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CHAPTER 6.0

CHEMICAL EQUILIBRIUM

CHEMISTRY 1
SK015

SESSION 2025/2026

STUDENT LEARNING TIME (SLT): LECTURE	
NON FACE-TO-FACE (PREPARATION)	FACE-TO-FACE (DURING CLASS)
2 HOURS	2 HOURS

Chemistry unit

CHEMISTRY UNIT, KMJ

6.0
CHEMICAL EQUILIBRIUM

6.1

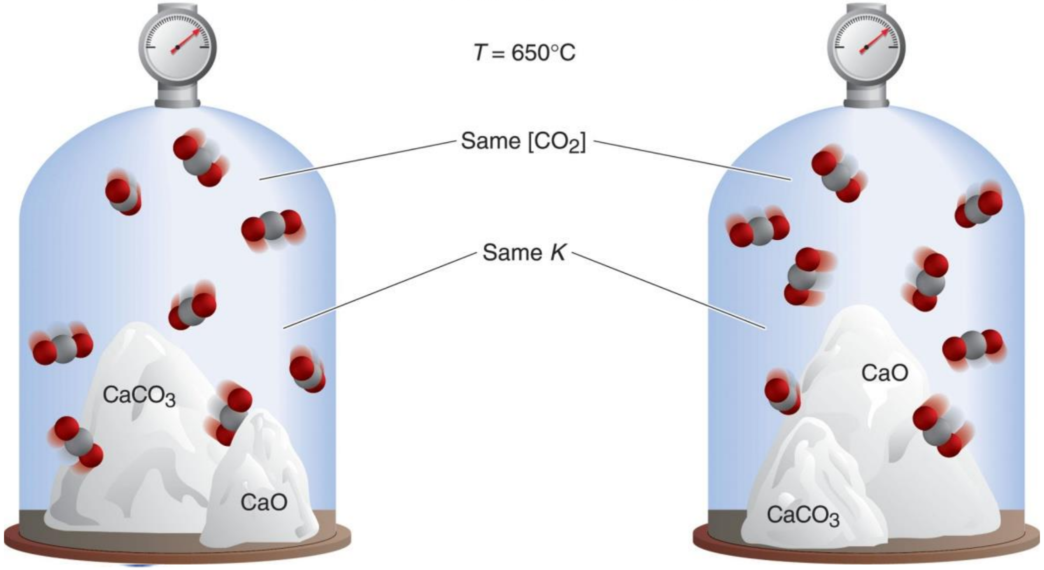
DINAMIC EQUILIBRIUM

6.2

EQUILIBRIUM CONSTANTS

6.3

LE CHATELIER’S PRINCIPLE



6.1 DYNAMIC EQUILIBRIUM

Teaching and learning outcomes

At the end of the lesson, student should be able to

6.1	**Dynamic Equilibrium**
a)	Explain the following terms: i) Reversible reaction ii) Dynamic equilibrium iii) Law of mass action
b)	State the characteristics of a system in equilibrium
c)	Interpret the curve of concentration reactants and products against time for a reversible reaction.
d)	Sketch the graph of concentration of reactants and products against time for a reversible reaction.

NON-REVERSIBLE REACTION

- **Non-reversible reactions**
  Chemical reaction proceed in only one direction.

$$A + B \longrightarrow C + D$$

Example:

$$C(s) + O_2\,(g) \rightarrow CO_2\,(g)$$

REVERSIBLE REACTION

- Reactions which take place in both forward and reverse directions.
- Most of the reactions are reversible reactions.

$$A + B \rightleftharpoons C + D$$

Example:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$\longrightarrow$ Forward reaction : reaction proceed from left to right

$\longleftarrow$ Backward / reverse : reaction proceeds from right to left

$$\underset{\text{reactant}}{A} \rightleftharpoons \underset{\text{Product}}{B}$$

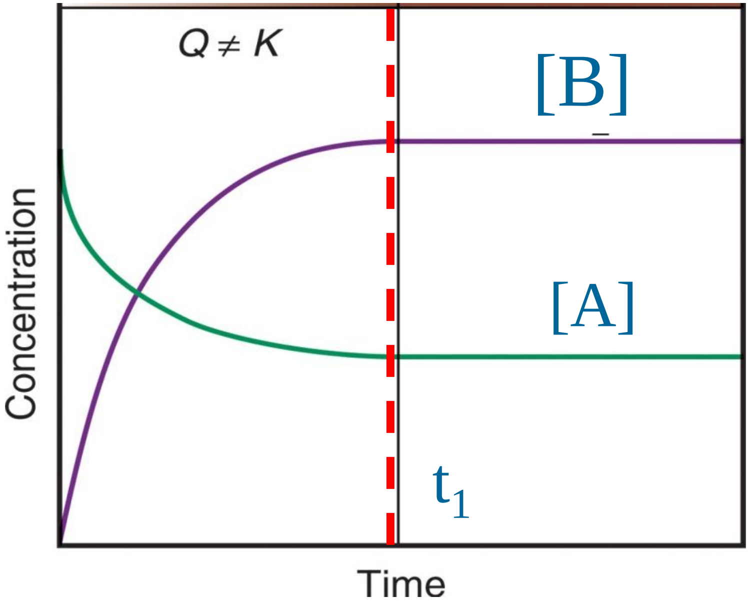
- **In a reversible reaction, initially the reaction proceeds toward the formation of the products.**

- **As soon as some product molecules formed, the reverse process begins to take place. Reactant molecules are formed from product molecules.**

Consider the following reversible reaction:

$$A \rightleftharpoons B$$

The graph of the concentration of A and B against time:



- **[A]** decrease with time
- **[B]** increase with time
- After time, $\mathbf{t_1}$, **[A]** and **[B]** remains unchanged
- **The system is in the state of <u>equilibrium</u>**

DYNAMIC EQUILIBRIUM

The reaction is said to be in a state of dynamic equilibrium when :

1. **The concentration of reactant and product stop changing (remain constant) over the time**

2. **The rate of forward reaction equals the rate of reverse reaction**

☞ **$\text{Rate}_{\text{fwd}} = \text{Rate}_{\text{rev}}$**

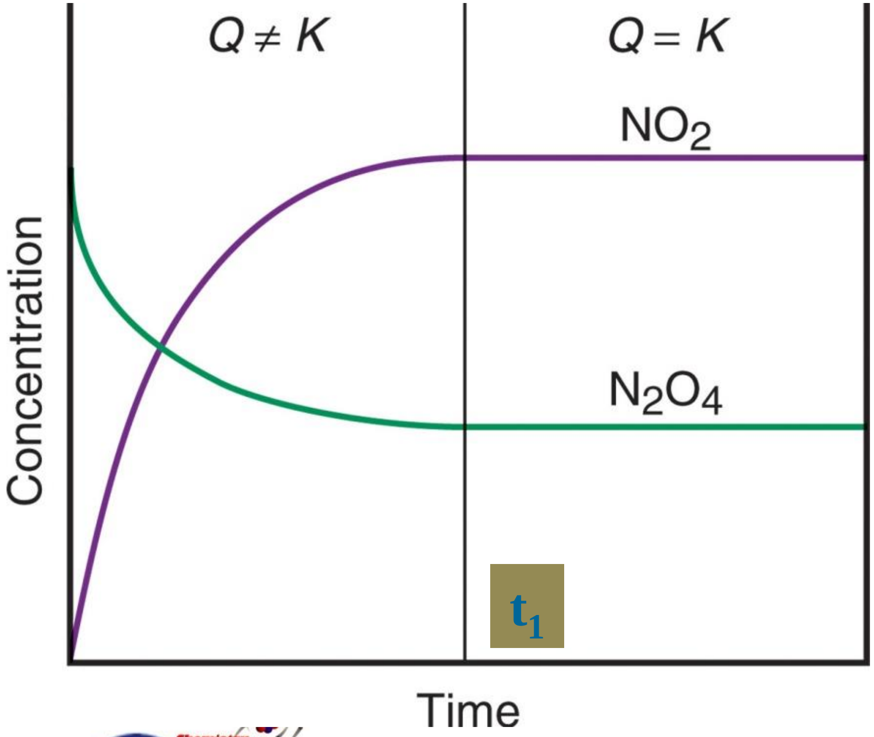
3. **The reaction quotient (Q) equals the equilibrium constant (*K*)**

