

# General Chemistry

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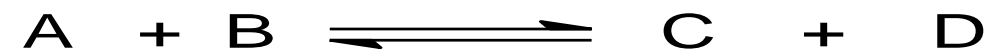
## **Chapter 3: Chemical Equilibrium**

# Chemical equilibrium

## Reversible reaction

$A + B \rightarrow C + D$  (forward reaction);

$A + B \leftarrow C + D$  (backward reaction)

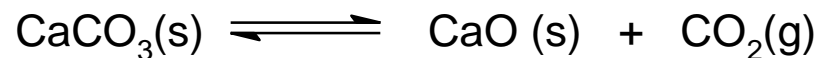
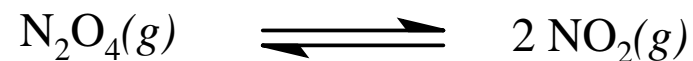
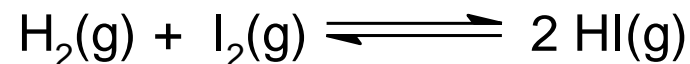
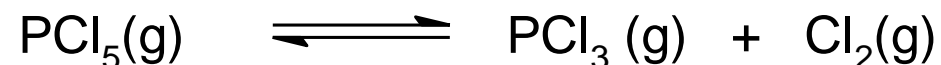


- A chemical reaction which **can go in the forward direction and backward direction** simultaneously is called a **reversible reaction**

## Irreversible reactions:

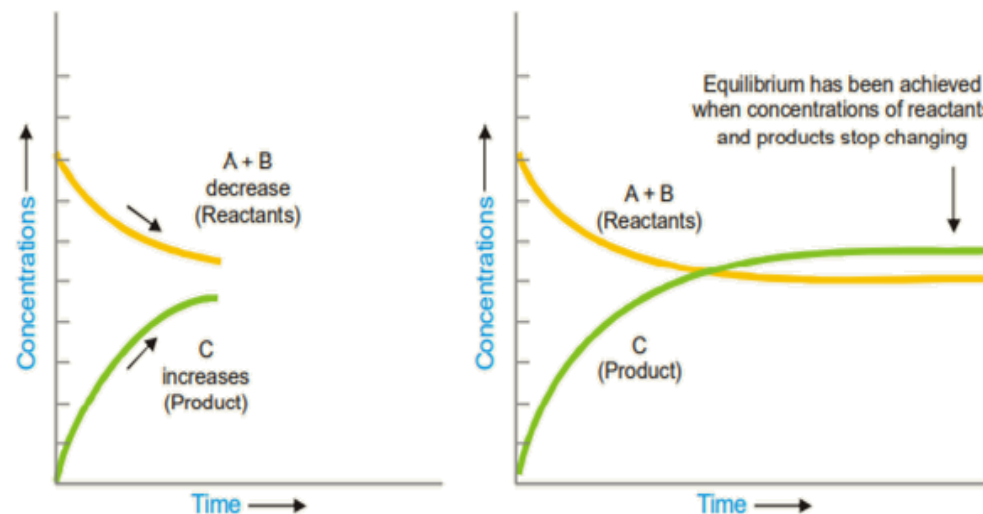
- That **proceeds in one direction only**. Like, precipitation reaction , neutralization reaction

