

# CHEMICAL EQUILIBRIUM



# Lecture 1

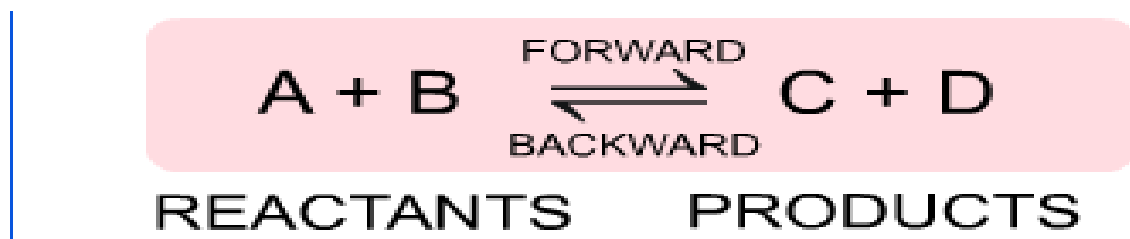
## 6.1 Dynamic Equilibrium

At the end of the lesson, students should be able to:

- 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) Explain the change of concentration of reactant and products based on the curve of concentration against time for a reversible reaction

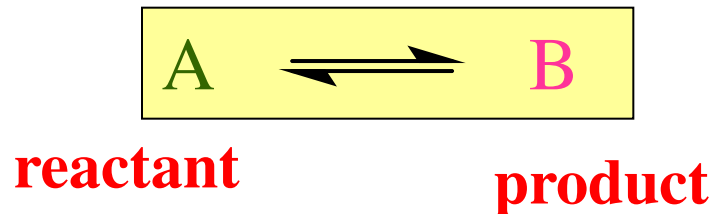
## 6.1.1 REVERSIBLE REACTION

- Reversible reaction can go in both direction.



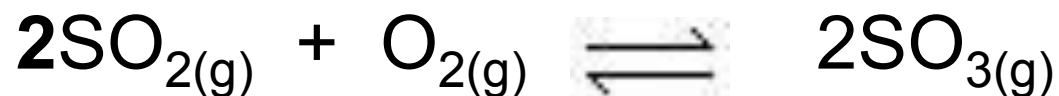
- Forward reaction : the reaction from left to right.
- Reverse reaction : the reaction from right to left.
- The reversible sign:



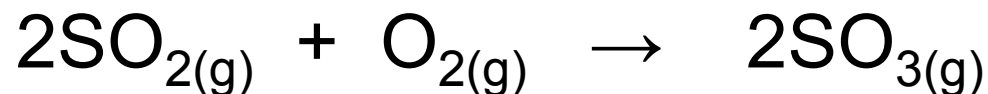


- In a reversible reaction, initially the reaction proceeds toward the formation of products
- As soon as some product molecules formed, the reverse process begins to take place
- Reactant molecules are formed from product molecules

## Example Reversible Reaction:



Forward reaction:



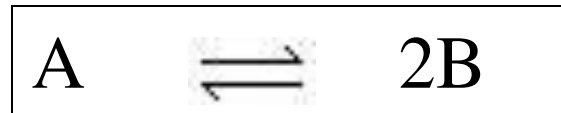
Reverse reaction:



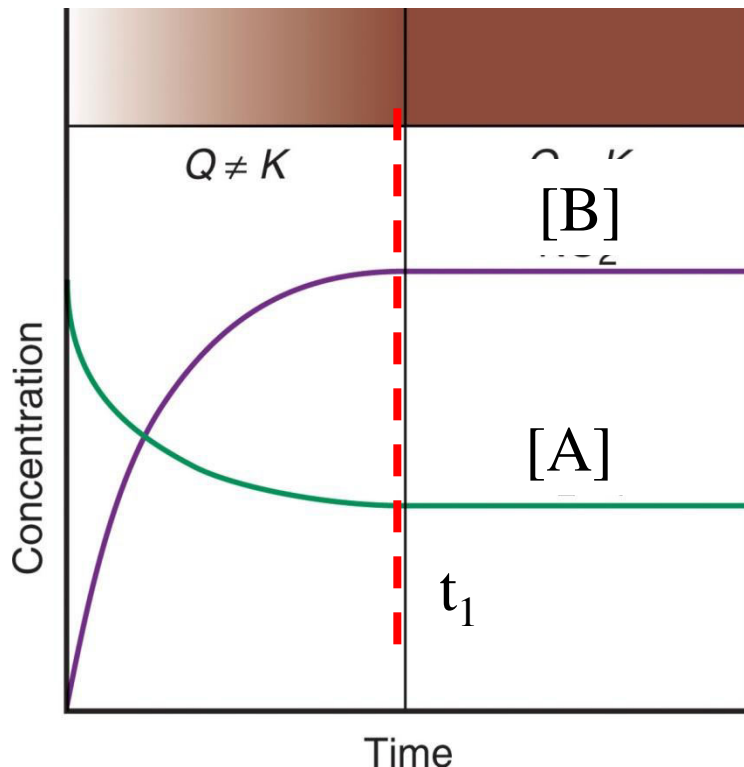
$\text{SO}_2$  and  $\text{O}_2$  combining to form  $\text{SO}_3$  at the same time as  $\text{SO}_3$  decomposed to form  $\text{SO}_2$  and  $\text{O}_2$

# REVERSIBLE REACTION

Consider the following reversible reaction:



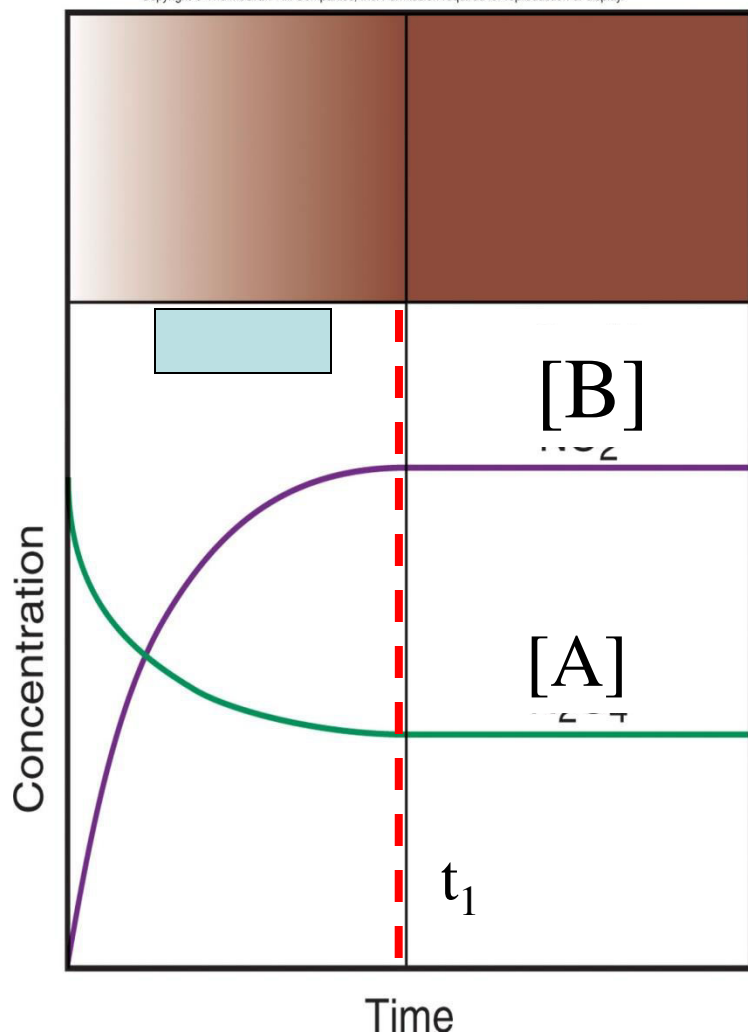
The graph of the concentration of A and B against time:



- $[A]$  decrease with time
- $[B]$  increase with time
- After time,  $t_1$ ,  $[A]$  and  $[B]$  remains unchanged
- The system is in the state of **equilibrium**

# Graph concentration vs time

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❖ The equilibrium is a dynamic equilibrium

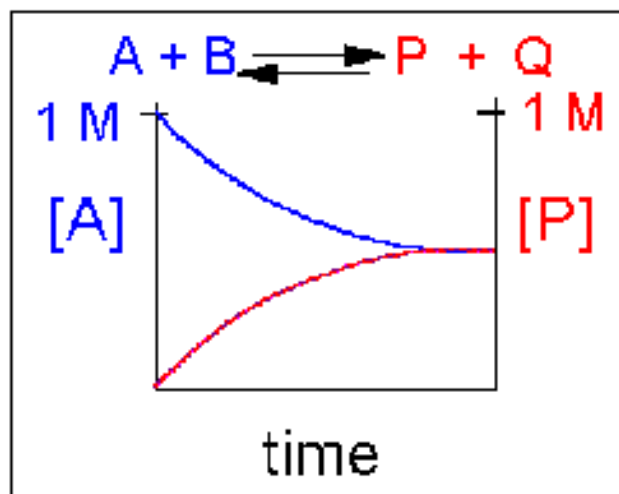
❖ Means that after  $t_1$ , the reaction did not stop

❖ But, the **rate of forward reaction = rate of reverse reaction**

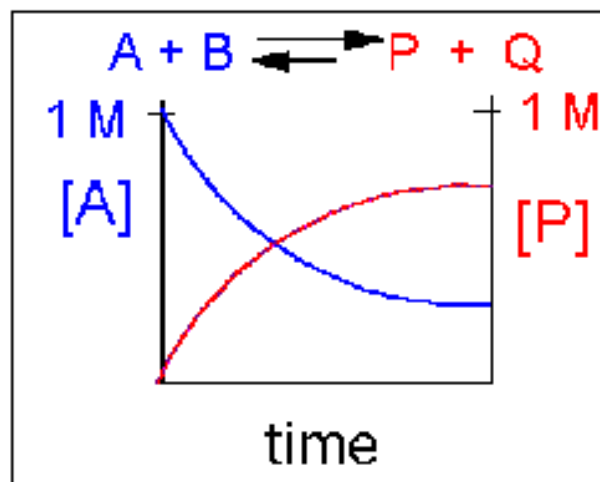
❖ There is **no net change in [A] and [B]**

# Graph for Dynamic equilibrium equation

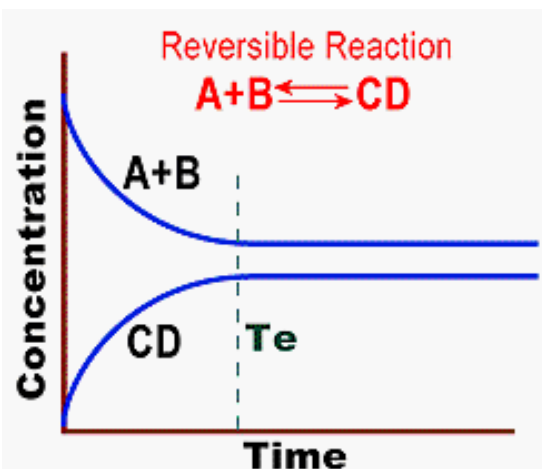
Shape 1



Shape 2



Shape 3



Shape of graph will depends on initial concentration and reaction stoichiometry.



## 6.1.2 Dynamic Equilibrium

- Equilibrium that exists in a closed system when the rate of the forward reaction is equal to the rate of the reverse reaction and the concentration of reactants and products remain constant over time.

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$



## 6.1.3 LAW OF CHEMICAL EQUILIBRIUM

Also known as law of mass action.

**The equilibrium law states :**

when a reversible reaction has achieved equilibrium, the ratio of the molar concentration of the products to the molar of the reactants is constant, at constant temperature.