☞ **$Q = K$**

will be discussed further in subtopic 6.2

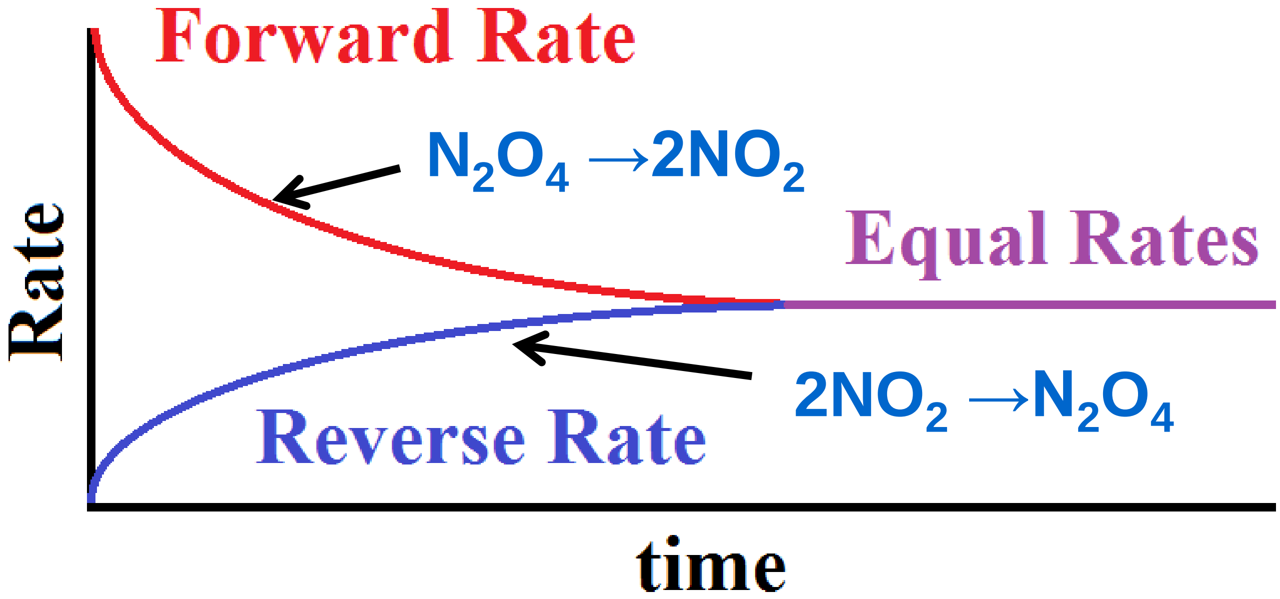
KEEP IN MIND!!

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$



- The equilibrium is a **dynamic equilibrium**
- Means that **after t_1, the reaction did not stop**
- But, the forward and reverse reaction occurring at the same rate
- The **[A] and [B] remain constant (no net change)**

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$



- As N_2O_4 is consumed, the rate of the forward reaction decreases
- As NO_2 is formed, the rate of the reverse reaction increases
- As the two rates become equal, an equilibrium state is attained and there are no further changes in concentrations.

LAW OF MASS ACTION

- Also known as law of chemical equilibrium.
- The relationship between the chemical equation and the expression of the equilibrium constant, *K*
- The law of mass action states that **for a reversible reaction at equilibrium and a constant temperature, a certain ratio of reactant and product concentrations has a constant value, *K* (the equilibrium constant)**

LAW OF MASS ACTION

- Consider this general reaction equation;

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

- At equilibrium;

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

K = equilibrium constant
[ ] = concentration of reactants and products at equilibrium
a, b, c, and d = stoichiometric coefficients for the reacting species A, B, C and D.

- **Although the concentrations may vary, as long as a given reaction is at equilibrium and the temperature does not change, the *K* remains constant.**

CURVE OF CONCENTRATION AGAINST TIME FOR REVERSIBLE REACTION

For a particular system and temperature, the same equilibrium state is attained regardless of how the reaction is run.

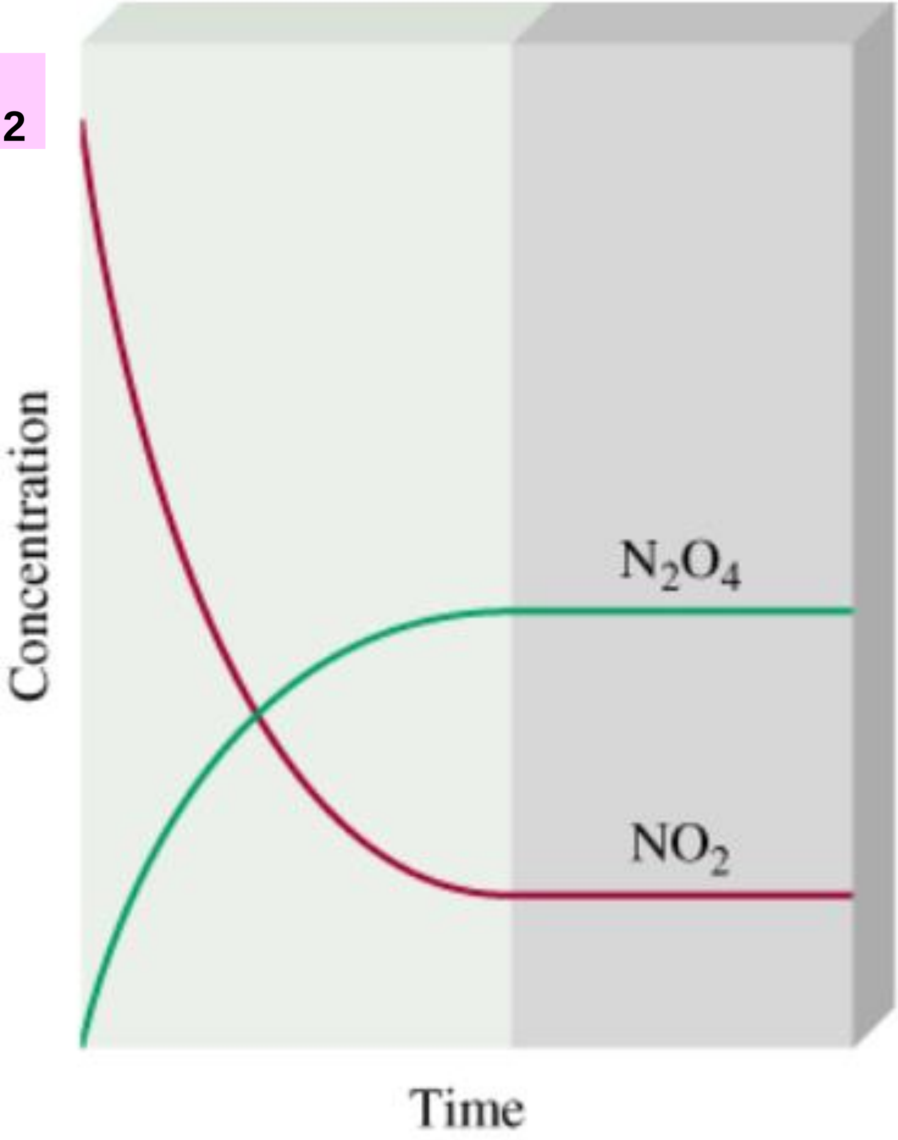
Example:

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

CASE 1:

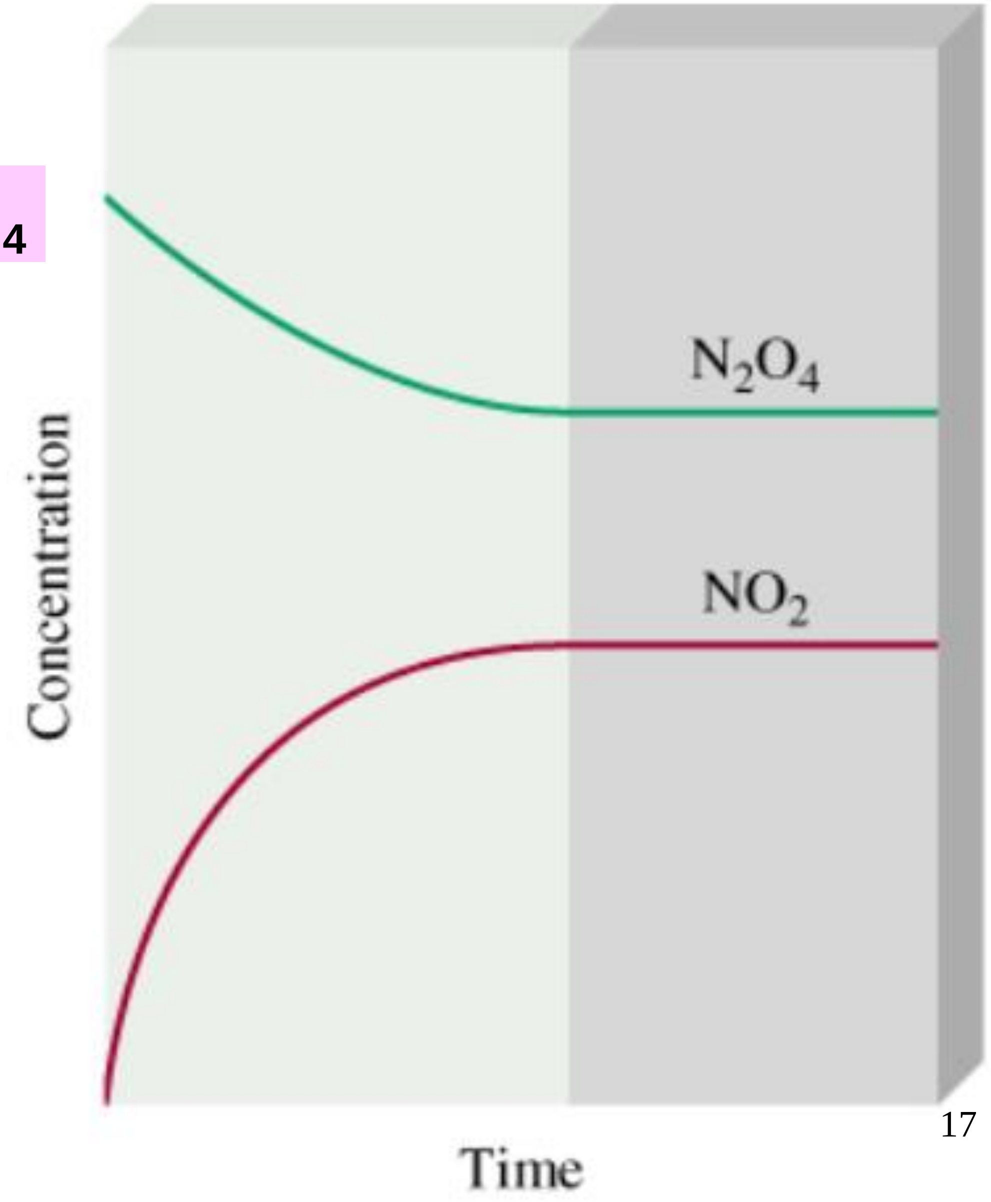
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Start with NO_2



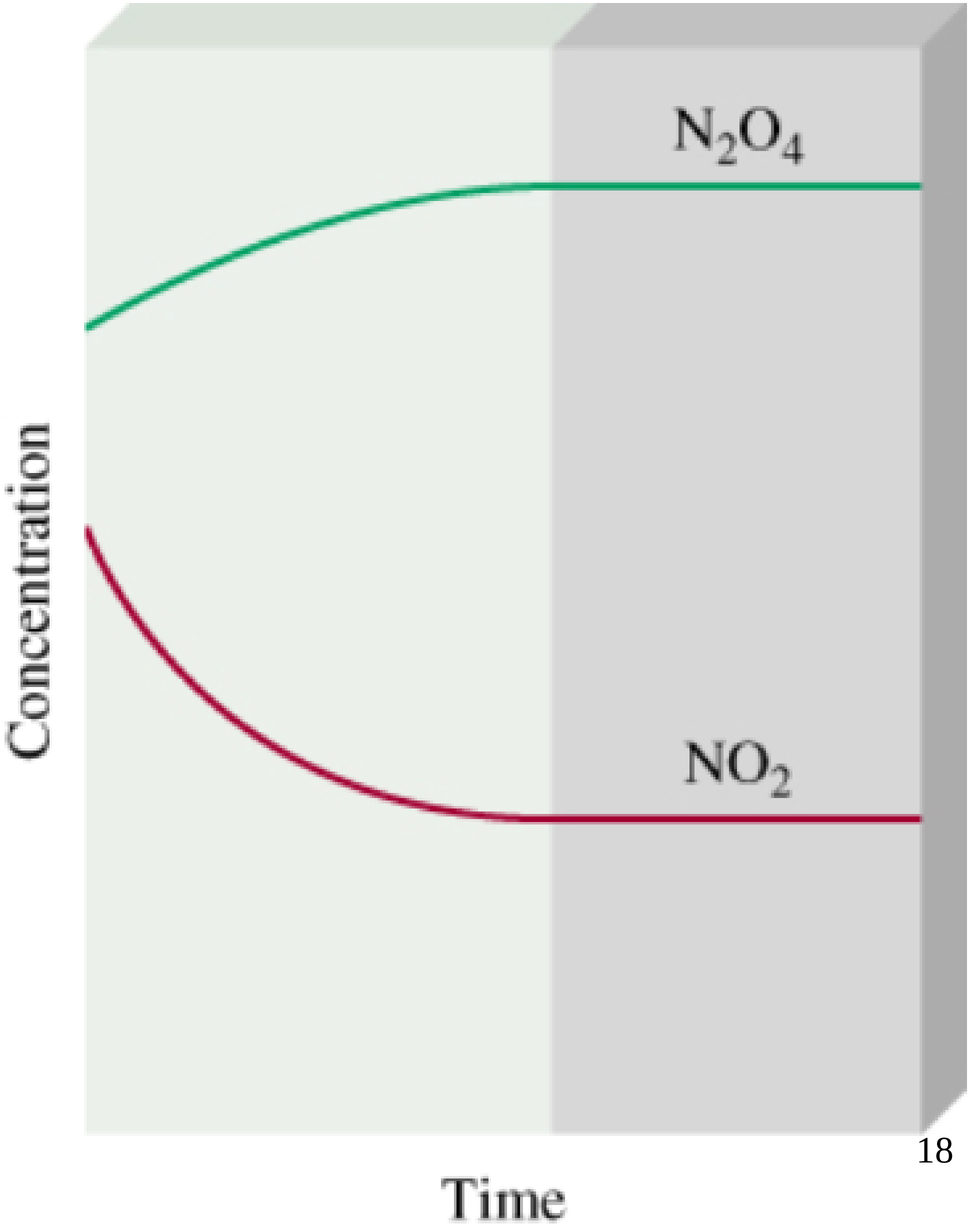
CASE 2: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Start with N_2O_4