Some examples of Reversible reactions

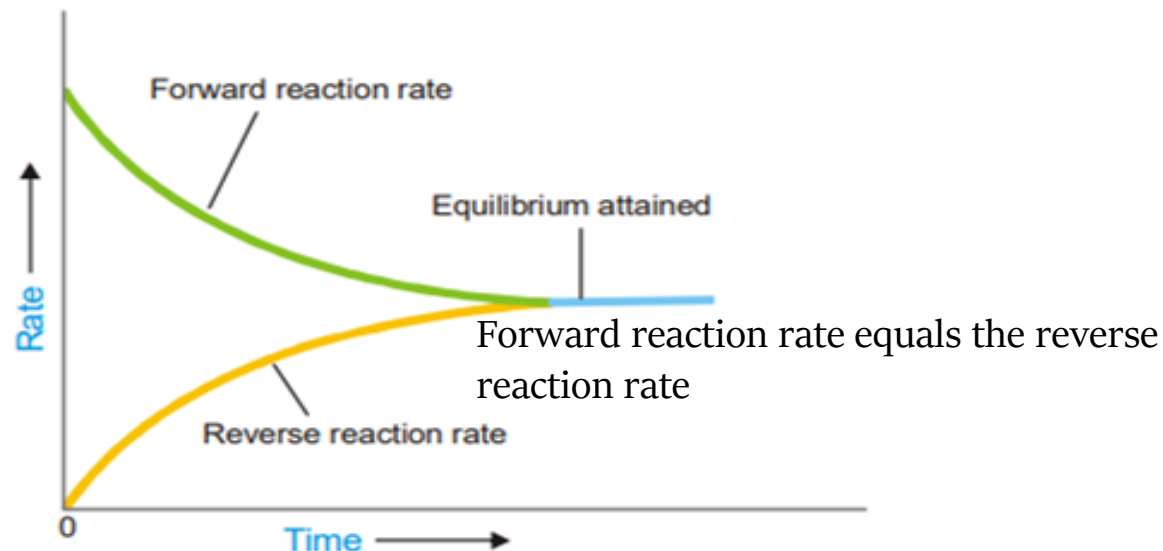


## Nature of chemical equilibrium:

- Let a chemical reaction between  **$\text{H}_2\text{O}(g)$  and  $\text{CO}(g)$  in a closed vessel**, represented as:  
$$\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)$$
- At certain time, the **system attains a state of equilibrium** in which **two opposing reactions proceed equally**
- Thus, chemical equilibrium may be defined as the state of a reversible in which the **rates of the forward and reverse reactions are equal** and the **concentrations of the reactants and products remain constant**.



**Fig:** The changes in concentrations with time for the reaction



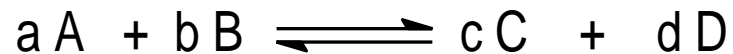
**Fig:** Reaction at equilibrium

## Characteristics of Chemical Equilibrium

- Cannot be attained in an Open Vessel
- Dynamic in nature (in constant motion)
- Reversible and attains equilibrium state spontaneously
- Can be approached from either side.
- Represents a compromise between opposing tendencies.
- A catalyst cannot change the equilibrium point
- Constancy of concentrations

### The Equilibrium Constant:

Let a general reaction



Where, molar concentration (active mass) of A, B, C and D at the equilibrium point be represented as, [A], [B], [C] and [D]

Contd...

- '**Active mass**' means the molar concentration of any substances which determines the rate of chemical reaction.
- **Law of Mass action** states that : the rate of a chemical reaction is proportional to the active masses of the reactants.
- According to law of mass action,  
rate of forward reaction =  $k_f[A]^a[B]^b$ .....(i)  
rate of reverse reaction =  $k_r[C]^c[D]^d$ .....(ii)
  - $k_f$  and  $k_r$  are called rate constants
- Eventually the two processes are proceeding at the same rate, and the reaction is at equilibrium:
  - rate of forward reaction = rate of reverse reaction  
*i.e.*  $k_f[A]^a[B]^b = k_r[C]^c[D]^d$

Contd...

