in a 5.00-L container at  $448^\circ\text{C}$  and allowed to come to equilibrium. Analysis of the equilibrium mixture shows that the concentration of  $\text{HI}$  is  $1.87 \times 10^{-3} \text{ M}$ .

Calculate the  $K_{\text{eq}}$  at  $448^\circ\text{C}$  for the reaction



# Class Practice Problem at Home

- Sulfur trioxide decomposes at high temperature in a sealed container:  $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$ . Initially the vessel is charged at 1000k with  $\text{SO}_3(g)$  at a concentration of  $6.09 \times 10^{-3} M$ . At equilibrium, the  $\text{SO}_3$  concentration is  $2.44 \times 10^{-3} M$ . Calculate the value for  $K_{\text{eq}}$  at 1000 K.

# Class Practice Problem

- A 1.00-L flask is filled with 1.000 mol of  $\text{H}_2$  and 2.000 mol of  $\text{I}_2$  at 448 °C. The value of the equilibrium constant,  $K_{\text{eq}}$ , for the reaction:

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  at 448 °C is 50.5. What are the concentration of HI,  $\text{H}_2$ , and  $\text{I}_2$  in the flask at equilibrium.



- A mixture of 0.100 mole of NO, 0.050 mole of H<sub>2</sub>, 0.1 mole of N<sub>2</sub> and 0.050 mole of H<sub>2</sub>O is placed in a 1.00-L vessel (at 25<sup>0</sup>C). The following equilibrium is established:



- Calculate the concentration at equilibrium of all substances in this reaction at the same temperature, knew the eq. constant  $K_C$  is 4.

# Predicting Direction of Reaction

- A mixture of products and reactants  $\rightarrow$  which direction?
- We define  $Q$ , the reaction quotient, for a general reaction



as

$$Q = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

- $Q = K$  only at equilibrium.

# Predicting Direction of Reaction

- We define  $Q$ , the reaction quotient, for a general reaction



as  $Q = \frac{\text{products}^{c,d}}{\text{reactants}^{a,b}}$

Similar to  $K$ ,

$K$  is evaluated using equilibrium amount

$Q$  is evaluated at any point (amount at any point):

we have a mixture  $\rightarrow Q$

- $Q = K$  only at equilibrium.

# Predicting Direction of Reaction

- K: primary  $K_{eq}$ .      Q: primary (formulae as  $K_{eq}$ )

If the rxn is gas only or gas + pure solid/liquid/solvent)

There are two K:  $K_P$  and  $K_C$

But the primary K is  $K_{eq}=K_P$  not  $K_C$

There are two Q:  $Q_P$  and  $Q_C$

Primary Q is  $Q_P$

In thermodynamic relation, we should use the primary K and Q (not secondary)

# Reaction Quotient and Gibbs Free Energy

- At any point:  $\Delta G = \Delta G^0 + RT \ln Q$
- At equilibrium:  $\Delta G=0$ ,  $Q=K$ :  
$$\Delta G^0 = -RT \ln K_{eq}$$
- Combine these equation:

$$\Delta G = RT \ln \frac{Q}{K_{eq}}$$

$R=8.314 \text{ J}/(\text{mol.K})$

Q/K: Q and K should be same type  
primary or secondary

# Reaction Quotient and Direction

- If  $Q > K$  then  $\Delta G > 0$ , the reverse reaction must occur to reach equilibrium (i.e., products are consumed, reactants are formed, the numerator in the equilibrium constant expression decreases and  **$Q$  decreases** until it equals  $K$ ).
- If  $Q < K$  then  $\Delta G < 0$ , the forward reaction must occur to reach equilibrium ( $Q$  increases to  $K$ ).
- If  $Q = K$  then  $\Delta G = 0$ : the system is at equilibrium, no net reaction

# Temperature Dependence of the Equilibrium Constant

- From  $\Delta G^0 = -RT \ln K_{eq} = \Delta H^0 - T\Delta S^0$
- Applying at two temperature T1 and T2

$$\ln K_1 = -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R} \text{ and } \ln K_2 = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R}$$

- Subtracting

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$R=8.314 \text{ (J/mol.K)}$$

# Class Practice Problem (1)

- At 448 °C the equilibrium constant,  $K_{eq}$ , for the reaction:  
$$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$$
 is 50.5. Predict how the reaction will proceed to reach equilibrium at 448 °C if we start with  $2.0 \times 10^{-2}$  mol of HI,  $1.0 \times 10^{-2}$  mol of  $\text{H}_2$ , and  $3.0 \times 10^{-2}$  mol of  $\text{I}_2$  in a 2.0-L container.



## Class Practice Problem (2)

- Calculate  $\Delta G$  for the reaction  $\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$  under the conditions:  $T = 423 \text{ K}$ ,  $[\text{NO}] = 0.01 \text{ M}$ ,  $[\text{O}_2] = 0.20 \text{ M}$ , and  $[\text{N}_2] = 1.00 \times 10^{-4} \text{ M}$ . The value of  $\Delta G^\circ$  for this reaction is  $+22.7 \text{ kJ}$ . In which direction will the reaction proceed to reach equilibrium?