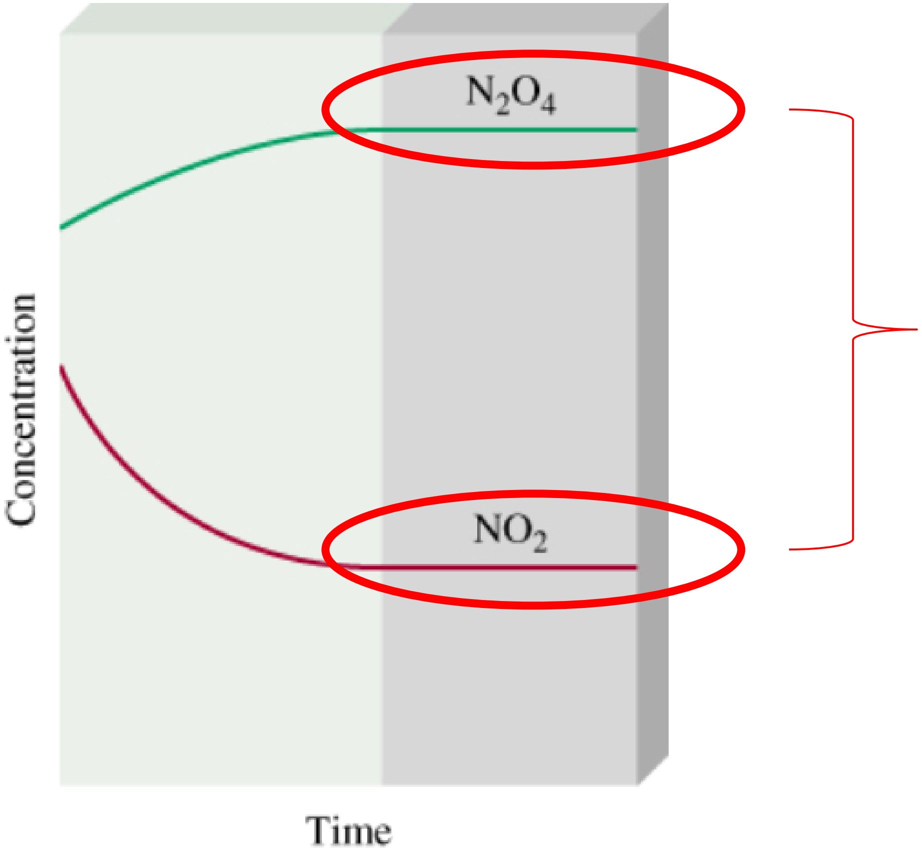


CASE 3: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Start with NO_2 & N_2O_4



- **Even though equilibrium is reach in all cases, the equilibrium concentrations of NO_2 and N_2O_4 are not same.**



Concentration of both solutions are not same

6.2 EQUILIBRIUM CONSTANT

Teaching and learning outcomes

At the end of the lesson, student should be able to

6.2 Equilibrium Constant

a) Define
  i. Homogeneous equilibria; and
  ii. heterogeneous equilibria

b) Write expressions for equilibrium constants in terms of concentration, *Kc* and partial pressure, *Kp* for homogeneous and heterogeneous systems.

c) Use the equation, $Kp = Kc(\mathrm{RT})^{Dn}$ to solve equilibrium problems.

d) Calculate *Kc*, *Kp* and the quantities of species present at equilibrium.

e) Determine the degree of dissociation, **a.**

f) Predict the direction of net reaction by comparing the values of reaction quotient, *Q* with *K*.

HOMOGENEOUS EQUILIBRIUM

- ☐ **Products and reactants are in the same phase**

EXAMPLE:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

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

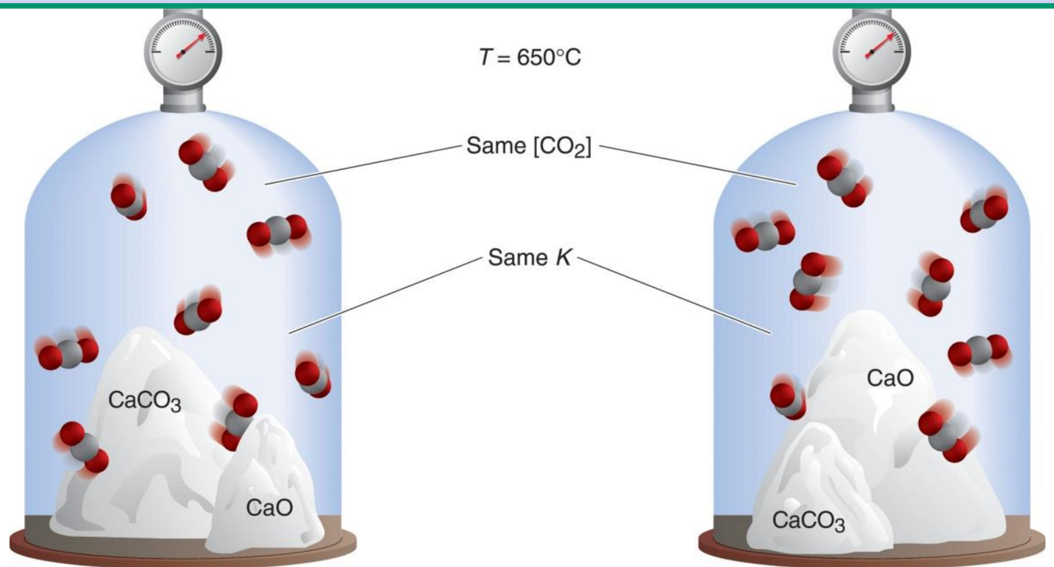
$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

HETEROGENEOUS EQUILIBRIUM

- Reactants and products are in **different phase**

EXAMPLE:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$



WRITING K_C EXPRESSIONS

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

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

[ ] = equilibrium concentration

- **Unit of concentration = *M* or mol L^{-1}**

WRITING K_P EXPRESSIONS

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

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

P = equilibrium partial pressure of the gas

☐ **Unit of pressure = atm**

- **The concentration of pure liquids and pure solids does not change (constant). Therefore it do not appear in the equilibrium constant expression**

EXAMPLE:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_C = \frac{\cancel{[CaO]}[CO_2]}{\cancel{[CaCO_3]}}$$

$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_C = [CO_2]$$

$$K_P = (P_{CO_2})$$

EXAMPLE 1

Write expressions for K_C, and K_P if applicable, for the following reversible reactions at equilibrium:
Note: balance the equations first.

(a) $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

(b) $NO(g) + O_2(g) \rightleftharpoons NO_2(g)$

(c) $H_2SO_4(l) + SO_3(g) \rightleftharpoons H_2S_2O_7(l)$

ANSWER EXAMPLE 1

(a) $HF(aq) \rightleftharpoons H^{+}(aq) + F^{-}(aq)$

$$K_C = \frac{[H^{+}][F^{-}]}{[HF]}$$

(b) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

$$K_C = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$K_P = \frac{(P_{NO_2})^2}{(P_{NO})^2(P_{O_2})}$$

EXAMPLE 1

(c) $H_2SO_4(l) + SO_3(g) \rightleftharpoons H_2S_2O_7(l)$

$$K_C = \frac{1}{[SO_3]}$$

$$K_P = \frac{1}{(P_{SO_3})}$$

K_P vs K_C

Equation to solve equilibrium problems

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

Hints:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad K_P = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$PV = nRT$$

EXAMPLE 2

The equilibrium concentrations for the reaction between carbon monoxide, CO and molecular chlorine, Cl_2 to form $COCl_2$ (*g*) at 74^{o}C are
[CO] = 0.012 *M*, [Cl_2] = 0.054 *M* and [$COCl_2$] = 0.14 *M*.