# LAW OF CHEMICAL EQUILIBRIUM

Consider this general reaction equation:



At equilibrium:

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

Where:

**a, b, c and d:** stoichiometric coefficients for the reacting species A, B, C and D

**$K$  = Equilibrium constant,  $[ ]$  = concentration**



# CHARACTERISTICS OF A SYSTEM IN EQUILIBRIUM

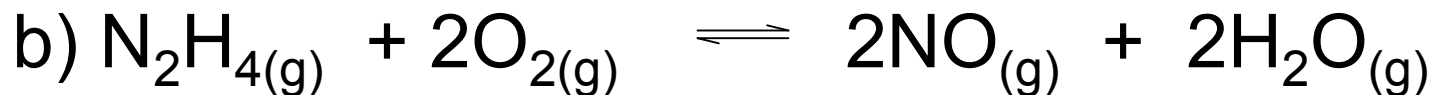
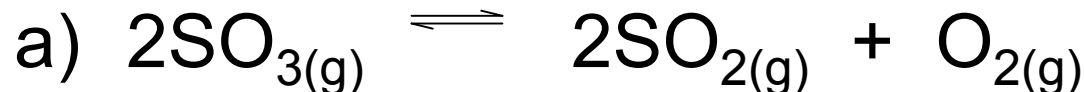
- i. Reactant and product concentrations are constant over time.
- ii. Forward reaction rate = reverse reaction rate
- iii. The reaction quotient ( $Q$ ) = The equilibrium constant ( $K$ )

$$Q = K$$

**( $Q$  will be discussed later in Topic 6.2)**

# Examples:

Write the equilibrium law for each reactions in terms of molar concentrations:



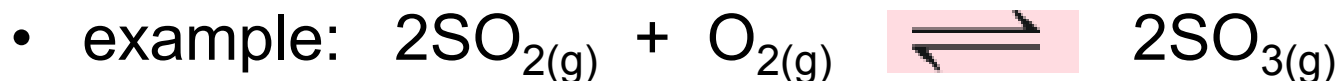
Answer: a)  $K =$

Unit of  $K = ?$

b)  $K =$

Unit of  $K = ?$

# Equilibrium law in term of pressure



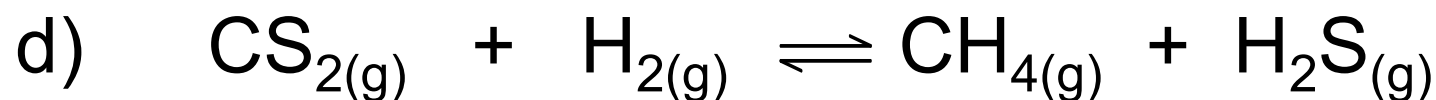
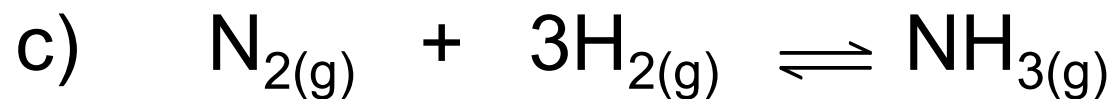
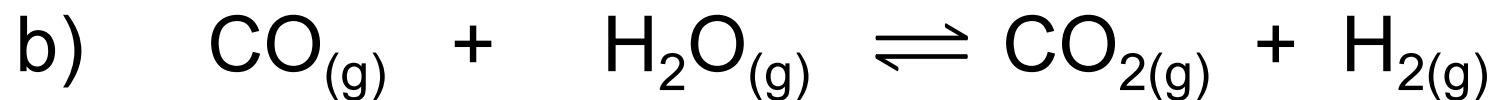
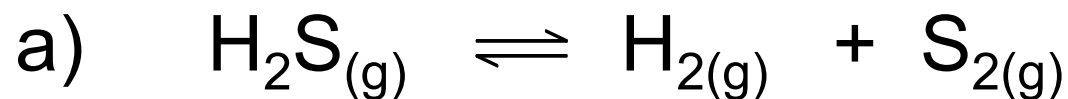
- $$K_p = \frac{(P_{\text{SO}_3})^2}{[P_{\text{SO}_2}]^2 \cdot [P_{\text{O}_2}]}$$

The units of  $K_p = \text{atm}^{-1}$

The value and units for  $K_c$  and  $K_p$  depend on the way in which the chemical equation is written.

## Exercises:

Write equilibrium constant expressions,  $K_c$ ,  $K_p$  and units for the following reactions:



# Lecture 2

## 6.2 Equilibrium Constants

At the end of the lesson, students should be able to:

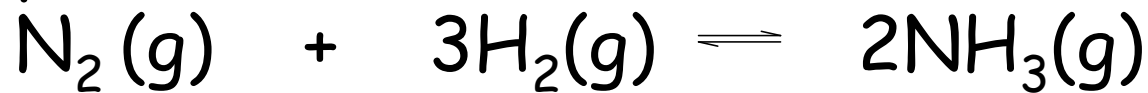
- (a) Define homogeneous and heterogeneous equilibria.**
- (b) Write expressions for equilibrium constants in terms of concentration,  $K_c$  and partial pressure,  $K_p$  for homogeneous and heterogeneous systems.**
- (c) Derive and use the equation,  $K_p = K_c (RT)^{\Delta n}$ .**



# Homogeneous Equilibrium

- All of the reactants and products are in same phase.

- Example :



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

# Heterogeneous Equilibrium

More than one phase exists in a reaction .

➤ Example :



➤ The concentration of pure substances, liquid or solid is constant, its not included in the equilibrium expression.

- Example :



the equilibrium constant as reactions

$$K_c = [\text{CO}_2]$$

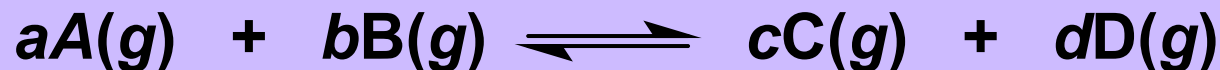
**Notes :** The equilibrium constant expression does not include the concentrations of pure solid and pure liquid phase

The equilibrium constant can  
expression into 2 way:

- i) Equilibrium involving concentrations
- ii) Equilibrium involving gases



# WRITING $K_p$ AND $K_c$ EXPRESSIONS



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



$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

[ ] in  $K_c$  = concentrations of the reacting species

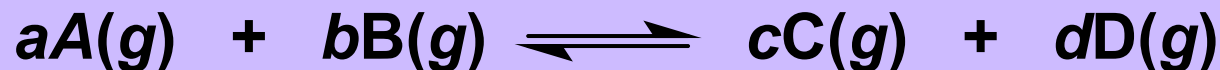


$$K_c = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Note: Unit of concentration = M (mol L<sup>-1</sup>)



# WRITING $K_p$ AND $K_c$ EXPRESSIONS

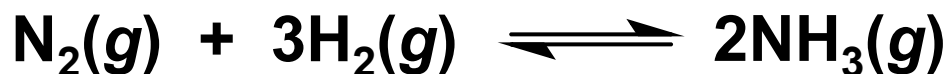


$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$



$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

$P$  in  $K_p$  = equilibrium partial pressure of the gas



$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

Note:

Equilibrium constant expression ( $K_c$  or  $K_p$ ) also called Equilibrium law expression

Note: Unit of pressure = atm.



# WRITING $K_p$ AND $K_c$ EXPRESSIONS

$$PV = nRT$$

So

$$P = \frac{n}{V} RT \quad \text{or} \quad \frac{P}{RT} = \frac{n}{V}$$

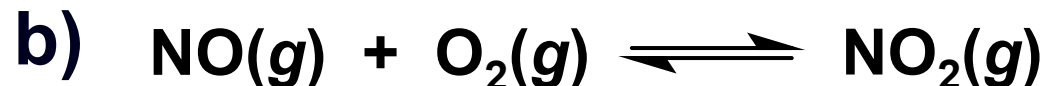
**At constant temperature,**

pressure (P) is **directly proportional** to molar concentration ( $n/V$ ).

The **equilibrium constant** for reaction involved **gases**, can be expressed based on **concentrations** ( $K_c$ ) and **pressures** ( $K_p$ ).

# EXERCISE - 1

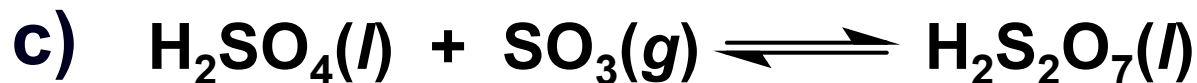
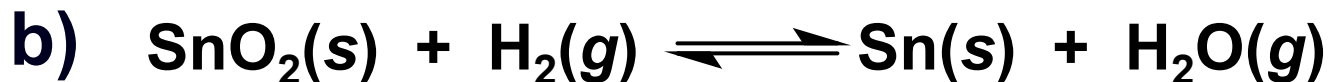
Write expressions for  $K_C$ , and  $K_P$  (if applicable), for the following reversible reactions at equilibrium:  
Note: balance the equations first.





## EXERCISE - 2

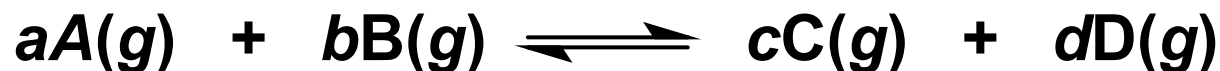
Balance each of the following equations and write its equilibrium constant expression,  $K_C$  and  $K_P$ :



# RELATION BETWEEN $K_p$ AND $K_c$

In most cases

$$K_c \neq K_p$$



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

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


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

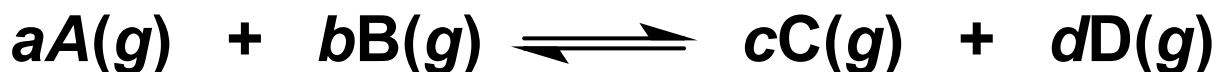
$\Delta n$  = moles of gaseous products  
– moles of gaseous reactants

$$= (c + d) - (a + b)$$

But, how do we derive  
this equation?

## Derivation of equation: $K_p = K_c(RT)^{\Delta n}$

Let us consider the following equilibrium in gas phase:



The equilibrium constant  $K_c$ :

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

The expression for  $K_p$ :

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

Assuming the gases behave as ideal gases:

$$PV = nRT$$



## Derivation of equation: $K_p = K_c(RT)^{\Delta n}$

$$\begin{aligned} P_A &= \frac{n_A}{V} RT & P_B &= \frac{n_B}{V} RT & P_C &= \frac{n_C}{V} RT & P_D &= \frac{n_D}{V} RT \\ &= [A]RT & &= [B]RT & &= [C]RT & &= [D]RT \end{aligned}$$

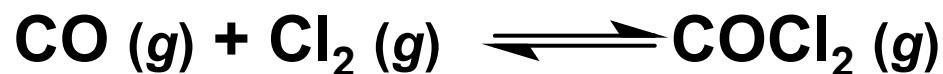
\*Notice that,  $n_A/V$ ,  $n_B/V$ ,  $n_C/V$  and  $n_D/V$  are concentration, [ ] and been replaced by [A], [B], [C] and [D]

By substituting these relations into the expression of  $K_p$ :

$$\begin{aligned} K_p &= \frac{P_C^c P_D^d}{P_A^a P_B^b} \\ &= \frac{([C]RT)^c \times ([D]RT)^d}{([A]RT)^a \times ([B]RT)^b} \end{aligned}$$
$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{(c+d)-(a+b)}$$
$$K_p = K_c(RT)^{\Delta n}$$

## EXAMPLE 1

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form  $\text{COCl}_2$  (g) at  $74^\circ\text{C}$  are  $[\text{CO}] = 0.012 \text{ M}$ ,  $[\text{Cl}_2] = 0.054 \text{ M}$ , and  $[\text{COCl}_2] = 0.14 \text{ M}$ . Calculate the equilibrium constants  $K_c$  and  $K_p$ .



$$K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{0.14}{0.012 \times 0.054} = 216$$

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

$$\Delta n = 1 - 2 = -1 \quad R = 0.0821 \quad T = 273 + 74 = 347 \text{ K}$$

$$K_p = 216 \times (0.0821 \times 347)^{-1} = 7.58$$

## EXAMPLE 2

- The equilibrium constant  $K_p$  for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine



Is found to be 1.05 at 250°C. If the equilibrium partial pressures of  $\text{PCl}_5$  and  $\text{PCl}_3$  are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of  $\text{Cl}_2$  at 250°C

# EXAMPLE

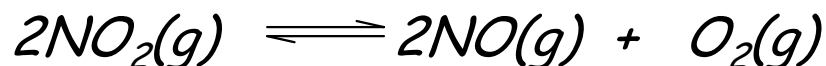
Solution :

$$K_p = \frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})}$$

$$P_{\text{Cl}_2} = \frac{(1.05)(0.875)}{(0.463)} = 1.98 \text{ atm}$$

# Exercise:

1. The equilibrium constant  $K_p$  for the following reaction is 158 at 1000K. Calculate  $P_{O_2}$  if  $P_{NO_2} = 0.400$  atm and  $P_{NO} = 0.270$  atm for the following reaction:



2. For the reaction above :

$K_p$  is  $4.3 \times 10^{-4}$  at  $375^\circ\text{C}$ . Calculate  $K_c$



# Lecture 3

## 6.2 Equilibrium Constants

At the end of the lesson, students should be able to:


- d) Calculate  $K_c$ ,  $K_p$  or the quantities of species present at equilibrium
- e) Define and determine the degree of dissociation,  $\alpha$
- f) Deduce the expression for reaction quotient,  $Q$  and predict the direction of nett reaction by comparing the values of  $Q$  and  $K_{eq}$ .

# EQUILIBRIUM PROBLEMS

Two types:

1  **Equilibrium quantities** ( concentrations , partial pressure ) are given

 Solve for  $K_C$  or  $K_P$

2  **Initial quantities** ( initial concentrations , initial partial pressure ) and  $K_P$  or  $K_C$  are given

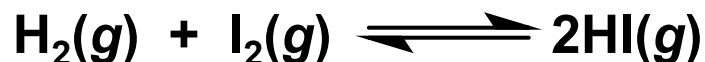
 Solve for **equilibrium quantities** ( concentrations , partial pressure )

# USING A REACTION (*ICE*) TABLE

1. Write down the balance equation and all species' initial concentration, (I).
2. Express the change in concentration, (C) using  $x$  (unknown) with referring to the species' stoichiometry coefficient, respectively.
3. Write the equilibrium constant expression ( $K_c$ ). Knowing the value of the equilibrium constant, **solve for  $x$** .
4. Having solved for  $x$ , calculate the (E) **equilibrium concentrations** of all species.

## EXAMPLE - 1

At a certain temperature, a mixture of  $\text{H}_2$  and  $\text{I}_2$  was prepared by placing 0.200 mol of  $\text{H}_2$  and 0.200 mol of  $\text{I}_2$  into a 2.00 L flask. After a period of time the equilibrium was established.



At equilibrium, the concentration of  $\text{I}_2$  had dropped to 0.020 M. What is the value of  $K_C$  for this reaction at this temperature?