## Example

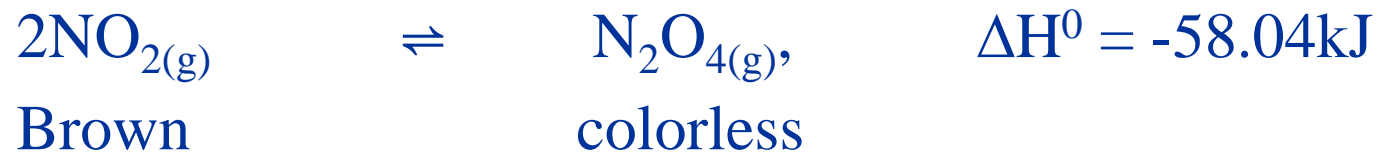


$$\Delta H_{298,f}^0 (kJ / mol) \quad -1205.93 \quad -634.94 \quad -392.92$$

$$S_{298}^0 (J / mol.K) \quad 92.63 \quad 39.71 \quad 213.31$$

estimate  $K_{eq}$  at 900 °C

## Example



- At 298K,  $K_p = 8.9$  . Estimate  $K_p$  at 273K



# Shift of equilibrium

System is at Equilibrium 1:  $\Delta G=0$

Disturb the system: change T, P, concentration

$\Delta G = \Delta G^0 + RT \ln Q$  because T changes or Q changes

→  $\Delta G \neq 0$

→ The system will react to establish new equilibrium

→ We call: the shift of equilibrium: from Equilibrium 1

→ equilibrium 2

→ Question: the shift of equilibrium: forward or reverse direction??

# Introducing Le Châtelier's Principle

- Consider the production of ammonia



- As the pressure increases, the amount of ammonia present at equilibrium increases.
- As the temperature decreases, the amount of ammonia at equilibrium increases.
- Can this be predicted?
  - Le Châtelier's Principle: if a system at equilibrium is disturbed, the system will move in such a way as to counteract the disturbance.

# Change in Reactant or Product Concentrations

- Consider the Haber process



- If  $\text{H}_2$  is added while the system is at equilibrium, the system must respond to counteract the added  $\text{H}_2$  (by Le Châtelier).
- The system must consume the  $\text{H}_2$  and produce products until a new equilibrium is established.
- So,  $[\text{H}_2]$  and  $[\text{N}_2]$  will decrease and  $[\text{NH}_3]$  increases.

# Effect of concentration

- At equilibrium 1:  $Q=K$ ,  $\Delta G=0$
- Add more product to system:  $Q$  increases  
( $Q=\text{product/reactant}$ ) now  $Q>K$  or  $\Delta G>0 \rightarrow$  rxn takes place in reverse direction
- Add reactant to system:  $Q$  decreases, now  $Q<K$  or  $\Delta G<0 \rightarrow$  rxn takes place in forward direction
- Remove product:  $Q$  decreases, now  $Q<K$  or  $\Delta G<0 \rightarrow$  rxn takes place in forward direction
- Remove reactant .....

# Application of Le Châtelier's Principle

- Adding a reactant or product shifts the equilibrium away from the increase (consume the increase).
- Removing a reactant or product shifts the equilibrium towards the decrease (produce the decrease).
- To optimize the amount of product at equilibrium, we need to flood the reaction vessel with reactant and continuously remove product (Le Châtelier).
- Reactive separation



# Effect of enthalpy on equilibrium constant

- $\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT\ln K_{eq}$
- Apply this formulae at two temperature T1 and T2
- $\ln K_1 = -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R}$       *and*       $\ln K_2 = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R}$
- $\ln \frac{K_2}{K_1} = -\frac{\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$

# Effect of Temperature

- Adding heat (i.e. heating the vessel) favors away from the increase:
  - if  $\Delta H > 0$ , adding heat favors the forward reaction,
  - if  $\Delta H < 0$ , adding heat favors the reverse reaction.
- Removing heat (i.e. cooling the vessel), favors towards the decrease:
  - if  $\Delta H > 0$ , cooling favors the reverse reaction,
  - if  $\Delta H < 0$ , cooling favors the forward reaction.

# Effect of Pressure

- Pressure only affect the gas (liquid and solid,  $V=\text{const}$ )
- Look at the gas in rxn
- System at equilibrium:  $Q=K$
- If increase the total pressure (P) 2 times, all of the partial pressure of gas species increases 2 times
- $$Q_{\text{new}} = \frac{p_C^c p_D^d}{p_A^a p_B^b} \frac{2^{c+d}}{2^{a+b}} = Q 2^{(c+d)-(a+b)} = Q \times 2^{\Delta n_{\text{gas}}}$$
- If  $\Delta n_{\text{gas}} > 0$ :  $Q_{\text{new}} > Q = K$ : rxn takes place in reverse direction (reduce the gas)
- If  $\Delta n_{\text{gas}} < 0$ :  $Q_{\text{new}} < Q = K$ : rxn takes place in forward direction (reduce the gas)

# Effect of Pressure

- Increase  $P \rightarrow$  direction that have less mole of gases (less pressure)
- Reduce  $P \rightarrow$  direction that have more moles of gas (more pressure)
- $\Delta n_{\text{gas}}=0$ : pressure has no effect ,  $Q_{\text{new}}=Q=K$

# Summary

- Add sth (concentration, T or heat, pressure)  
→ equilibrium will shift away from the increase (consume the increase)
- Remove sth (concentration, T or heat, pressure)  
→ Equilibrium will shift toward the decrease (produce the decrease)
- Le Châtelier's Principle: if a system at equilibrium is disturbed, the system will move in such a way as to counteract the disturbance.

# **The Effect of Catalysis**

- A catalyst lowers the activation energy barrier for the reaction.
- Therefore, a catalyst will decrease the time taken to reach equilibrium.
- A catalyst does not affect the composition of the equilibrium mixture.