Calculate the equilibrium constants K_C and K_P.

EXAMPLE 2

$$\mathrm{CO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons \mathrm{COCl_2}(g)$$

$$K_\mathrm{C} = \frac{[\mathrm{COCl_2}]}{[\mathrm{CO}][\mathrm{Cl_2}]}$$

$$= \frac{0.14}{0.012 \times 0.054}$$

$$= 216$$

EXAMPLE 2

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

$$K_C = 216$$

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

$\Delta n = 1 - 2 = -1$

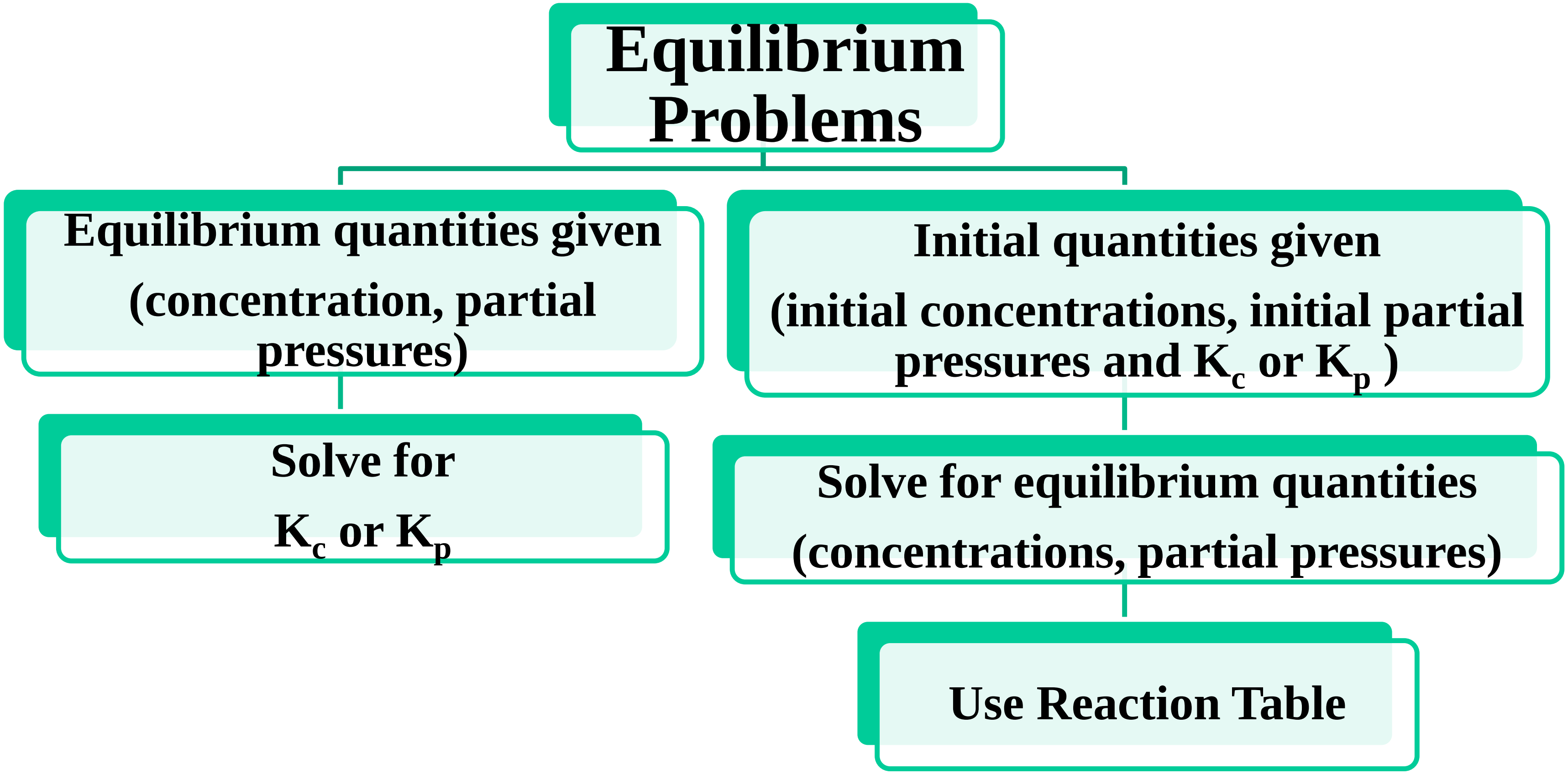
$T = (273.15 + 74)\ K$
$= 347.15\ K$

$R = 0.0821\ atm.L.mol^{-1}K^{-1}$

$$K_P = 216 \times (0.0821 \times 347.15)^{-1}$$

$$= 7.58$$

EQUILIBRIUM PROBLEMS



Equilibrium Problems

Equilibrium quantities given

(concentration, partial pressures)

Solve for

K_c or K_p

Initial quantities given

(initial concentrations, initial partial pressures and K_c or K_p)

Solve for equilibrium quantities

(concentrations, partial pressures)

Use Reaction Table

Solving equilibrium problems by using REACTION TABLE

❑ **Reaction Table contains:**

- **Initial quantities**
- **Change in quantities**
- **Equilibrium quantities**

Quantities = concentration, pressure

EXAMPLE 3

Consider the gas phase reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Suppose that a flask containing H_2 and I_2 has been heated to 425^{o}C and the initial concentrations of H_2 and I_2 were each 0.0175 mol/L. At equilibrium [HI] = 0.0276 mol/L. Use this experimental information to calculate the equilibrium constant.

EXAMPLE 3

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial Concentration, $[\ \ ]_i$ (mol/L)	**0.0175**	**0.0175**	**0**
Change in Concentration, Δ (mol/L)	$-x$	$-x$	$+2x$
Equilibrium Concentration, $[\ \ ]_{\rightleftharpoons}$ (mol/L)	$0.0175 - x$	$0.0175 - x$	$0 + 2x$ $= 0.0276$

EXAMPLE 3

Equilibrium concentrations:

[HI] = 0.0276 mol/L

= $2x$ So, x = 0.0138 mol/L

[H_2] = 0.0175 – x

= (0.0175 – 0.0138) mol/L = 0.0037 mol/L

[I_2] = 0.0175 – x

= (0.0175 – 0.0138) mol/L = 0.0037 mol/L

EXAMPLE 3

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$[H_2] = 0.0037$ mol/L **$[HI] = 0.0276$ mol/L**

$[I_2] = 0.0037$ mol/L

$$K_C = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$= \frac{(0.0276)^2}{0.0037 \times 0.0037}$$

$$= 55.6$$

DEGREE OF DISSOCIATION (α)

- ☐ **Fraction** **of a molecule** **dissociate** **or decompose** **into smaller molecules / ions / atoms**

$$\alpha = \frac{\text{Change in concentration of reactant}}{\text{Initial concentration of reactant}}$$

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

Suppose you know the value of *K* at the temperature of the reaction

How do you know if the reaction has reached equilibrium?

If it hasn't, how do you know in which direction it is progressing to reach equilibrium?

ANS: Compare the value of *K* and *Q*

PREDICTING THE DIRECTION OF A REACTION

The direction of a reaction can be predicted by comparing the equilibrium constant, K_c or K_p with the value of reaction quotient, Q_c or Q_p.

The expression for Q is the same as that for the equilibrium constant, K.

The reaction quotient (Q) is defined as the numerical value of the equilibrium expression - Evaluated at any time not necessarily at equilibrium.