# EXAMPLE - 1

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	
I nitial (M)	$\frac{0.200 \text{ mol}}{2.00 \text{ L}}$ $= 0.100$		$\frac{0.200 \text{ mol}}{2.00 \text{ L}}$ $= 0.100$	0.000
C hange (M)	$-x$		$-x$	$+ 2x$
E quilibrium (M)	$0.100 - x$		$0.100 - x$ $= 0.020$	$0.000 + 2x$ $= 2x$

$$\text{So, } x = 0.100 - 0.020$$

$$= 0.080$$

$$[\text{I}_2] = 0.020 \text{ M}$$

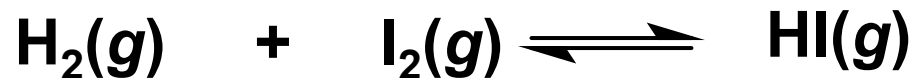
$$[\text{H}_2] = (0.100 - 0.080) \text{ M}$$

$$= 0.020 \text{ M}$$

$$[\text{HI}] = 2 \times 0.080 \text{ M}$$

$$= 0.160 \text{ M}$$

## EXAMPLE - 1



$$[\text{H}_2] = 0.020 \text{ M} \quad [\text{I}_2] = 0.020 \text{ M} \quad [\text{HI}] = 0.160 \text{ M}$$

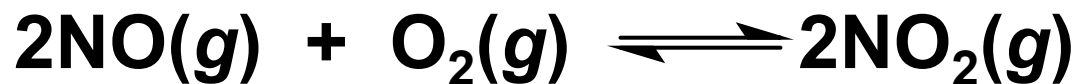
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2] [\text{I}_2]}$$

$$= \frac{(0.160)^2}{0.020 \times 0.020}$$

$$= 64.0$$

## EXAMPLE - 2

The atmospheric oxidation of nitric oxide,



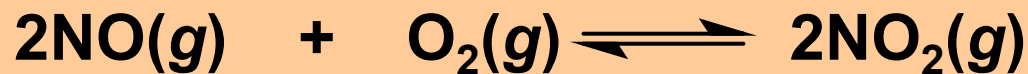
was studied at  $184^\circ\text{C}$  with pressure of 1.000 atm of NO and 1.000 atm of  $\text{O}_2$ .

At equilibrium,  $P_{\text{O}_2} = 0.506$  atm.

Calculate  $K_p$ .



## EXAMPLE - 2



Initial (atm)	1.000	1.000	0.000
Change (atm)	$-2x$	$-x$	$+2x$
Equilibrium (atm)	$1.000 - 2x$	$1.000 - x$ $= 0.506$	$0.000 + 2x$ $= 2x$

$$\text{So, } x = 1.000 - 0.506$$

$$= 0.494$$

$$P_{\text{NO}} = (1.000 - 2 \times 0.494) \text{ atm}$$

$$= 0.012 \text{ atm}$$

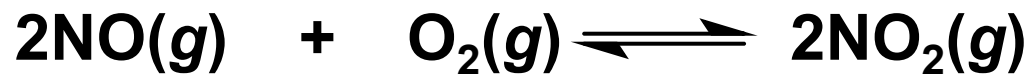
$$P_{\text{NO}_2} = 2 \times 0.494 \text{ atm}$$

$$= 0.988 \text{ atm}$$

$$P_{\text{O}_2} = 0.506 \text{ atm}$$



## EXAMPLE - 2

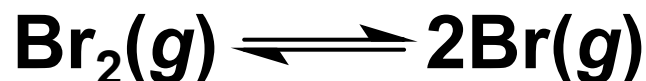


$$P_{\text{NO}} = 0.012 \text{ atm} \quad P_{\text{O}_2} = 0.506 \text{ atm} \quad P_{\text{NO}_2} = 0.988 \text{ atm}$$

$$\begin{aligned} K_p &= \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 P_{\text{O}_2}} \\ &= \frac{(0.988)^2}{(0.012)^2 \times 0.506} \\ &= 1.34 \times 10^4 \text{ atm}^{-1} \end{aligned}$$

## EXAMPLE - 3

At 1280°C the equilibrium constant ( $K_c$ ) for the reaction



is  $1.1 \times 10^{-3}$ . If the initial concentrations are  $[\text{Br}_2] = 0.063 \text{ M}$  and  $[\text{Br}] = 0.012 \text{ M}$ , calculate the concentrations of these species at equilibrium.

Let  $x$  be the change in concentration of  $\text{Br}_2$

	$\text{Br}_2(g) \rightleftharpoons 2\text{Br}(g)$	
Initial ( $M$ )	0.063	0.012
Change ( $M$ )	$-x$	$+2x$
Equilibrium ( $M$ )	$0.063 - x$	$0.012 + 2x$

## EXAMPLE - 3

	$\text{Br}_2(g) \rightleftharpoons 2\text{Br}(g)$	
Initial (M)	0.063	0.012
Change (M)	$-x$	$+2x$
Equilibrium (M)	$0.063 - x$	$0.012 + 2x$

$$K_c = \frac{[\text{Br}]^2}{[\text{Br}_2]} \quad K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3}$$

 Solve for  $x$

## EXAMPLE - 3

Given in question

$$K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3}$$

$$4x^2 + 0.048x + 0.000144 = 0.0000693 - 0.0011x$$

$$4x^2 + 0.0491x + 0.0000747 = 0$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = -0.0105$$

$$x = -0.00178$$

} try substitute both into answer

## EXAMPLE -3

👉 Determine **chemically meaningful x value**

	$\text{Br}_2(\text{g}) \rightleftharpoons 2\text{Br}(\text{g})$	
Initial (M)	0.063	0.012
Change (M)	$-x$	$+2x$
Equilibrium (M)	$0.063 - x$	$0.012 + 2x$
<del><math>(x = -0.0105)</math></del>	<del><math>= 0.0705</math></del>	<del><math>= -0.009</math></del>
$(x = -0.00178)$	$= 0.0648$	$= 0.00844$

**WRONG  
WAY**

☒ **correct**

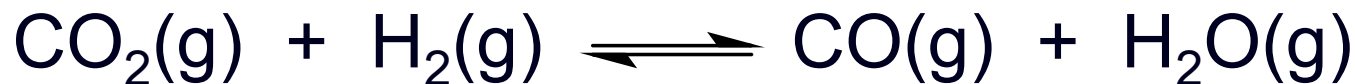
Note: Only **one x value makes sense chemically!**

At equilibrium,  $[\text{Br}] = 0.00844 \text{ M}$

$[\text{Br}_2] = 0.0648 \text{ M}$

## EXERCISE - 1

Consider the following equilibrium process at 686°C:

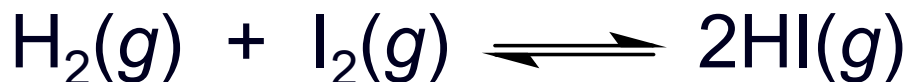


The equilibrium concentrations of the reacting species are  $[\text{CO}] = 0.050 \text{ M}$ ,  $[\text{H}_2] = 0.045 \text{ M}$ ,  $[\text{CO}_2] = 0.086 \text{ M}$ , and  $[\text{H}_2\text{O}] = 0.040 \text{ M}$ .

- Calculate  $K_C$  for the reaction at 686°C.
- If we add  $\text{CO}_2$  to increase its concentration to 0.50 M, what will be the concentrations of all gases be when equilibrium is reestablished?

## EXERCISE - 2

A 1.000L flask is filled with 1.000 mol of  $\text{H}_2$  and 2.000 mol of  $\text{I}_2$  at  $448^\circ\text{C}$ .



$$K_C = 50.5 \text{ at } 448^\circ\text{C}.$$

What is the concentration of  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$  at equilibrium?

## EXERCISE - 3

Hydrogen iodide decomposes according to the reaction



A sealed 1.50-L container initially holds 0.00623 mol of  $\text{H}_2$ , 0.00414 mol of  $\text{I}_2$ , and 0.0244 mol of  $\text{HI}$  at 703 K.

When equilibrium is reached, the concentration of  $\text{H}_2(\text{g})$  is 0.00467 M.

What are the equilibrium concentrations of  $\text{HI}(\text{g})$  and  $\text{I}_2(\text{g})$ ?



## EXERCISE - 4

0.500 mol of ICl was placed in a 5.00-L flask and allowed to decompose at a high temperature:



Calculate the equilibrium concentrations of  $\text{I}_2$ ,  $\text{Cl}_2$ , and ICl. ( $K_C = 0.110$  at this temperature)



# EQUILIBRIUM CALCULATIONS WHEN $K_c$ IS VERY SMALL

👉 The **concentration change** ( $x$ ) can often be **neglected**.

$$[A]_{\text{initial}} - x = [A]_{\text{equilibrium}} \approx [A]_{\text{initial}}$$

Note: You must **check** that the **assumption** is **justified** or not.

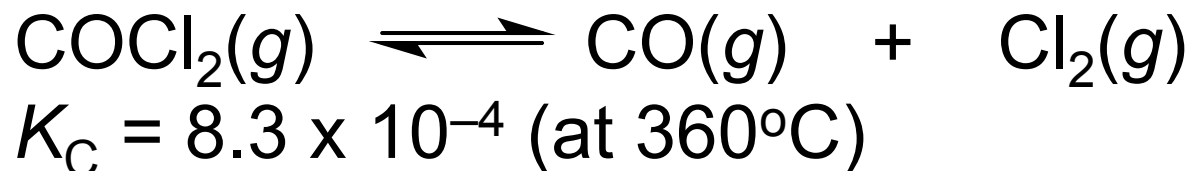
**CHECK:**  
**5% rule**

$$\frac{x}{[A]_{\text{initial}}} \times 100 < 5\% \quad \text{👉 Assumption is OK}$$

$$\frac{x}{[A]_{\text{initial}}} \times 100 > 5\% \quad \begin{array}{l} \text{👉 Assumption is NOT OK} \\ \text{👉 Use quadratic formula} \end{array}$$

## EXAMPLE - 4

Phosgene is a potent chemical warfare agent that is now outlawed by international agreement. It decomposes by the reaction



Calculate  $[\text{CO}]$ ,  $[\text{Cl}_2]$ , and  $[\text{COCl}_2]$ , when the following amounts of phosgene decompose and reach equilibrium in a 10-L flask:

- a) 5.000 mol of  $\text{COCl}_2$
- b) 0.100 mol of  $\text{COCl}_2$

## EXAMPLE -4

a)



Initial (M)	$\frac{5.000 \text{ mol}}{10.0 \text{ L}}$ $= 0.500$	0.000	0.000
-------------	---	-------	-------

Change (M)	$-x$	$+x$	$+x$
------------	------	------	------

Equilibrium (M)	$0.500 - x$	$x$	$x$
-----------------	-------------	-----	-----

$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

$$K_c = \frac{x^2}{(0.500 - x)} = 8.3 \times 10^{-4}$$



**Solve for  $x$**

## EXAMPLE - 4

$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

$$K_c = \frac{x^2}{(0.500 - x)} = 8.3 \times 10^{-4}$$

👉 Solve for  $x$

$K_c$  is very small

Assume  $x$  very small,  $0.500 - x \approx 0.500$

$$K_c = \frac{x^2}{0.500} = 8.3 \times 10^{-4}$$

$$x^2 = 8.3 \times 10^{-4} \times 0.500$$

$$x = 2.0 \times 10^{-2}$$

Checking the assumption:

$$\frac{2.0 \times 10^{-2}}{0.500} \times 100 = 4 \% (< 5\%)$$

**OK!**

## EXAMPLE - 4

	$\text{COCl}_2(\text{g})$	$\rightleftharpoons$	$\text{CO}(\text{g})$	+	$\text{Cl}_2(\text{g})$
Initial (M)	= 0.500		0.000		0.000
Change (M)	- x		+ x		+ x
Equilibrium (M)	$0.500 - x$		x		x

$$(x = 2.0 \times 10^{-2})$$

$$[\text{CO}] = 2.0 \times 10^{-2} \text{ M}$$

$$[\text{Cl}_2] = 2.0 \times 10^{-2} \text{ M}$$

$$\begin{aligned} [\text{COCl}_2] &= (0.500 - 2.0 \times 10^{-2}) \text{ M} \\ &= 0.480 \text{ M} \end{aligned}$$

## EXAMPLE - 4

b)



Initial (M)	$\frac{0.100 \text{ mol}}{10.0 \text{ L}}$ $= 0.010$	0.000	0.000
-------------	---	-------	-------

Change (M)	$-x$	$+x$	$+x$
------------	------	------	------

Equilibrium (M)	$0.010 - x$	$x$	$x$
-----------------	-------------	-----	-----

$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

$$K_c = \frac{x^2}{(0.010 - x)} = 8.3 \times 10^{-4}$$



Solve for  $x$

## EXAMPLE - 4

$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

$$K_c = \frac{x^2}{(0.010 - x)} = 8.3 \times 10^{-4}$$

👉 Solve for  $x$

$K_c$  is very small

Assume  $x$  very small,  $0.010 - x \approx 0.010$

$$K_c = \frac{x^2}{0.010} = 8.3 \times 10^{-4}$$

$$x^2 = 8.3 \times 10^{-4} \times 0.010$$

$$x = 2.9 \times 10^{-3}$$

Checking the assumption:


$$\frac{2.9 \times 10^{-3}}{0.010} \times 100 = 29 \% (> 5\%)$$

**NOT OK!**<sub>6</sub>



## EXAMPLE - 4

$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} \quad K_c = \frac{x^2}{(0.010 - x)} = 8.3 \times 10^{-4}$$