Now, the above eqn. is written ,  $k_f/k_r = [C]^c[D]^d / [A]^a[B]^b$ .....(iii)

- At specific temperature,  $k_f$  and  $k_r$  are constant and the ratio of  $k_f/k_r$  is also constant. Then, this ratio  $k_f/k_r$  is replaced by new constant term,  $K_{eqm}$ . which is known as **equilibrium constant** and the equation is called **equilibrium constant expression** or **equilibrium law**.
- $K_{eqm} = [C]^c[D]^d / [A]^a[B]^b$ .....(iv)
- Thus, **equilibrium constant** may be defined as the ratio of product of equilibrium concentration of the products to the product of equilibrium concentration of the reactants, with each concentration term raised to a power equal to the coefficient of the species in the balanced chemical equation.
- **Characteristics of equilibrium constant:**
  - The value of  **$K_{eqm}$** . of a reaction **at constant temperature and pressure is same**.
  - The value of  **$K_{eqm}$** . of a reaction does not **depend upon the initial concentration** of reacting species in the reaction.

## Contd...

- **Characteristics of equilibrium constant:**
  - The value of  $K_{eqm}$  does **not depend upon the use of catalyst.**
  - *The value of  $K_{eqm}$  in fact **depends on temperature and identity of the reactants and products.***
  - *The value of  $K_{eqm}$  of a reversible reaction provides following ideas.*
    - ⇒ If the  $K_c$  value is large ( $K_c \gg 1$ ), the equilibrium lies to the right and the reaction mixture contains mostly products.
    - ⇒ If the  $K_c$  value is small ( $K_c \ll 1$ ), the equilibrium lies to the left and the reaction mixture contains mostly reactants.
    - ⇒ If the  $K_c$  value is close to 1 ( $0.10 < K_c < 10$ ), the mixture contains appreciable amounts of both reactants and products.

## Writing Equilibrium constant expressions:

- **1.**  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$   $K_c = [\text{NO}_2]^2 / [\text{N}_2\text{O}_4]$  ;  $K_p = [\text{P}_{\text{NO}_2}]^2 / [\text{P}_{\text{N}_2\text{O}_4}]$
- **2.**  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$   $K' = [\text{CO}_2][\text{CaO}] / [\text{CaCO}_3]$ 
  - **Since, concentrations of *pure solids and liquids* are fixed by their density and molar mass (*both constants*) and *do not vary with the amount, and their concentration taken to be unity.***
- *Therefore, equilibrium constant expression is given as.*
  - $[\text{CO}_2] = [\text{CaCO}_3] / [\text{CaO}] \cdot K' = K_p$
- **3.**  $\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightleftharpoons \text{Cu}(s) + \text{Zn}^{2+}(aq)$  ;  $K_c = [\text{Zn}^{2+}] / [\text{Cu}^{2+}]$
- **4.**  $3\text{Cu}(s) + 2\text{NO}_3^-(aq) + 8\text{H}^+(aq) \rightleftharpoons 3\text{Cu}^{2+}(aq) + 2\text{NO}(g) + 4\text{H}_2\text{O}(l)$  **?????**



## Reaction quotient (Q) and Equilibrium constant (K<sub>eqm</sub>):

- The reaction quotient, Q, is the resulting value when we substitute reactant and product concentrations into the equilibrium expression at any instance.

**1. If  $Q > K$ ,** *the reaction will go to the left.*

- The ratio of products over reactants is too large & the reaction will move toward equilibrium by forming more reactants.

**2. If  $Q < K$ ,** the reaction will go to the right.

- The ratio of products over reactants is too small & the reaction will move toward equilibrium by forming more products.

**3. If  $Q = K$ ,** the reaction mixture is already at equilibrium, so no shift occurs.

## Example

1. For the reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$K = 6.0 \times 10^{-2}$  at  $500^\circ\text{C}$ . Predict the direction in which the system will shift to reach equilibrium. if  $[\text{NH}_3] = 1.0 \times 10^{-5} \text{ M}$ ,  $[\text{N}_2] = 1.0 \times 10^{-5} \text{ M}$  and  $[\text{H}_2] = 2.0 \times 10^{-3} \text{ M}$ .