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

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

[A], [B], [C], [D] :
equilibrium concentrations

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

[A], [B], [C], [D] :
any (initial) concentrations

To determine the direction in which the net reaction will proceed to achieve equilibrium, the values of Q_c and Q_p must be compared.

Q < K	✓ **The system is not at equilibrium.** ✓ **Initially, there are more reactants in the reaction mixture.** ✓ **To reach equilibrium Q=K, the reaction proceeds from left to right.**

$Q > K$	✓ **The system is not at equilibrium.** ✓ **Initially, there are more product in the reaction mixture** ✓ To reach equilibrium $Q=K$, **the reaction proceeds from right to left** .
$Q = K$	✓ The system is **at equilibrium**. No nett change.

EXAMPLE 7

At a very high temperature, K_C = 65.0 for the following reaction.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The following concentrations were detected in a mixture. Is the system at equilibrium?
If not, in which direction must the reaction proceed for equilibrium to be established?

$[HI] = 0.500\ M$, $[H_2] = 2.80\ M$, and $[I_2] = 3.40\ M$

EXAMPLE 7

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad K_C = 65.0$$

$$Q_C = \frac{[H_2][I_2]}{[HI]^2}$$

$[HI] = 0.500\ M$ $\qquad [H_2] = 2.80\ M$ $\qquad [I_2] = 3.40\ M$

$$Q_C = \frac{2.80 \times 3.40}{0.500^2}$$

$$= 38.1$$

EXAMPLE 7

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad K_C = 65.0$$

$$Q_C = 38.1$$

$$K_C = 65.0$$

$$Q_C < K_C$$

The reaction is not at equilibrium and will proceed to the forward (right) until the equilibrium is reached ($Q = K$).

CHAPTER 6.3 : OVERVIEW

6.3 Le Chatelier's Principle

- **State Le Chatelier's Principle**
- **Explain the effect on a system at equilibrium using Le Chatelier's**
  - Concentration
  - Pressure/Volume
  - Temperature
  - Catalyst
  - Addition of inert gas
    - Constant Volume
    - Constant Pressure

6.3 Le CHÂTELIER'S PRINCIPLES

Teaching and learning outcomes

At the end of the lesson, student should be able to

6.3	Le Chatelier's Principles
a)	State Le Châtelier's principle
b)	Explain the effect of the following factors on a system at equilibrium using Le Chatelier's principle : i. Concentration of reacting species; ii. Pressure by changing volume; iii. Addition of inert gas at constant volume; iv. Addition inert gas at constant pressure; v. Temperature; and vi. Catalyst.

LE CHÂTELIER’S PRINCIPLE

- When a chemical system is **disturbed**, it reattains **equilibrium** by undergoing a net reaction that **reduces** the **effect** of the disturbance

disturbance → reduce the effect

Henry Louis Le Châtelier (1850 – 1936). French chemist.

DISTURBANCE

- **Three common disturbance:**
  - **Change in concentration**
  - **Change in pressure**
    (caused by change in volume)
  - **Change in temperature**

A) CHANGES IN CONCENTRATION

Changing the concentration of any of the reactants or products will cause:

The equilibrium position shift to the direction that will reduce the effect of the disturbance in order to achieve a new equilibrium.

When the **concentration of reactant/s** being **increased;**

- the **equilibrium position will shift forward (from left to right),**
- in order **to reduce the effect of the added reactant** by **<u>forming more products</u>** until a new equilibrium is reached.

The **value of K at this temperature remains the same.**
(Refer to the expression of K_c or K_p)

HOT!

EXAMPLE:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

add Cl_2

$$Q_C = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

Disturbance : Addition of Cl_2 ($[Cl_2]$ increase)

- $Q_c < K_C$ (not at equilibrium)
- system will reduce the disturbance by reducing $[Cl_2]$
- Equilibrium position shift to the right until $Q_c = K_c$
- consuming some additional Cl_2
    - $[PCl_5]$ increase
    - $[PCl_3]$ decrease

EXAMPLE:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

remove PCl_3

$$Q_C = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

Disturbance : Removal of PCl_3 ($[PCl_3]$ decrease)

- $Q_C > K_C$ (not at equilibrium)
- system will reduce the disturbance by increasing $[PCl_3]$
- Equilibrium position shift to the left until $Q_C = K_C$
  - $[PCl_3]$ and $[Cl_2]$ increase
  - $[PCl_5]$ decrease

EXAMPLE – 01

To improve air quality and obtain a useful product, sulfur is often removed from coal and natural gas by treating the fuel contaminant hydrogen sulfide with O_2:

$$2H_2S(g) + O_2(g) \rightleftharpoons 2S(s) + H_2O(g)$$

What happen to

(a) $[H_2O]$ if O_2 is added?
(b) $[H_2S]$ if O_2 is added?
(c) $[O_2]$ if H_2S is removed?
(d) $[H_2S]$ if sulfur is added?

Explain.

ANSWER : EXAMPLE – 01

$$2H_2S(g) + O_2(g) \rightleftharpoons 2S(s) + H_2O(g)$$

(a) $[H_2O]$ if O_2 is added?

- **Disturbance:** $[O_2]$ increase
- **Equilibrium:**

  Will reduce the disturbance by reducing $[O_2]$

  Equilibrium position will shift to right

  ☞ $[H_2O]$ **increase**

ANSWER :

EXAMPLE – 01

$$2H_2S(g) + O_2(g) \rightleftharpoons 2S(s) + H_2O(g)$$

(b) $[H_2S]$ if O_2 is added?

- **Disturbance: $[O_2]$ increase**
- **Equilibrium:**

  Will reduce the disturbance by reducing $[O_2]$

  Equilibrium position will shift to right

☞ **$[H_2S]$ decrease**

ANSWER : EXAMPLE – 01

$$2H_2S(g) + O_2(g) \rightleftharpoons 2S(s) + H_2O(g)$$

(c) $[O_2]$ if H_2S is removed?

- Disturbance: $[H_2S]$ decrease
- Equilibrium:

Will reduce the disturbance by increasing $[H_2S]$

Equilibrium position will shift to left

☞ $[O_2]$ increase

ANSWER : EXAMPLE – 01

$$2H_2S(g) + O_2(g) \rightleftharpoons 2S(s) + H_2O(g)$$

(d) $[H_2S]$ if sulfur is added?

No disturbance because sulfur (S) is a solid; it has no effect on equilibrium

☞ **$[H_2S]$ unchanged**

B) CHANGES IN PRESSURE

- Significant only for system involving gaseous components

- Pressure of an equilibrium system can be changed by changing the volume of reaction vessel

Larger volume
Lower pressure

(fewer collisions per unit volume)

Smaller volume
Higher pressure

(more collisions per unit volume)

Changes in Volume

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 mol gas **1 mol gas**

<u>CASE 1:</u>

- **Disturbance: Volume of the system is decreased**
- **Gas pressure immediately increases**
- **$Q_C \neq K_C$ (not at equilibrium)**

According to Le Chatelier principle;

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 mol gas 1 mol gas

- System will reduce the disturbance by :

  Reducing the number of gas molecules in order to reduce the gas pressure

- Equilibrium position shift to the right (side with fewest no. of mole) until a new equilibrium is achieved ($Q_c = K_c$)