 Solve for  $x$  using **quadratic formula**

$$x^2 + (8.3 \times 10^{-4})x - 8.3 \times 10^{-6} = 0$$

**Do it yourself**

$x = 2.5 \times 10^{-3}$  (the only **meaningful value of  $x$** )

$$[\text{CO}] = 2.5 \times 10^{-3} \text{ M}$$

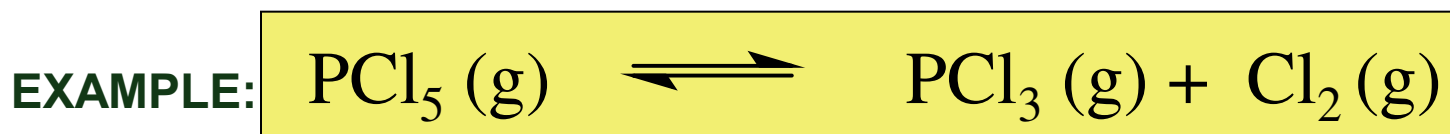
$$[\text{Cl}_2] = 2.5 \times 10^{-3} \text{ M}$$

$$[\text{COCl}_2] = (0.010 - 2.5 \times 10^{-3}) \text{ M}$$

$$= 7.5 \times 10^{-3} \text{ M}$$

# DEGREE OF DISSOCIATION, $\alpha$

**Dissociation reaction**: a molecule is broken down into smaller molecules, atoms or ions



Fraction or the percentage of molecules that dissociate is called **degree of dissociation,  $\alpha$**

$\alpha = 1$  or 100% if complete dissociation occurs

If incomplete dissociation occurs:

- $\alpha = \frac{[\text{changes}]}{[\text{initial}]} \times 100\%$

- The number of moles of reactants that has dissociated will be (  $ca$  ) where  $c$  is the reactant concentration

## EXAMPLE - 5

The degree of dissociation of dinitrogen tetroxide at  $250^{\circ}\text{C}$  and 1 atm is 0.15. Calculate the degree of dissociation at  $250^{\circ}\text{C}$  and 5 atm.

## EXAMPLE - 5



Initial (mol)	1	0
Changes	-0.15	+2(0.15)
Equilibrium (mol)	$1 - 0.15 = 0.85$	$2(0.15) = 0.30$

Total number of moles after dissociation

$$= 0.85 + 0.30$$

$$= 1.15 \text{ mol}$$

## EXAMPLE - 5

According to Dalton's law of partial pressure:

Partial pressure of  $\text{NO}_2 = 0.3/1.15 \times 1\text{atm} = 0.261 \text{ atm}$

Partial pressure of  $\text{N}_2\text{O}_4 = 0.85/1.15 \times 1\text{atm} = 0.739 \text{ atm}$

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

$$K_p = \frac{0.261^2}{0.739}$$

$$= \underline{\underline{9.21 \times 10^{-2} \text{ atm}}}$$

$K_p$  remain constant (no change in T)

$K_p$  needed for next calculation

## EXAMPLE -5

Let the degree of dissociation,  $\alpha$  at 5 atm =  $x$



Initial (mol)	1	0
Changes	$-x$	$+x$
Equilibrium (mol)	$1-x$	$2x$

## EXAMPLE - 5

$$P_{\text{NO}_2} = \frac{2x}{1 - x + 2x} \quad (5 \text{ atm})$$

$$P_{\text{N}_2\text{O}_4} = \frac{1x}{1 - x + 2x} \quad (5 \text{ atm})$$

$$K_p = \frac{(2x / 1 + x)^2 (5^2)}{(1 - x / 1 + x) (5)} = 9.21 \times 10^{-2}$$

$$x = 0.068$$

$$\alpha = \frac{0.068}{1} \times 100$$
$$= 6.8\%$$

**Only 6.8% of dinitrogen tetroxide dissociates at 250°C and 5 atm**



## EXERCISE - 7

- At a pressure of  $4.4 \times 10^5$  Pa and a temperature of  $150^\circ\text{C}$ , phosphorus pentachloride is 25% dissociated. Calculate the partial pressure equilibrium constant for this reaction.

## EXERCISE - 8

The dissociation of molecular iodine into iodine atoms represented as



At 1000K,  $K_C$  for the reaction is  $3.80 \times 10^{-5}$ .

Suppose you start with 0.0456 mol of  $\text{I}_2$  in a 2.30L flask at 1000K.

What are the concentrations of the gases at equilibrium?

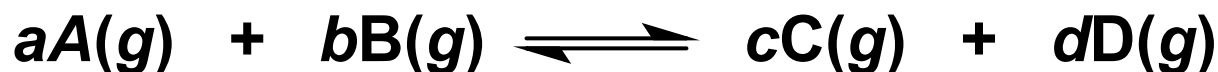
# PREDICTING THE REACTION OF A REACTION

- For predicting the direction of reaction, we compare  $K_c$  or  $K_p$  with the value of reaction quotient,  $Q$
- The expression for  $Q$ , known as the reaction quotient, is the same as that for the equilibrium constant,  $K$
- The difference is that the  $Q$  is determined from non-equilibrium.



# REACTION QUOTIENT (Q)

👉 Calculated by substituting the **initial concentrations** (or **pressures**) of the reactants and products into  $K_c$  or  $K_p$  expression.



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

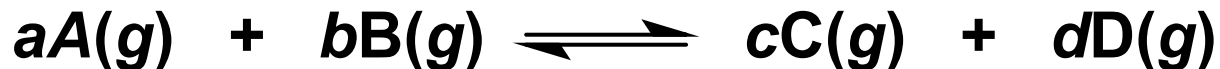
[A], [B], [C], [D] :  
**equilibrium  
concentrations**

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

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



# COMPARING Q AND K



Suppose you know the value of  $K_c$  at any given temperature of the reaction.



How do you know if the **reaction has reached equilibrium**?

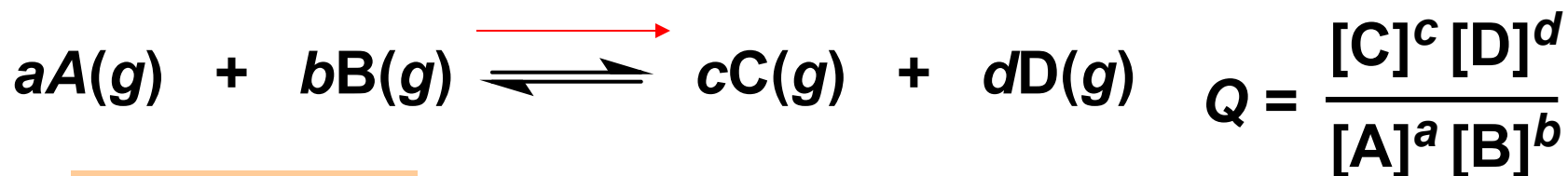


If it hasn't, how do you know in which **direction it is progressing to reach equilibrium**?

👉 Compare the value of  $K_c$  and  $Q_c$ .



## COMPARING Q AND K



$$Q < K$$

👉 Denominator (reactants) is large relative to numerator (products)

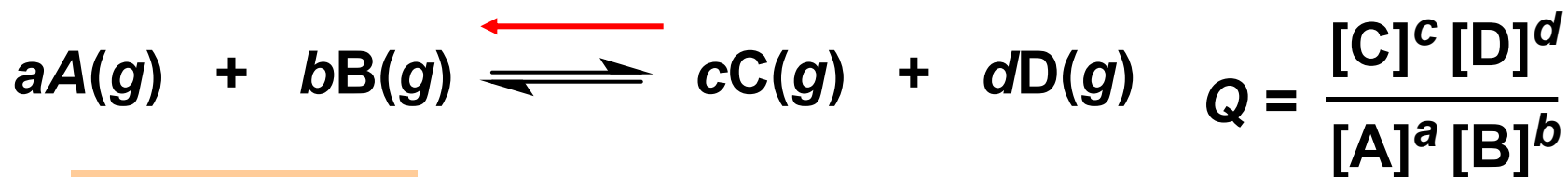
👉 To reach equilibrium,  $Q = K$ :  
the products must increase, reactants decrease.

If  $Q < K$ , reactants  $\longrightarrow$  products

The reaction will progress to the right (more product forms) until equilibrium is reached.



## COMPARING Q AND K



$$Q > K$$

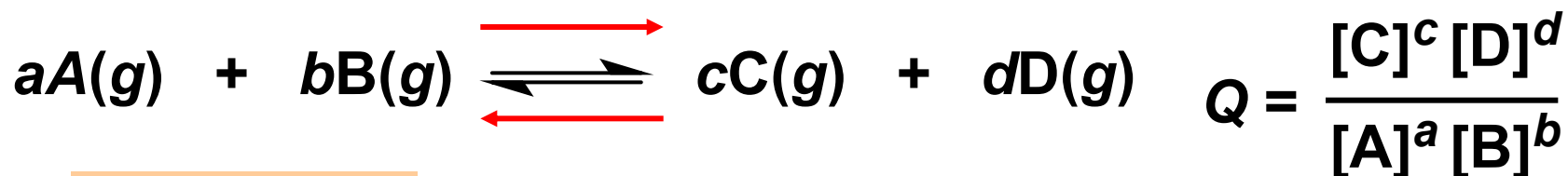
- 👉 Denominator (reactants) is small relative to numerator (products)
- 👉 To reach equilibrium,  $Q = K$ :  
the products must decrease, reactants increase.

If  $Q > K$ , reactants  $\longleftarrow$  products

The reaction will progress to the left (more reactant forms) until equilibrium is reached.



## COMPARING Q AND K



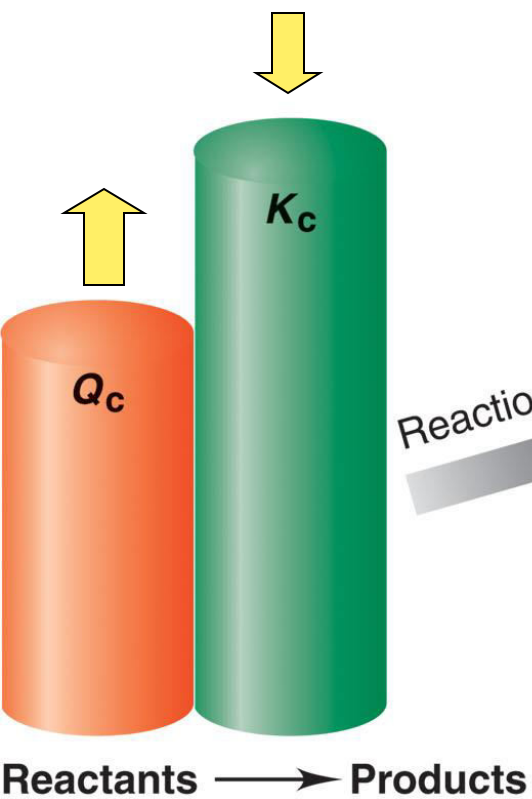
$$Q = K$$

👉 When the reactant and product concentrations (or pressures) has **attained** their **equilibrium** values.

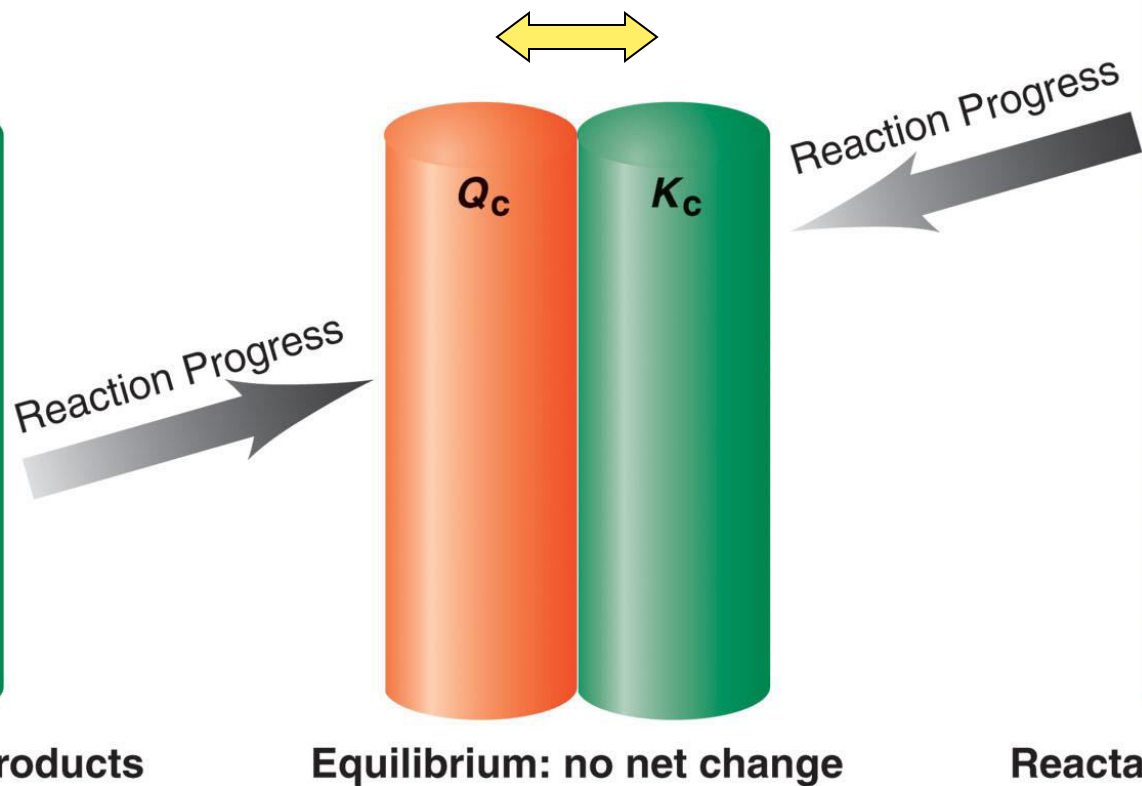
If  $Q = K$ , reactants  $\rightleftharpoons$  products