- Therefore, since  $Q > K$  the direction goes towards the reactants ( $Q = 1.3 \times 10^3$ )

2. For the reaction,  $\text{B} \rightleftharpoons 2\text{A}$ ,

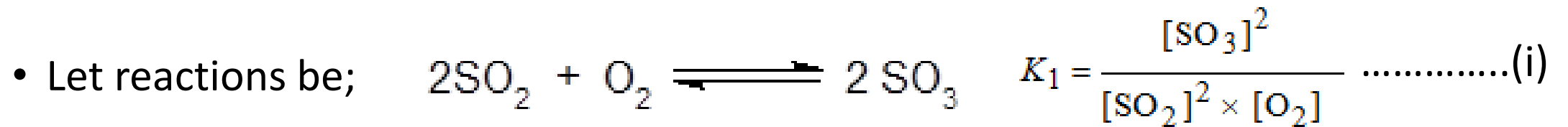
$K_c = 2$ . Suppose 3.0 moles of A and 3.0 moles of B are introduced into a 2.00 L flask. (a) In which direction will the reaction proceed to attain equilibrium? (b) Will the concentration of B increase, decrease or remain the same as the system moves towards equilibrium?

- Try yourself

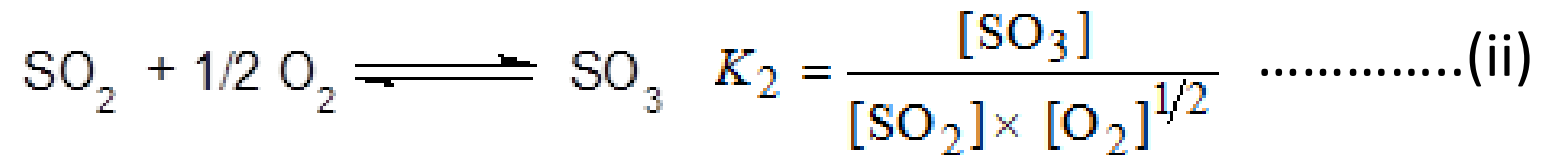
# Modifying equilibrium constant expressions

## 1. Changing stoichiometric coefficients

- If a reaction is multiplied by a certain number, its equilibrium constant must be raised to a power equal to that number in order to obtain the new equilibrium constant, for the new reaction.



- If this reaction is multiplied by  $\frac{1}{2}$  the new chemical reaction and new equilibrium constant will be



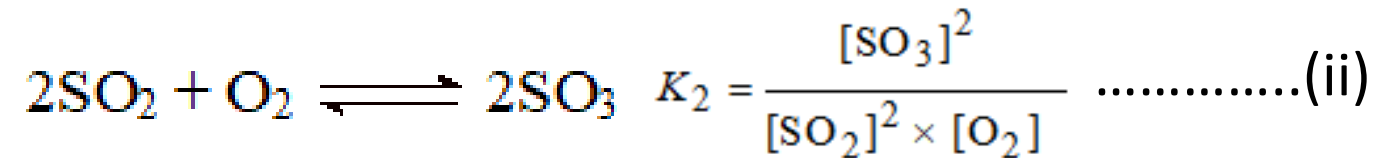
- Now, by the comparison of these expressions (i) and (ii), we may write;  
 $K_2 = (K_1)^{1/2}$  to justify the above statement.

## 2. Reversing the reaction

- The equilibrium constant for a reaction and its reverse are reciprocals to each other

- Let reactions be;  $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$   $K_1 = \frac{[\text{SO}_2]^2 \times [\text{O}_2]}{[\text{SO}_3]^2}$  .....(i)