  - $[PCl_3]$ and $[Cl_2]$ decrease
  - $[PCl_5]$ increase

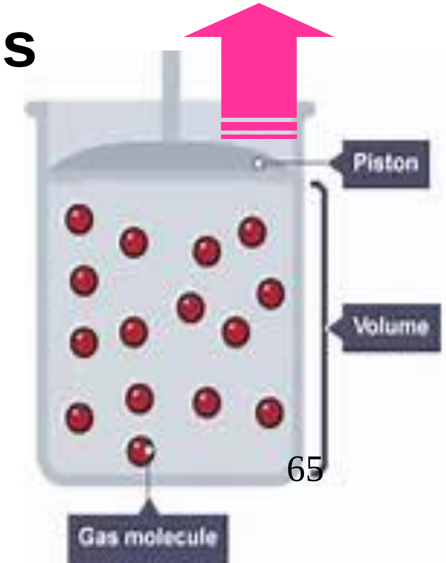
Changes in Volume

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 mol gas **1 mol gas**

CASE 2:

- **Disturbance: Volume of the system is increased**
- **Gas pressure immediately decreases**
- $Q_C \neq K_C$ **(not at equilibrium)**



According to Le Chatelier principle;

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 mol gas

1 mol gas

- **System will reduce the disturbance by :**

Increasing the number of gas molecules in order to increase the pressure

- **Equilibrium position shift to the left (side with more no. of mole) until a new equilibrium is achieved ($Q_C = K_C$)**

  - **$[PCl_3]$ and $[Cl_2]$ increase**
  - **$[PCl_5]$ decrease**

EXAMPLE:

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

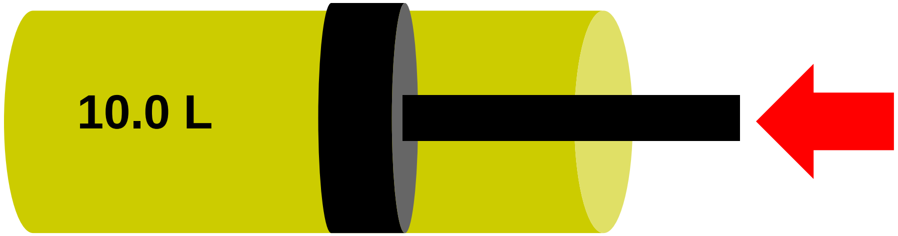
$K_C = 2.8 \times 10^2$ at 1000 K

At original equilibrium:

0.68 mol SO_3

0.32 mol SO_2

0.16 mol O_2



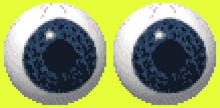
At new equilibrium:

0.83 mol SO_3

0.17 mol SO_2

0.085 mol O_2

Keep in mind!



Change	Shifts the Equilibrium
Increase pressure	Side with fewest moles of gas
Decrease volume	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas

C) ADDITION OF INERT GAS

At constant volume

- Has no effect on the equilibrium position
- Adding inert gas does not change the volume
- All reactant and product concentrations remain the same
- Their partial pressures does not change (even though the total gas pressure increase)

C) ADDITION OF INERT GAS

At constant pressure

- Has same effect as in the increase in volume
- The partial pressure of each gas decreases
- Equilibrium shift to the side with more moles of gas to increase the pressure

- When inert gas is added, the total number of moles of gaseous molecules in the system will increase (the total pressure should increase).

- But since the total pressure is kept constant, the volume of the container will expand (volume increase).

- The partial pressure of each gas in the container will decrease.

- The equilibrium position shift to the side with more moles of gas molecules to increase the pressure.

Example

$$2A(g) \rightleftharpoons B(g)$$

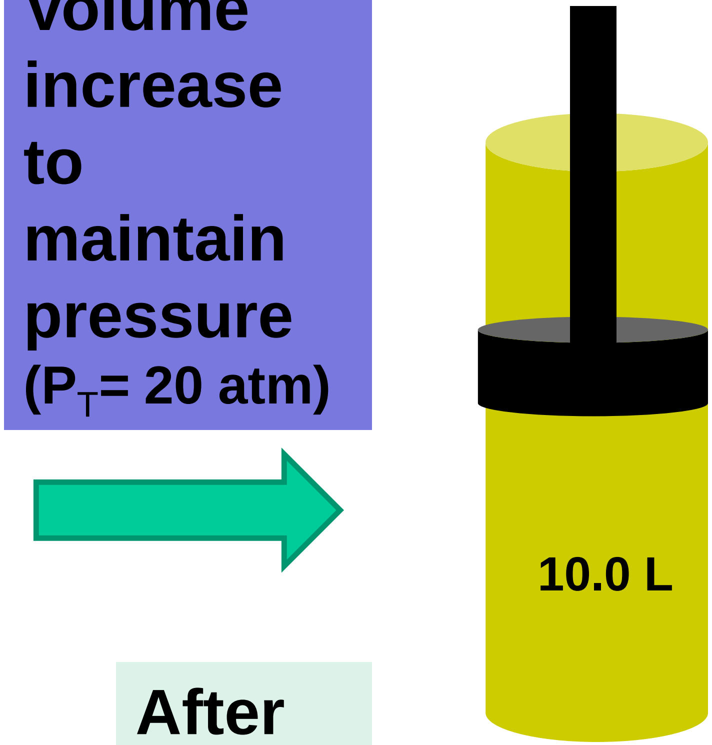
Add He (inert gas)

Before

$$P_T = P_A + P_B$$

20 = 10 atm + 10 atm

Volume increase to maintain pressure (P_T= 20 atm)



After

$$P_T = P_A + P_B + P_{He}$$

20 = (a) atm + (b) atm + P_{He}

Effect: **decreased in partial pressure (P_A and P_B)**

How to overcome:
increase pressure by produce more moles

D) CHANGES IN TEMPERATURE

- **Only temperature changes can alter *K*.**
- **The effect of temperature on an equilibrium depends on the type of reactions, whether it is:**

i. $\underset{\text{exo}}{\overset{\text{endo}}{\rightleftharpoons}}$ **ΔH= + kJ**

or

ii. $\underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}}$ **ΔH= - kJ**

Example 1

Consider the following system:

$$N_2O_{4(g)} \underset{\text{exo}}{\overset{\text{endo}}{\rightleftharpoons}} 2NO_{2\,(g)} \qquad \Delta H = +57\text{ kJ}$$

- **'+ve'** indicates that heat is **absorbed** for the **forward** reaction.
- The forward reaction above is **endothermic**

KEEP IN MIND !!

- When the temperature of the system is increased, endothermic reaction is favorable as to reduce the temperature of the system by absorbing the added heat

- When the temperature of the system is decreases, exothermic reaction is favorable as to increase the temperature of the system by releasing more heat

Increasing the temperature of the system:

$$N_2O_{4(g)} \underset{\text{exo}}{\overset{\text{endo}}{\rightleftharpoons}} 2NO_{2\,(g)} \qquad \Delta H = +57\text{ kJ}$$

- **When the temperature of the system is increased, endothermic reaction is favorable**

- So, it will cause the equilibrium position **shift forward/ right** as **to reduce** the temperature of the system by **absorbing the added heat**

- **More N_2O_4 will be consumed and NO_2** gas will produced.

- The **value of K_c and K_p** of the system will **increase**. (since the amount of product increases)

$$N_2O_{4(g)} \overset{\longrightarrow}{\rightleftharpoons} 2NO_{2\,(g)} \qquad \Delta H = +57\ \text{kJ}$$

colorless **brown**

At room temperature (Equilibrium)

T of the system is increased

Lowering the temperature of the system:

$$N_2O_{4(g)} \underset{\text{exo}}{\overset{\text{endo}}{\rightleftharpoons}} 2NO_{2\,(g)} \qquad \Delta H = +57\ \text{kJ}$$

- **When the temperature of the system is decreased, exothermic reaction is favorable**

- So it will cause the **equilibrium position shift to the left** as **to increase the temperature of the system by releasing more heat.**

- **More N_2O_4** will be formed.