**No further net change.**

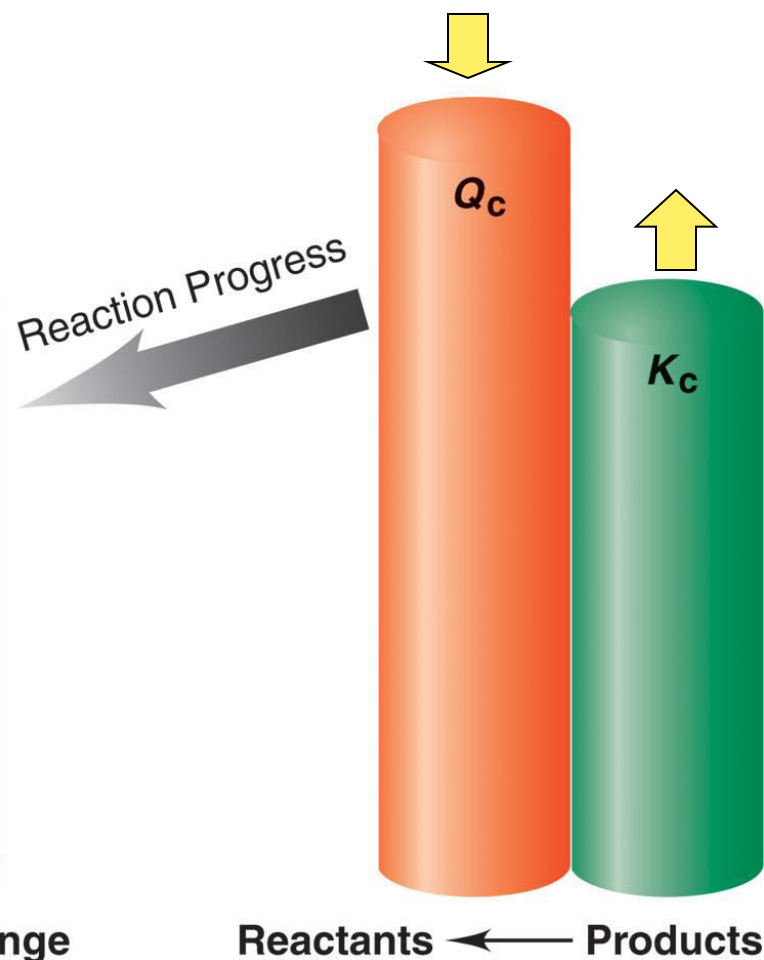




$Q < K$



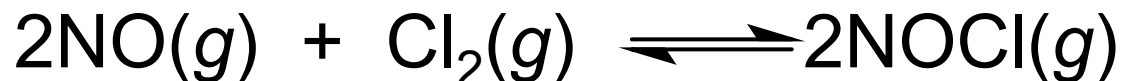
$Q = K$



$Q > K$

## EXAMPLE - 1

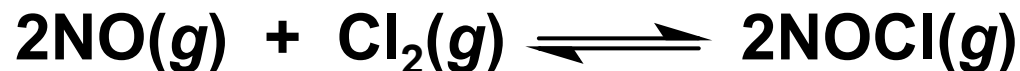
$K_C$  for the formation of nitrosyl chloride, an orange–yellow compound, from nitric oxide and molecular chlorine



is  $6.5 \times 10^4$  at  $35^\circ\text{C}$ . In certain experiment,  $2.0 \times 10^{-2}$  mole of NO,  $8.3 \times 10^{-3}$  mole of  $\text{Cl}_2$ , and 6.8 moles of NOCl are mixed in a 2.0L flask.

In which direction will the system proceed to reach equilibrium?

## EXAMPLE - 1



$$K_c = 6.5 \times 10^4$$

$$Q_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2 [\text{Cl}_2]}$$

Initial concentrations:

$$\begin{aligned} [\text{NOCl}_2] &= \frac{6.8 \text{ mol}}{2.0 \text{ L}} \\ &= 3.4 \text{ M} \end{aligned}$$

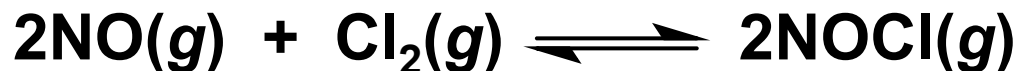
$$[\text{NO}] = \frac{2.0 \times 10^{-2} \text{ mol}}{2.0 \text{ L}}$$

$$= 0.01 \text{ M}$$

$$[\text{Cl}_2] = \frac{8.3 \times 10^{-3} \text{ mol}}{2.0 \text{ L}}$$

$$= 0.0042 \text{ M}$$

## EXAMPLE - 1



$$K_c = 6.5 \times 10^4$$

Initial concentrations:

$$[\text{NOCl}_2] = 3.4 \text{ M}$$

$$[\text{NO}] = 0.01 \text{ M}$$

$$[\text{Cl}_2] = 0.0042 \text{ M}$$

$$\begin{aligned} Q_c &= \frac{[\text{NOCl}]^2}{[\text{NO}]^2 [\text{Cl}_2]} \\ &= \frac{3.4^2}{0.01^2 \times 0.0042} \\ &= 2.75 \times 10^7 \end{aligned}$$

$$\begin{array}{ccc} Q_c & > & K_c \\ (2.75 \times 10^7) & & (6.5 \times 10^4) \end{array}$$

The reaction is not at equilibrium and will proceed to the left( to reactant) until  $Q_c = K_c$ .

## EXERCISE - 1

State the reaction  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ ,  
 $K_C = 0.21$  at  $100^\circ\text{C}$ . At a point during the reaction,  
 $[\text{N}_2\text{O}_4] = 0.12 \text{ M}$  and  $[\text{NO}_2] = 0.55 \text{ M}$ .

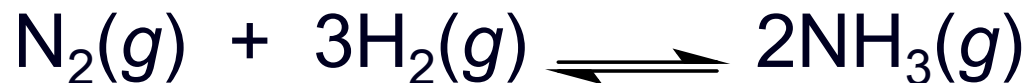
Is the reaction at equilibrium?

If not, in which direction is it progressing?

## EXERCISE - 2

At the start of a reaction, there are 0.249 mol  $\text{N}_2$ ,  $3.21 \times 10^{-2}$  mol  $\text{H}_2$ , and  $6.42 \times 10^{-4}$  mol  $\text{NH}_3$  in a 3.50L reaction vessel at  $375^\circ\text{C}$ .

If  $K_C$  for the reaction



is 1.2 at this temperature, decide whether the system is at equilibrium.

If not, predict which way the net reaction will proceed.

## EXERCISE - 3

At 425°C,  $K_p = 4.18 \times 10^{-9}$  for the reaction



In one experiment, 0.20 atm of  $\text{HBr}(g)$ , 0.010 atm of  $\text{H}_2(g)$ , and 0.010 atm of  $\text{Br}_2(g)$  are introduced into a container.

Is the system at equilibrium?

If not, in which direction will it proceed?

## EXERCISE -4

At 100°C,  $K_p = 60.6$  for the reaction



In a given temperature, 0.10 atm of each component is placed in a container.

Is the reaction at equilibrium?

If not, in which direction will it proceed?





## Lecture 4 & 5

### **6.3** Le Chatelier's Principle

At the end of the lesson, students should be able to:

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



# LE CHÂTELIER'S PRINCIPLE

When a chemical system in equilibrium is disturbed, it regains equilibrium by undergoing a net reaction that reduces the effect of the disturbance.

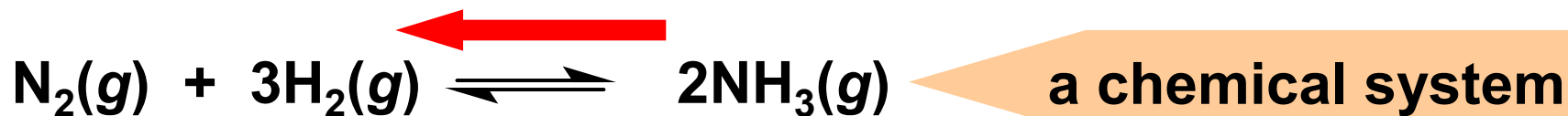
Three common disturbances:

- Change in concentration
- Change in pressure  
(caused by change in volume)
- Change in temperature

“net reaction” = shift in the equilibrium position of the system to either right or left



# LE CHÂTELIER'S PRINCIPLE



Add  $\text{NH}_3$

Original equilibrium:  $Q = K$

Disturbance:

➡ Add  $\text{NH}_3$

➡  $[\text{NH}_3]$  increase

➡  $Q \neq K$

Reduce Disturbance:

➡ reduce increase of  $[\text{NH}_3]$

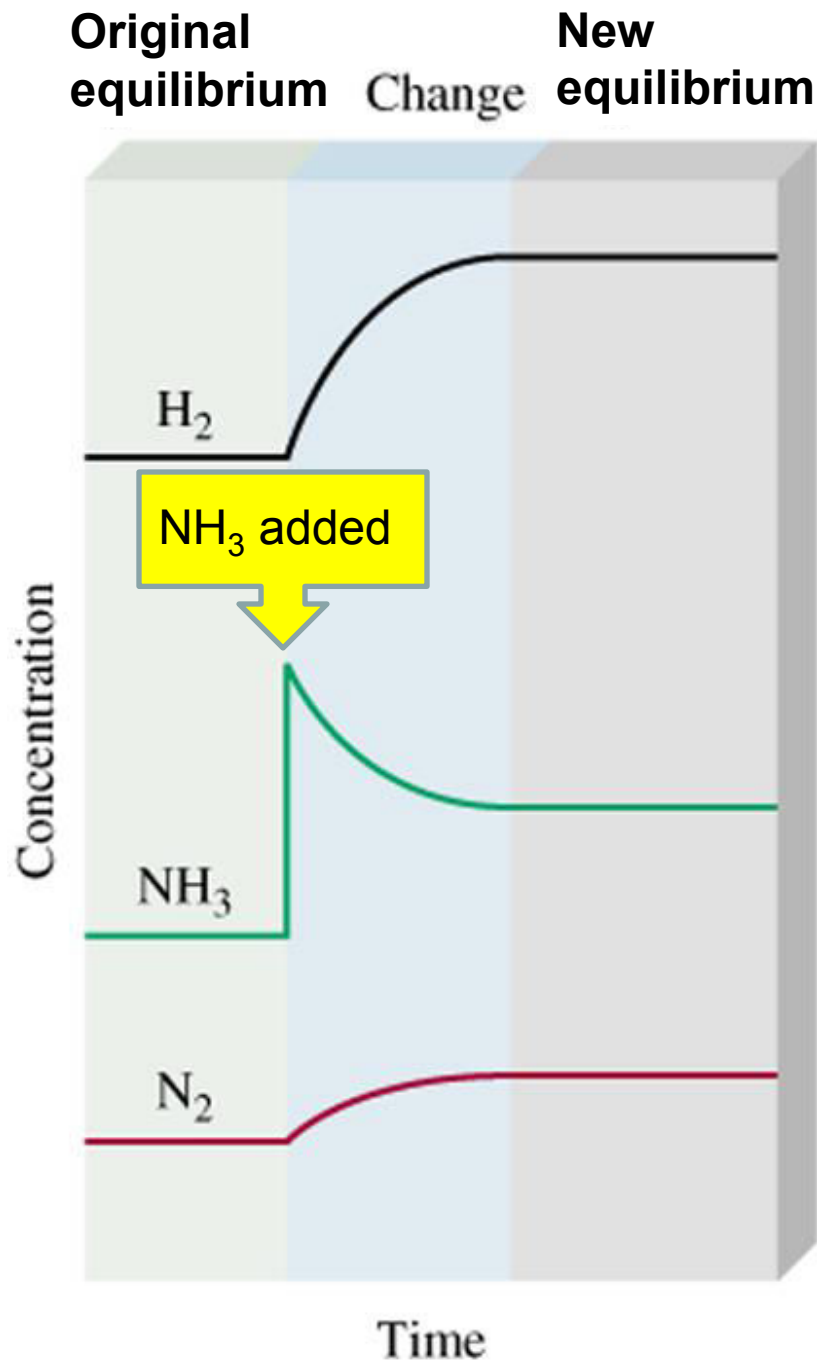
➡ net reaction proceeds to the left

New equilibrium:

$Q = K$

# Keep in mind!

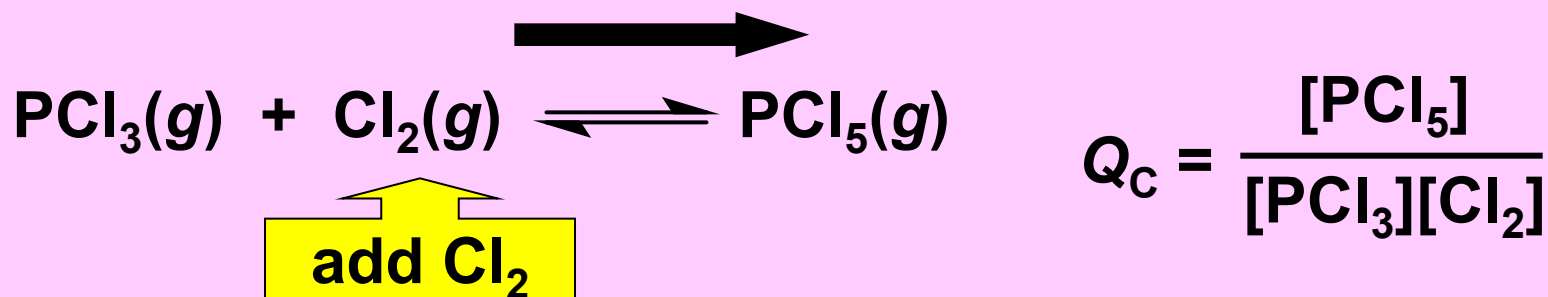
The **disturbance** (addition of  $\text{NH}_3$ ) is **reduced** but **not eliminated**.