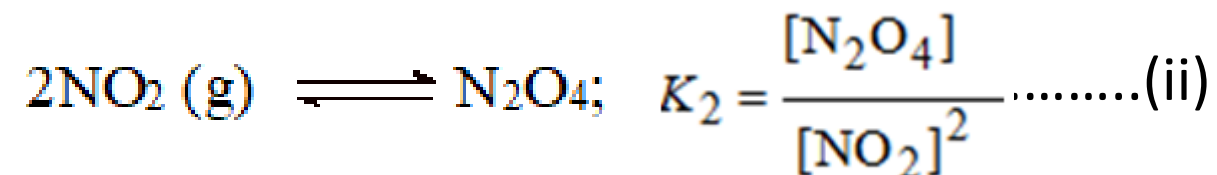
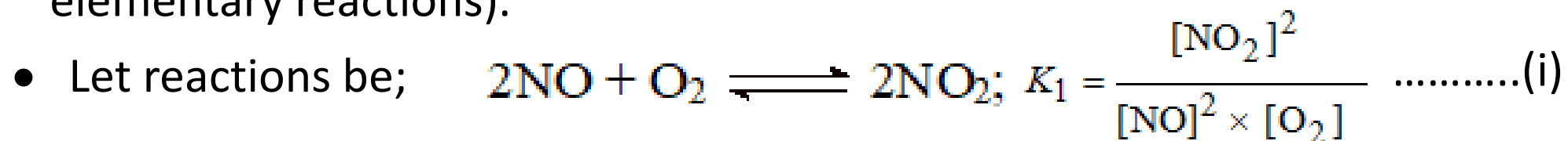
- Its reverse reaction is;



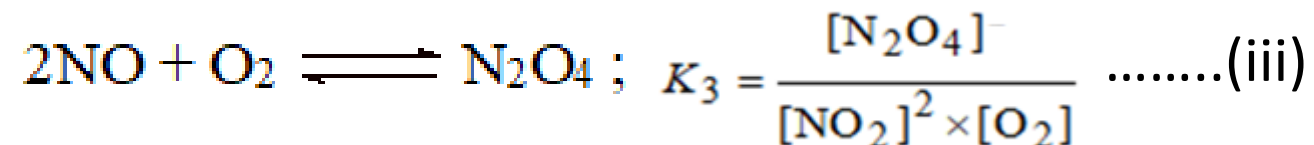
- Then, by comparison of above expressions 'i' and 'ii',  
we may write  $K_2 = (1/K_1)$  to justify the above statement

### 3. Adding the multiple equilibrium reactions to get final reaction

- When two or more elementary reactions are added, their equilibrium constants must be multiplied to give the equilibrium constant of overall reaction (a complex reaction proceeding with successive reversible elementary reactions).



- Final reaction is;

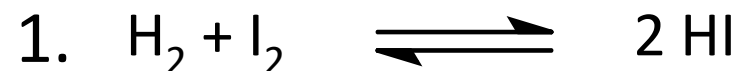


- Then, by comparison of above expressions (i), (ii) and (iii), we may write  $K_3 = K_1 \times K_2$  to justify the above statement.

## Relation between equilibrium constants, $K_p$ and $K_c$ :

- Deduce the relation,  $K_p = K_c \times [RT]^{\Delta n}$  where, symbols have their usual meanings. (**Attempt yourself**)
- Actually,  $\Delta n$  is the difference between the total moles of the products and the total moles of the reactants,  $R$  is universal gas constant and  $T$  is absolute temperature
  - *If the unit of concentration is changed, the equilibrium constant for a chemical reaction will change if  $\Delta n \neq 0$ . The new equilibrium constant is obtained as:*
    - $K_{new} = K_{previous} [\text{conversion factor}]^{\Delta n}$
- For the reaction,  $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$ 
  - If equilibrium constant in **atm unit** is to be changed to equilibrium constant in **torr unit**. Then, the unit relation is  $P_{(\text{Torr})} = 760 \times P_{(\text{Atm.})}$ , so the equilibrium constant also holds following relation,  $K_{P(\text{Torr})} = K_{P(\text{Atm.})} \times [760]^2$

Predict the relation between  $K_p$  and  $K_c$  for the reactions:

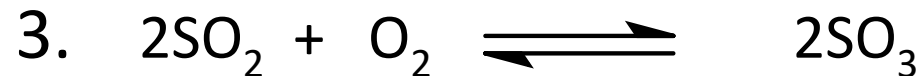


$$\Delta n = 2 - 2 = 0; K_p = K_c (RT)^{\Delta n} \text{ or } K_p = K_c (RT)^0 \text{ or } K_p = K_c.$$



$$\Delta n = 2 - 1 = 1 \text{ (+ve)}; K_p = K_c (RT)^{\Delta n} \text{ or } K_p = K_c (RT)^1 \text{ or } K_p > K_c.$$

Try yourself for others!



$$\Delta n = 2 - 3 = -1 \text{ (-ve)}; K_p = K_c (RT)^{\Delta n} \text{ or } K_p = K_c (RT)^{-1} \text{ or } K_p < K_c.$$

## Factors affecting the chemical equilibrium: Le Chatelier's Principle

- **Le Chatelier's Principle**

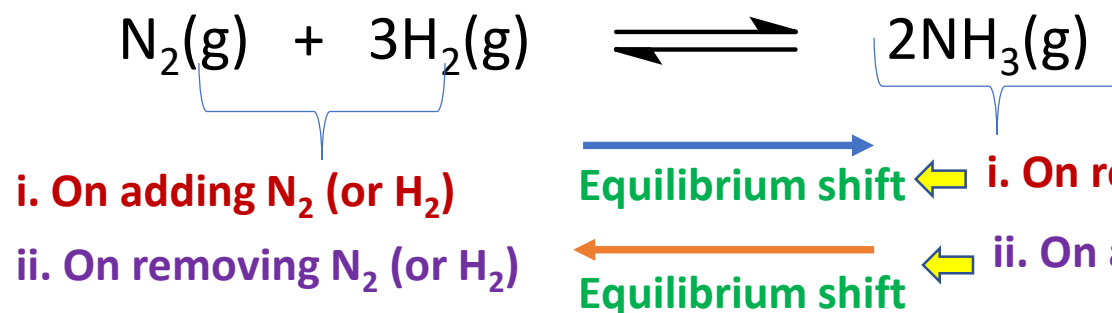
- If a system at equilibrium is subjected to a change of pressure, temperature, or the number of moles of a substance, there will be a tendency for a net reaction in the direction that tends to reduce the effect of this change
- There are three factors:
  - (1) Changing the **concentration of a reactant or product**.
  - (2) Changing the **pressure (or volume) of the system**.
  - (3) Changing the **temperature**.
- On applying to a chemical reaction in equilibrium, Le Chatelier's principle can be stated as: if a **change in concentration, pressure or temperature** is caused to a chemical reaction in equilibrium, the equilibrium will **shift to the right or the left** so as **to minimise the change**.



# Application of Le-chatelier principle to illustrate the effect of change of concentration, pressure and temperature on equilibrium of chemical reactions

## 1. The effect of a change in Concentration:

- Let us illustrate this effect on a system at equilibrium with example:



Equilibrium I		Equilibrium II
$[\text{N}_2] = 0.399 \text{ M}$		$\text{N}_2 = 1.348 \text{ M}$
$[\text{H}_2] = 1.197 \text{ M}$	$\xrightarrow{\text{1 mole/L of N}_2 \text{ added}}$	$[\text{H}_2] = 1.044 \text{ M}$
$[\text{NH}_3] = 0.202 \text{ M}$		$[\text{NH}_3] = 0.304 \text{ M}$

Increase in concentration of any of reactants  $\xrightarrow{\text{shifts the equilibrium towards}}$  forward direction.

Increase in concentration of any of products  $\xrightarrow{\text{shifts the equilibrium towards}}$  backward direction.

contd...

## 2. The effect of a change in Pressure:

- There are ***three ways to affect a change in the pressure of gaseous reaction mixture.***

### i. Addition or removal of gaseous reactants or products

- This process is similar to the change in concentration of reactant and product. Remember, that the **pressure of gases is related directly to the concentration** by  $P = n/V$ .



contd...