- The **value of K_p and Kc decreases.**

$$\underset{\text{colorless}}{N_2O_{4(g)}} \underset{\longleftarrow}{\rightleftharpoons} \underset{\text{brown}}{2NO_{2\,(g)}} \qquad \Delta H = +57\ kJ$$

At room temperature (Equilibrium)

T of the system is decreased

Example 2

Consider the following system:

$$N_{2\,(g)} + 3H_{2(g)} \xrightleftharpoons[\text{endo}]{\text{exo}} 2NH_{3(g)} \qquad \Delta H = -\,92\text{kJ}$$

- Has a **‘–ve’** sign to indicate **energy is given off (heat release)** for the **forward** reaction.

- The forward reaction above is **exothermic.**

Increasing the temperature of the system

$$N_{2\,(g)} + 3H_{2(g)} \underset{\text{(endo)}}{\overset{\text{(exo)}}{\rightleftharpoons}} 2NH_{3(g)} \qquad \Delta H = -\ 92kJ$$

- **When the temperature of the system is increased, endothermic reaction is favorable**

- So it will cause the equilibrium position **shift** to the **left as to reduce the temperature of the system** by **absorbing the added heat.**
- **More N_2 and H_2** will formed and the amount of **NH_3 is decreased.**
- The value of **K_p or K_c decreases.**

Lowering the temperature of the system

$$N_{2\,(g)} \quad + \quad 3H_{2(g)} \underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}} 2NH_{3(g)} \qquad \Delta H = -\ 92kJ$$

- **When the temperature of the system is decreased, exothermic reaction is favorable**

- So it will cause **the equilibrium position shifts forward/ right as to increase the temperature of the system by releasing more heat.**
- **More NH_3** produced and **amount of N_2 and H_2 reduced**.
- **K_c or K_p increases**.

EXAMPLE 3

$$PCl_3(g) + Cl_2(g) \underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}} PCl_5(g) \qquad \Delta H = -111 \text{ kJ}$$

$$K_C = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

- **Disturbance: rise in temperature (adding heat)**
- **According to Le Chatelier's principle, to achieve equilibrium;**
  - ☞ **endothermic reaction is favorable**
  - ☞ **Equilibrium position will shift to the left**
  - ☞ **K_C decrease**

EXAMPLE 4:

$$\mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}} \mathrm{PCl_5}(g) \qquad \Delta H = -111\ \text{kJ}$$

$$K_C = \frac{[\mathrm{PCl_5}]}{[\mathrm{PCl_3}][\mathrm{Cl_2}]}$$

- **Disturbance: drop in temperature (removing heat)**
- **According to Le Chatelier's principle, to achieve equilibrium;**
  - ☞ **exothermic reaction is favorable**
  - ☞ **Equilibrium position will shift to the right**
  - ☞ **K_C increase**

EXAMPLE 5

$$\mathrm{SO_2}(g) \underset{\text{exo}}{\overset{\text{endo}}{\rightleftharpoons}} \mathrm{S}(s) + \mathrm{O_2}(g) \qquad \Delta H = +178\ \mathrm{kJ}$$

$$K_C = \frac{[\mathrm{O_2}]}{[\mathrm{SO_2}]}$$

- **Disturbance: rise in temperature ☞ adding heat**

EXAMPLE 5

$$\mathrm{SO_2}(g) \underset{\textbf{exo}}{\overset{\textbf{endo}}{\rightleftharpoons}} \mathrm{S}(s) + \mathrm{O_2}(g) \qquad \Delta H = +178\ \mathrm{kJ}$$

$$K_\mathrm{C} = \frac{[\mathrm{O_2}]}{[\mathrm{SO_2}]}$$

- **Equilibrium:**
  - **Endothermic reaction is favorable**
  - **Equilibrium position will shift to the right**
  - K_C **increase**

EXAMPLE 6

$$\mathrm{SO_2}(g) \underset{\text{exo}}{\overset{\text{endo}}{\rightleftharpoons}} \mathrm{S}(s) + \mathrm{O_2}(g) \qquad \Delta H = +178\ \text{kJ}$$

$$K_C = \frac{[\mathrm{O_2}]}{[\mathrm{SO_2}]}$$

- **Disturbance: drop in temperature ☞ removing heat**

EXAMPLE 6

$$SO_2(g) \underset{\text{exo}}{\overset{\text{endo}}{\rightleftharpoons}} S(s) + O_2(g) \qquad \Delta H = +178\text{ kJ}$$

$$K_C = \frac{[O_2]}{[SO_2]}$$

- **Equilibrium:**
  - ☞ **Exothermic reaction is favorable**
  - ☞ **Equilibrium position will shift to left**
  - ☞ **K_C decrease**

E) EFFECTS OF CATALYST

- Catalyst speeds up a reaction by providing an alternative pathway which has lower activation energy.
- It increase the forward and reverse rates to the same extent.
- Shorten the time taken to reach equilibrium.
- A catalyst will not shift an equilibrium position because both rates are equally increased.
- Catalyst has no effect on the value of K_c or K_p

HABER PROCESS

- ☐ Industrial preparation of ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -91.8\ \text{kJ}$$

Fritz Haber (1868 – 1934). German chemist.

MAXIMIZING YIELD OF NH_3
(based on Le Chậtelier’s Principle)

$$N_2(s) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -91.8\ \text{kJ}$$

- **Reduce [NH_3]**
  - **Remove NH_3 produced**

- **Reduce volume (increase pressure)**

Equilibrium shift toward fewer moles of gas ☞ formation of NH_3

Reduce temperature

- Formation of NH_3 ☞ exothermic
- Exothermic reaction favors cooling

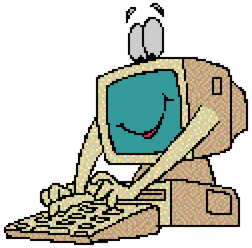
The yield is favored by low temperature
BUT, the rate formation is not

In fact, NH_3 forms so slowly at low temperature that the process become impractial and uneconomical

HABER PROCESS
(INDUSTRIAL CONDITIONS)

$$N_2(s) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -91.8\ \text{kJ}$$

High pressure and continuous removal of NH_3 are use to increase yield, but the temperature is raised to moderate level and a catalyst is used to increase the rate.



$$N_2(s) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -91.8\ \text{kJ}$$

Achieving the same rate without a catalyst requires much higher temperatures and results in a much lower yield

As a result, the optimum conditions are applied in most of the industrial ammonia plants :

- **Temperature : 400°C – 500°C**
- **Pressure : 500 – 1000 atm**
- **Catalyst : Iron (Fe)**

EXAMPLE – 02

Consider the following equilibrium:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H < 0$$

How will each of the following changes affect an equilibrium mixture of the three gases?

(a) $O_2(g)$ **is added to the system**
(b) **the reaction mixture is heated**
(c) **the volume of the reaction vessel is doubled**
(d) **a catalyst is added to the mixture**
(e) **the total pressure of the system is increased by adding a noble gas**
(f) $SO_3(g)$ **is removed from the system**

ANSWER : EXAMPLE – 02

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H < 0$$

(a) **$O_2(g)$ is added to the system**

The equilibrium position shift to the right

(b) **The reaction mixture is heated**

The equilibrium position shift to the left

☞ **K_C decrease**

ANSWER : EXAMPLE – 02

$$2SO_2(g) \quad + \quad O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H < 0$$

(c) The volume of the reaction vessel is doubled

The equilibrium position shift to the left

(d) A catalyst is added to the mixture

The equilibrium position unchanged

ANSWER : EXAMPLE – 02

$$2SO_2(g) \quad + \quad O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H < 0$$

(e) The total pressure of the system is increased by adding a noble gas

The equilibrium position unchanged

(f) $SO_3(g)$ is removed from the system

The equilibrium position shift to the right

Thanks!

For Attention

See You The Next Chapter

End Slide

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