# CHANGES IN CONCENTRATION

If the **concentration increases**, the system reacts to **consume** some of it.



$$Q_c < K_c \text{ (not at equilibrium)}$$

System will **reduce the disturbance** (increase of  $[\text{Cl}_2]$ ) by:

- ☞ proceeding to the **right**
- ☞ Consuming some additional  $\text{Cl}_2$
- ☞  $[\text{PCl}_5]$  increase
- ☞  $[\text{PCl}_3]$  decrease

	■ Original equilibrium	■ New initial (just after $\text{Cl}_2$ added)	■ New equilibrium
--	------------------------	--	-------------------

$[\text{PCl}_5]$	0.600 M	0.600 M	0.637 M
------------------	---------	---------	---------

$[\text{Cl}_2]$	0.125 M	0.200 M	0.163 M
-----------------	---------	---------	---------

$[\text{PCl}_3]$	0.200 M	0.200 M	0.163 M
------------------	---------	---------	---------

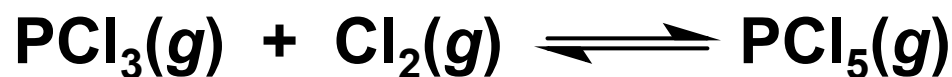
At the new equilibrium:  $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$

☞  $[\text{PCl}_5]$  is **higher** than its original concentration.

☞  $[\text{Cl}_2]$  is **higher** than its original concentration but **lower** than the concentration just after the  $\text{Cl}_2$  added (**disturbance is reduced but not eliminated**).

☞  $[\text{PCl}_3]$  is **lower** than its original concentration because some reacted with the added  $\text{Cl}_2$ .

	■ Original equilibrium	■ New initial (just after Cl <sub>2</sub> added)	■ New equilibrium
[PCl <sub>5</sub> ]	0.600 M	0.600 M	0.637 M
[Cl <sub>2</sub> ]	0.125 M	0.200 M	0.163 M
[PCl <sub>3</sub> ]	0.200 M	0.200 M	0.163 M



$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

At the **original equilibrium**:

$$K_c = \frac{0.600}{(0.200)(0.125)} = 24.0$$

At the **new equilibrium**:

$$K_c = \frac{0.637}{(0.163)(0.163)} = 24.0$$

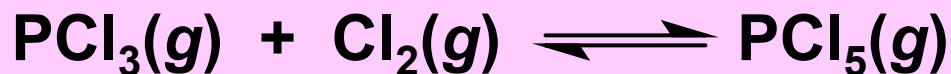
At a given temperature,  
 **$K_c$  does not change** with  
a change in concentration.



# CHANGES IN CONCENTRATION

If the **concentration decreases**, the system reacts to **produce** some of it.

remove  $\text{PCl}_3$



$$Q_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

$Q_c > K_c$  (not at equilibrium)

System will **reduce the disturbance** (decrease of  $[\text{PCl}_3]$ ):

👉 proceeding to the **left**

👉  $[\text{PCl}_3]$  and  $[\text{Cl}_2]$  increase

👉  $[\text{PCl}_5]$  decrease



## EXERCISE - 1

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



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?



# CHANGES IN PRESSURE (VOLUME)

- ☞ Only involve systems with **gaseous components**.
- ☞ Liquids and **solids** are **nearly incompressible**.

**Pressure changes** can occur in 3 ways:

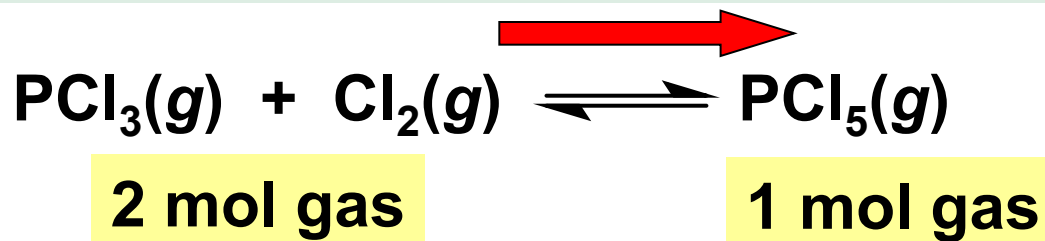
- Changing **concentration** of a **gaseous component**.
- Adding **inert gas**.
- Changing the **volume** of the **reaction vessel**.



a cylinder–piston  
assembly



# CHANGES IN PRESSURE (VOLUME)



**Disturbance:** volume decrease

☞ gas pressure immediately increases.

☞  $Q_c \neq K_c$  (not at equilibrium)

System will **reduce the disturbance**

☞ **Reduce** number of gas molecules

☞ proceeding to the **right**

☞  $[\text{PCl}_3]$  and  $[\text{Cl}_2]$  decrease

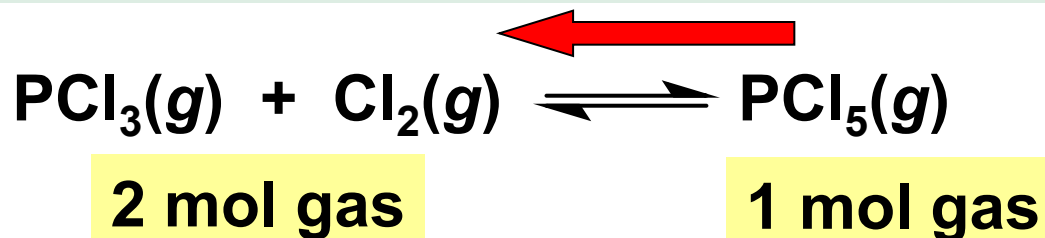
☞  $[\text{PCl}_5]$  increase

Push down





# CHANGES IN PRESSURE (VOLUME)



**Disturbance:** volume increase

☞ gas pressure immediately decreases.

☞  $Q_c \neq K_c$  (not at equilibrium)

System will **reduce the disturbance**

☞ **Increase** number of gas molecules

☞ proceeding to the **left**

☞  $[\text{PCl}_3]$  and  $[\text{Cl}_2]$  increase

☞  $[\text{PCl}_5]$  decrease



# KEEP IN MIND!

## Changes

**Decrease volume/  
Increase pressure**

**Increase volume/  
Decrease pressure**

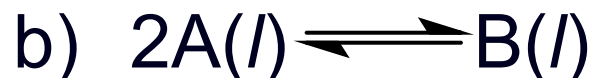
## Shifts in the Equilibrium

**To side with fewest moles of gas**

**To side with most moles of gas**

## EXERCISE - 2

What effect does an increase in pressure have on each of the following systems at equilibrium? The temperature is kept constant and in each case, the reactants are in a cylinder fitted with a movable piston.



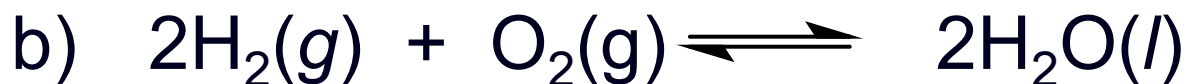
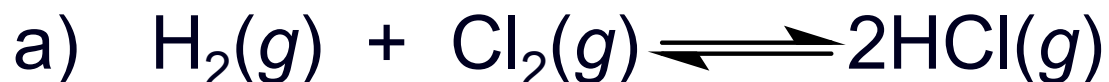
## EXERCISE - 3

Predict the effect of increasing the container volume on the amounts of each reactant and product in the following:



## EXERCISE - 4

Predict the effect of decreasing the container volume on the amounts of each reactant and product in the following:





## EXERCISE - 5

Consider the following equilibrium systems:



Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing volume) on the system at constant temperature.

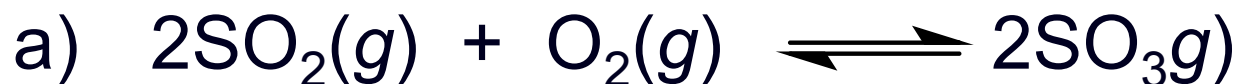
## EXERCISE - 6

How would you change the volume of each of the following reaction to increase the yield of the products?



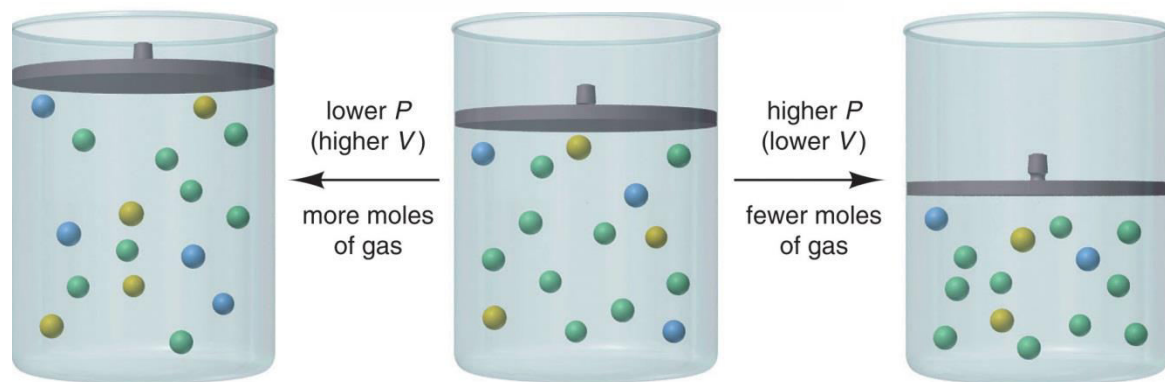
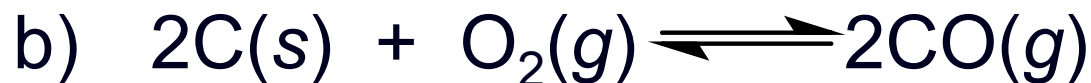
## EXERCISE - 7

How would you change the pressure (via a volume change) the following reaction to decrease the yield of the products?



## EXERCISE - 8

How would you adjust the volume of the reaction vessel in order to maximize product yield in the following reactions?





# ADDITION OF INERT GAS

- The total pressure of an equilibrium system can be changed without changing its volume by **adding an inert gas**.
- However, adding an inert gas has no effect on the equilibrium position
- The effect of the addition of an inert gas to the equilibrium system can be studied based on these two conditions:
  - I. At constant pressure
  - II. At constant volume

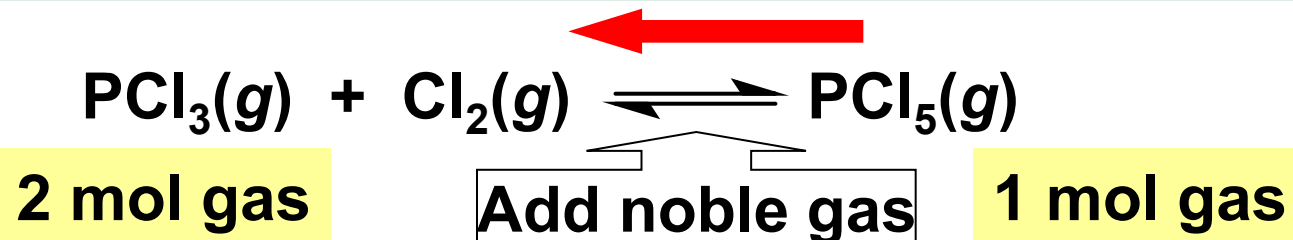


# THE EFFECT OF THE ADDITION OF INERT GAS ON EQUILIBRIUM

- **At constant pressure:**
  - \* The partial pressures for the gases in the system are lowered
  - \* The **net effect** is as though the gases at equilibrium are subjected to a **lower total pressure**
  - \* According to Le Chatelier's principle, **addition of a noble gas favours the direction that increases the number of moles of gas**



# ADDITION OF INERT GAS AT CONSTANT PRESSURE



**Disturbance:** addition of inert gas

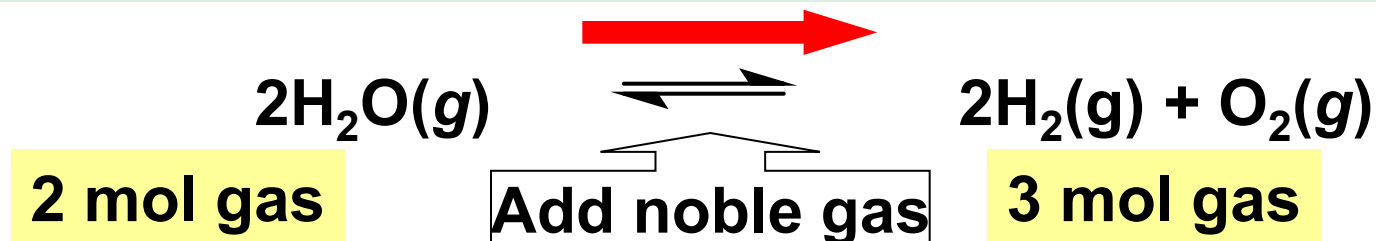
☞ Total gas pressure decreases.

System will reduce the disturbance

- ☞ By increasing the number of gas molecules
- ☞ proceeding to the left (less products will be produced)
- ☞  $[\text{PCl}_3]$  and  $[\text{Cl}_2]$  increase
- ☞  $[\text{PCl}_5]$  decrease
- ☞ Equilibrium favours the reactants



# ADDITION OF INERT GAS AT CONSTANT PRESSURE



**Disturbance:** addition of inert gas

☞ Total gas pressure decreases.

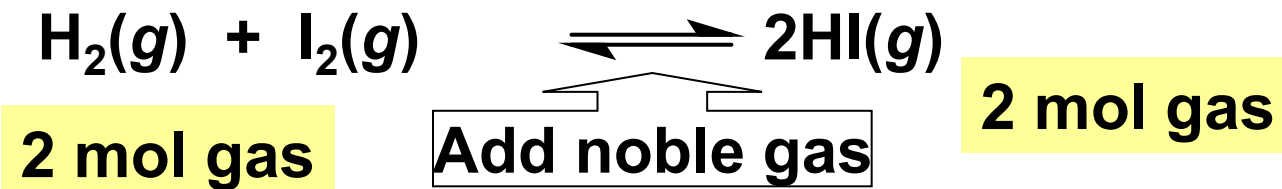
System will reduce the disturbance

- ☞ By increasing the number of gas molecules
- ☞ proceeding to the right (more products produced)
- ☞  $[\text{H}_2]$  and  $[\text{O}_2]$  increase
- ☞  $[\text{H}_2\text{O}]$  decrease
- ☞ Equilibrium favours the products





# ADDITION OF INERT GAS AT CONSTANT PRESSURE



**Disturbance:** addition of inert gas

- 👉 The equilibrium position is **not affected**
- 👉 Number of moles of reactants and products are the same



# THE EFFECT OF A NOBLE GAS ON EQUILIBRIUM

## At constant volume:

- The total number of gaseous molecules **increases**
- The total pressure of the equilibrium system **increases**
- However, the partial pressures of each of the gases in the equilibrium system **remains unchanged**

# KEEP IN MIND!!!

- From Dalton's law:

$$P_A = n_A (RT/V)$$

$P_A$  = partial pressure of any gas, A

- Adding inert gas at constant volume **does not change any of the quantities on the right side of the above equation**
- So,  $P_A$  remains constant
- Therefore, **addition of inert gas at constant volume has no effect on the equilibrium position and the composition of the equilibrium mixture**

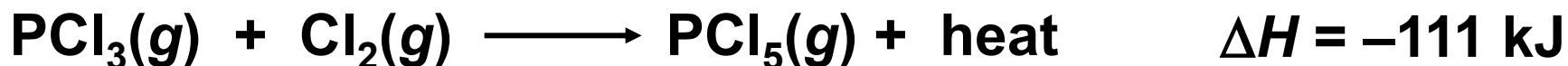


# CHANGES IN TEMPERATURE

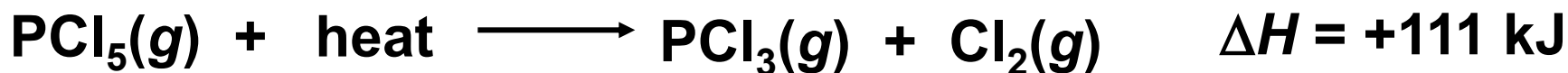
☞ Only temperature changes can alter  $K$ .



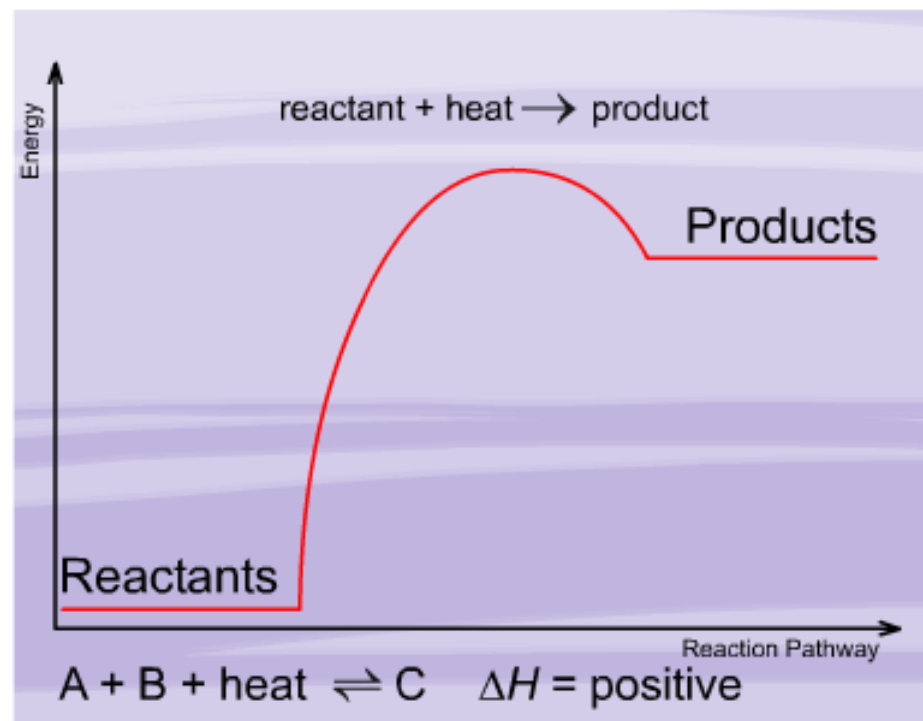
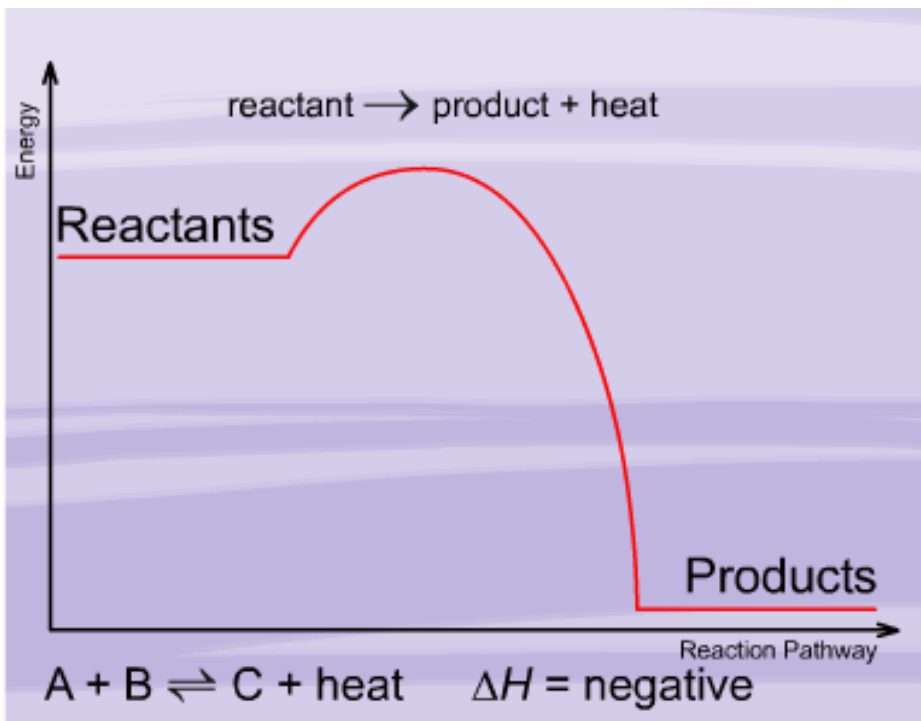
forward reaction is **exothermic**  
(heat released)



**Exothermic** ☞ heat **released**



**Endothermic** ☞ heat **absorbed**





# CHANGES IN TEMPERATURE

**Exothermic** ☞ **heat released**

heat released



**Disturbance:**

☞ **rise in temperature**

☞ **“adds” heat to the system**

☞ **exothermic reaction is not favorable**

**Disturbance:**

☞ **drop in temperature**

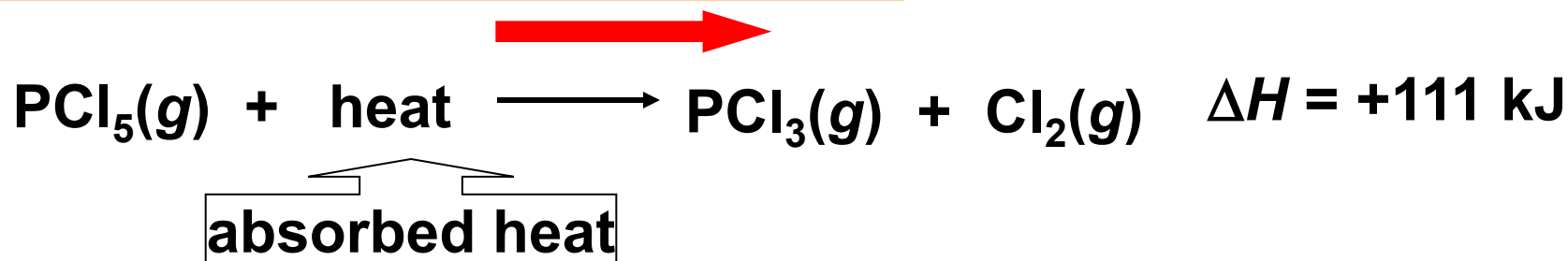
☞ **“removes” heat from the system**

☞ **exothermic reaction is favorable**



# CHANGES IN TEMPERATURE

**Endothermic** ➡ heat absorbed



**Disturbance:**

➡ rise in temperature

➡ “adds” heat to the system

➡ endothermic reaction is favorable

**Disturbance:**

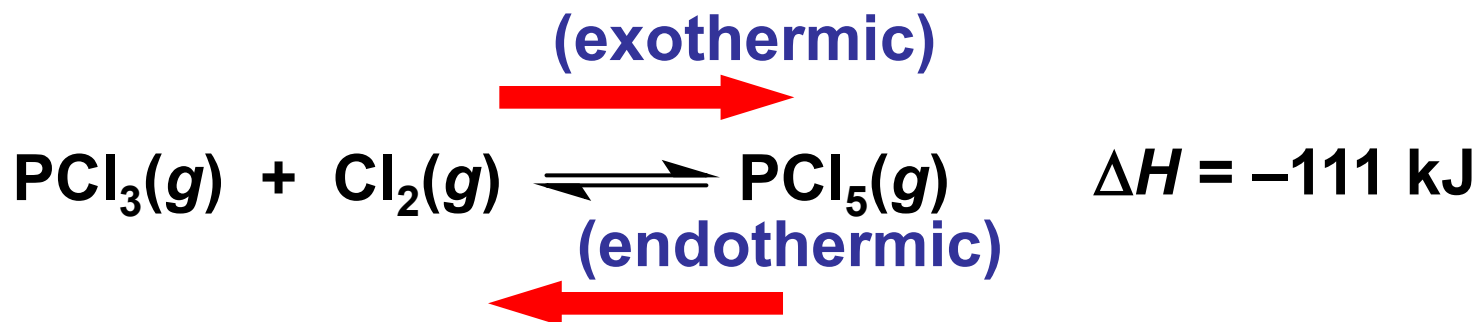
➡ drop in temperature

➡ “removes” heat from the system

➡ exothermic reaction is not favorable



# CHANGES IN TEMPERATURE



$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

<u>Changes</u>	<u>Net reaction</u>	<u>Exothermic</u>
Increase temperature	Left	$K$ decreases
Decrease temperature	Right	$K$ increases



Temperature decrease favors an exothermic reaction.





# CHANGES IN TEMPERATURE

(endothermic)



(exothermic)



$$K_c = \frac{[\text{O}_2]}{[\text{SO}_2]}$$

## Changes

## Net reaction

## Endothermic

Increase temperature

Right

*K* increases

Decrease temperature

Left

*K* decreases



Temperature increase favors an endothermic reaction.



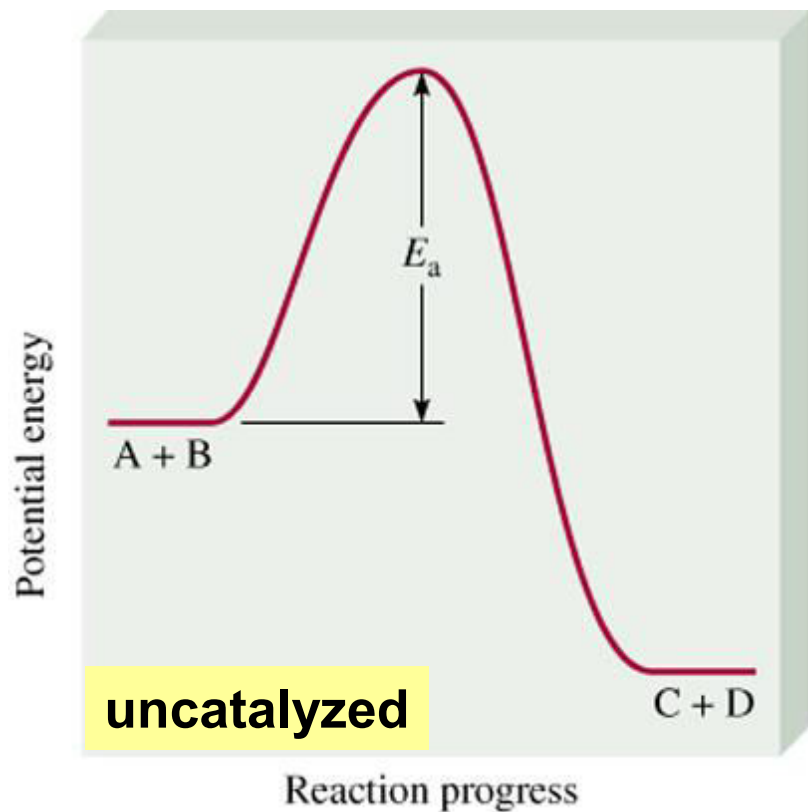
# EFFECT OF CATALYST

Catalyst **speeds up** a reaction.

- ☞ by providing **alternative mechanism** with **lower activation energy**.
- ☞ Increasing forward and reverse rates to the **same extent**.
- ☞ Shorten the time taken to reach equilibrium.

**BUT, REMEMBER...**

Catalyst has **no effect on the equilibrium position and value of  $K_c$** .



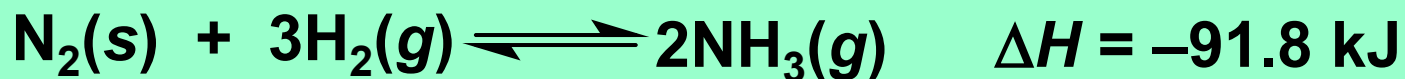
**Catalyst lowers activation energy,  $E_a$  for both forward and reverse reactions.**

# Keep in MIND

<u>Changes</u>	<u>Shift Equilibrium</u>	<u>Change Equilibrium Constant (value of <math>K</math>)</u>
Concentration	yes	no
Pressure	yes	no
Volume	yes	no
Temperature	yes	yes
Catalyst	no	no

# APPLICATION OF CHEMICAL EQUILIBRIUM: SYNTHESIS OF AMMONIA HABER PROCESS

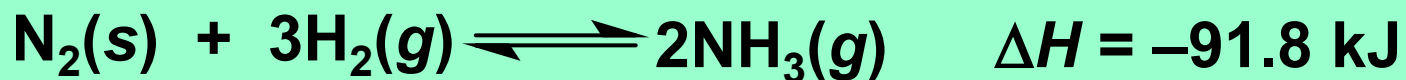
- Over 80% of ammonia is used as fertilizers. When applied to soil, it helps provide increased yields of crops.



- Nearly 13% of nitrogen fixation on earth is accomplished industrially through the Haber process for the formation of ammonia from its elements:
- The process was developed by Fritz Haber (German chemist) in 1913

# APPLICATION OF EQUILIBRIUM PRINCIPLES IN THE HABER PROCESS

- How to make an industrial process **economically** worthwhile? (cheap and fast)

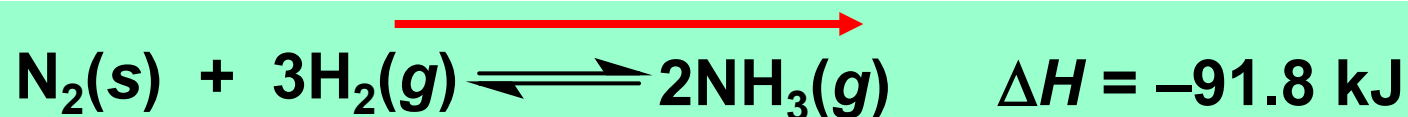


## Application of Le Chatelier's principle

Three ways to **maximize** the **yield** of ammonia:

- ✓ Decrease  $[\text{NH}_3]$
- ✓ Decrease volume (increase pressure)
- ✓ Decrease temperature

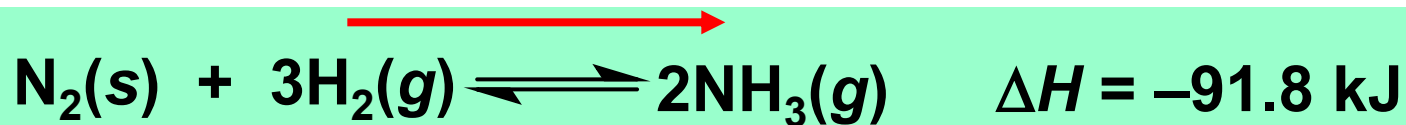
# APPLICATION OF EQUILIBRIUM PRINCIPLES IN THE HABER PROCESS



## 1. Decrease [NH<sub>3</sub>]

- Product: Ammonia
- By removing ammonia, the system will produce more in continual drive to reattain equilibrium
- The equilibrium will shift to the right

# APPLICATION OF EQUILIBRIUM PRINCIPLES IN THE HABER PROCESS



4 mol of gas

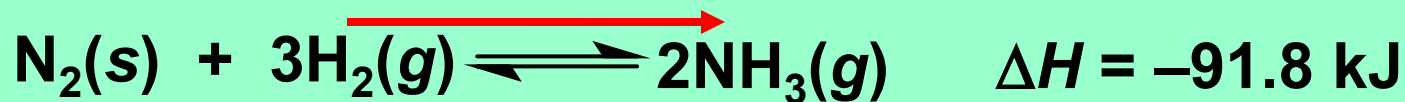
2 mol of gas

## 2. Decrease volume (increase pressure)

- 4 mol of gas reacts to form 2 mol of gas
- **Decreasing the volume** will shift the equilibrium towards fewer moles of gas
- Produces more ammonia



# APPLICATION OF EQUILIBRIUM PRINCIPLES IN THE HABER PROCESS



## 3. Decrease temperature

- Formation of ammonia is **exothermic**
- Decreasing temperature (removing heat) will **shift the equilibrium to the right**
- $K_C$  will increase

Table B17.1 Effect of Temperature on  $K_c$  for Ammonia Synthesis

$T$ (K)	$K_c$
200.	$7.17 \times 10^{15}$
300.	$2.69 \times 10^8$
400.	$3.94 \times 10^4$
500.	$1.72 \times 10^2$
600.	$4.53 \times 10^0$
700.	$2.96 \times 10^{-1}$
800.	$3.96 \times 10^{-2}$

## EXERCISE - 9

How does an increase in temperature affect the equilibrium concentration of the underlined substance and the value of  $K$ :

- a)  $\text{CaO(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{Ca(OH)}_2\text{(g)} \quad \Delta H = -82 \text{ kJ}$   
b)  $\text{CaCO}_3\text{(g)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)} \quad \Delta H = 178 \text{ kJ}$   
c)  $\text{C(s)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} \quad \Delta H = -75 \text{ kJ}$   
d)  $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)} \quad \Delta H = 181 \text{ kJ}$   
e)  $\text{P}_4\text{(s)} + 10\text{Cl}_2\text{(g)} \rightleftharpoons 4\text{PCl}_5\text{(g)} \quad \Delta H -1528 \text{ KJ}$



## EXERCISE - 10

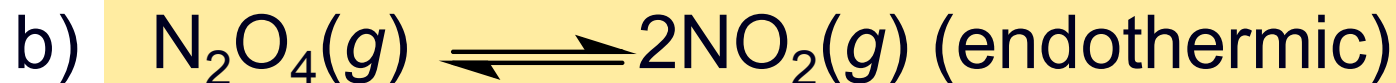
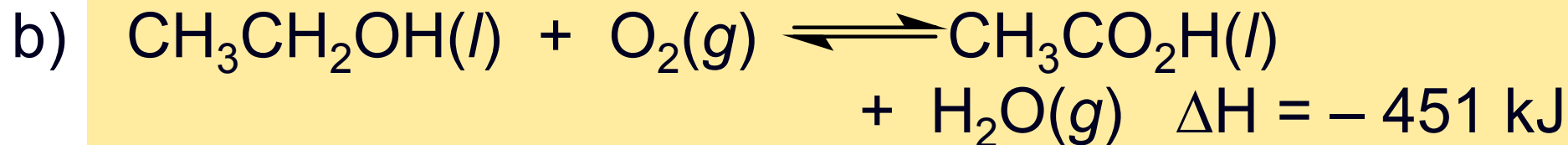
Predict the effect of increasing the temperature on the amounts of products in the following reactions:

- a)  $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) \quad \Delta H = -90.7 \text{ kJ}$
- b)  $\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g) \quad \Delta H = 131 \text{ kJ}$
- c)  $2\text{NO}_2(g) \rightleftharpoons 2\text{NO}(g) + \text{O}_2(g) \text{ (endothermic)}$
- d)  $2\text{C}(s) + \text{O}_2(g) \rightleftharpoons 2\text{CO}(g) \text{ (exothermic)}$



## EXERCISE - 11

Predict the effect of decreasing the temperature on the amounts of products in the following reactions:

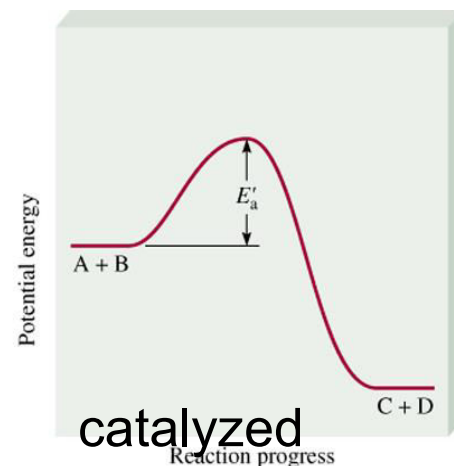
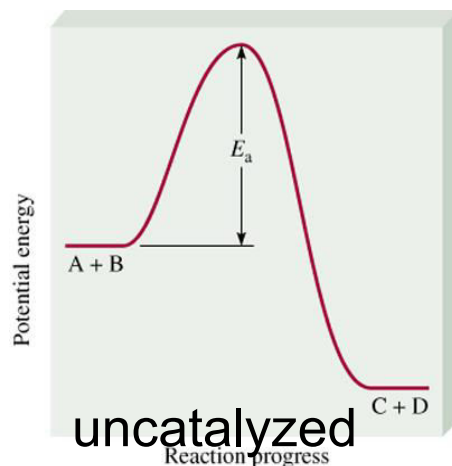


## EXERCISE - 12

In the uncatalyzed reaction



the pressure of the of the gases at equilibrium are  $P_{\text{N}_2\text{O}_4} = 0.377$  atm and  $P_{\text{NO}_2} = 1.5$  atm at  $100^\circ\text{C}$ . What would happen to these pressures if a catalyst to the mixture ?



## EXERCISE - 13

**Consider the following equilibrium process between dinitrogen tetrafluoride ( $\text{N}_2\text{F}_4$ ) and nitrogen difluoride ( $\text{NF}_2$ ):**

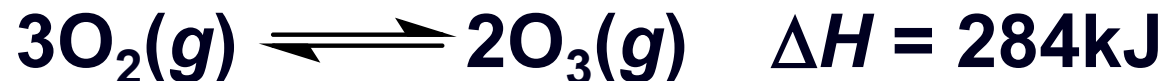


**Predict the changes in equilibrium if**

- a) the reaction mixture is heated**
- b)  $\text{NF}_2$  gas is removed**
- c) the pressure decrease**
- d) inert gas, such as He, is added**

## EXERCISE - 14

**Consider the equilibrium between molecular oxygen and ozone**



**What would be the effect of**

- a) increasing pressure by decreasing volume**
- b) increasing pressure by adding  $\text{O}_2$**
- c) decreasing the temperature**
- d) adding a catalyst**

## EXERCISE - 15

**Heating solid sodium bicarbonate in a closed vessel establishes the following equilibrium:**



**What would happen to the equilibrium position if**

- a) some of the  $\text{CO}_2$  were removed**
- b) some solid  $\text{Na}_2\text{CO}_3$  were removed**
- c) some solid  $\text{NaHCO}_3$  were removed**



## EXERCISE - 16

**Consider the following equilibrium process:**



**Predict the direction of the shift in equilibrium when**

- a) the temperature is raised
- b) more chlorine gas is added
- c) some  $\text{PCl}_3$  is removed
- d) pressure on the gases is increased
- e) a catalyst is added to the reaction mixture

## EXERCISE - 17

**Consider the following equilibrium reaction in a closed container:**



**What happen if**

- a) the volume is increased
- b) some CaO is added
- c) some CO<sub>2</sub> is added
- d) a few drops of a NaOH solution are added
- e) a few drops of a HCl solution is added
- f) temperature is increased

**Note: Decomposition reactions are endothermic.**

## EXERCISE - 18

Lime (CaO) used primarily in the manufacture of steel, glass, and high-quality paper. It is produced in an endothermic reaction by thermal decomposition of limestone:



How would control reaction conditions to produce the maximum amount of lime?