## ii. Change the volume of container.

- If the pressure of a gas is reduced, its volume will increase; **the pressure and volume are inversely proportional**.
- If **P** increases (**V** decreases), the equilibrium of the system will **shift in the direction of less number of gas molecules** (among reactant and product), since this effectively reestablishes equilibrium by ***decreasing the pressure***.
- If **P** decreases (**V** increases), the system **shifts to the side with a greater number of gas molecules**.
- For example,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}); \Delta\text{H} = - 22.4 \text{ Kcal}$   
**Q.** Does the equilibrium shift left or right if the pressure is increased?

contd...

- For example,  $2\text{NO}_2 (\text{g}) \rightleftharpoons \text{N}_2\text{O}_4$ ;

**Q.** Does the equilibrium shift left or right if we double the pressure, by compressing the mixture to a smaller volume?

- For the chemical reactions with  $\Delta n = 0$ , **change of pressure has no any effect on the equilibrium condition. Example**  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$

Increase in pressure (decrease in volume)	shifts the equilibrium towards $\rightarrow$	lesser number of gaseous molecules
Decrease in pressure (increase in volume)	shifts the equilibrium towards $\leftarrow$	larger number of gaseous molecules

System	Pressure increased	Pressure decreased
(1) $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$	$\leftarrow$	$\rightarrow$
(2) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$	$\leftarrow$	$\rightarrow$
(3) $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	$\rightarrow$	$\leftarrow$
(4) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$	$\rightarrow$	$\leftarrow$
(5) $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$	No effect	No effect
(6) $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$	No effect	No effect

contd...

- **iii. Addition of Inert gas.**

- a. Addition of an inert gas into a system at eqm. under **constant volume** causes, **an increase in the pressure of the system and an increase in the total no. of moles in the system**. i.e.  $P_t V = n_t RT$  or  $n_t / P_t = V / RT$  Here, the ratio of  $n_t / P_t$  remains constant even on addition of any inert gas. In this case the **equilibrium constant is not affected by the inert gas**.
  - If the **volume of the system is increased** then *partial pressure of each component is decreased* and **shifts the eqm. towards the side with greater no. of gaseous molecules**.
- b. When **inert gas is added without disturbing the total pressure (constant P)**, in this case partial pressure of reactant and product decreases by certain factor (***increases the volume of the system***). The equilibrium condition will be disturbed if  **$\Delta n \neq 0$** .

contd...

<u>Reaction having</u> <u><math>\Delta n</math> value</u>	<u>Direction of shift in eqm.</u>
<u><math>\Delta n = +ve</math></u>	Right hand side (Product side)
<u><math>\Delta n = -ve</math></u>	Left hand side ( Reactant side)
<u><math>\Delta n = 0</math></u>	Remains constant

- Here according to **Le-chateliers principle** **equilibrium will shift towards more number of mole side** (among reactant and product), which minimizes the stress to some extent. {Here the **stress is the decrease in partial pressure**}.

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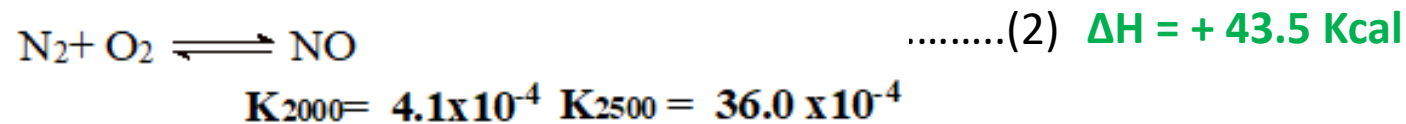
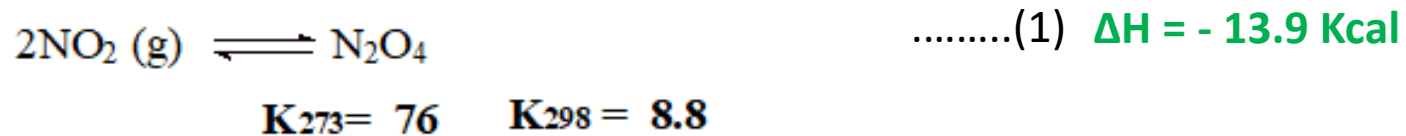
### 3. The effect of a change in Temperature:

- For a reversible reactions if **the forward reaction proceeds by the evolution of heat (exothermic)**, the **reverse reaction occurs by the absorption of heat (endothermic)**.
- The **change of temperature** affects the equilibrium state of **both exothermic and endothermic** reaction.
- The **magnitude of the equilibrium constant is also affected** by the change of temperature for such kind of reactions.
- When **temperature of a reaction is increased**, **the equilibrium shifts in a direction in which heat is absorbed**

Increase in temperature	shifts the equilibrium towards	⇨	endothermic reaction
Decrease in temperature	shifts the equilibrium towards	⇨	exothermic reaction

contd...

- Consider following reactions, in which **energy is released. (i.e. exothermic) in 1<sup>st</sup>** and **energy is absorbed (i.e. endothermic) in 2<sup>nd</sup>.**



- Since the new eqm. has less products than the old one, the new K constant < old one. **As T rises, K drops**
- Since the new eqm. has more products than the old one, the new K constant > old one. **As T rises, K also increases**

**Direction of equilibrium shift with increase in Temperature**

Reaction	Equilibrium Shift
$4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Cl}_2 + 284 \text{ kcal}$	←
$\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl} + 44.2 \text{ kcal}$	←
$\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O} + 212.8 \text{ kcal}$	←
$2\text{CO}_2 + 135.2 \text{ kcal} \rightleftharpoons 2\text{CO} + \text{O}_2$	→
$\text{N}_2\text{O}_4 + 14 \text{ kcal} \rightleftharpoons 2\text{NO}_2$	→
$\text{H}_2 + \text{I}_2 + 12.4 \text{ kcal} \rightleftharpoons 2\text{HI}$	→



## Effect of a Catalyst

- Catalysts lower  $E_a$  for the reaction, so a catalyst **decreases the amount of time taken to reach equilibrium for both** the forward and reverse reactions.
- The catalyst **does not affect the equilibrium concentrations** of reactants and products in the equilibrium mixture; thus, the  **$K_c$  value does not change**.

# Calculation with the equilibrium constant for gaseous reaction

( in terms of Total pressure (P) of reactants & products, and 'f' fractional amount dissociated of reactant)

- The **equilibrium constant** of a reaction between gases are often expressed in terms of the **partial pressure of reagent** and generally **units are atmosphere**

- Thus for the reaction,  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$

- We have,  $K_P = \frac{P_{(\text{NO}_2)}^2}{P_{(\text{N}_2\text{O}_4)}} = 0.14$  where the pressure are expressed in atm.

- Here,  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$

At initial,      1                      0

At eqm.        1-f                      2f

- To express in terms of total pressure,  $P_T$  and 'f' of the original  $\text{N}_2\text{O}_4$  dissociated,
- Total no. of moles of all particles present at eqm. is proportional to total fraction of all i. e. (1-f+2f) or **(1+f)**.

contd...

- Then, **mole fraction** of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are :
  - $X_{\text{N}_2\text{O}_4} = (1-f) / (1+f)$  , and  $X_{\text{NO}_2} = (2f) / (1+f)$
- Now, **partial pressure** of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  in terms of total pressure,  $P_T$ .
  - $P_{\text{NO}_2} = X_{\text{NO}_2} \cdot P_T = [(2f) / (1+f)] \cdot P_T$  ;  $P_{\text{N}_2\text{O}_4} = X_{\text{N}_2\text{O}_4} \cdot P_T = [(1-f) / (1+f)] \cdot P_T$
- Now, putting the values of  $P_{\text{NO}_2}$  and  $P_{\text{N}_2\text{O}_4}$  in eqn.  $K_P = \frac{P_{(\text{NO}_2)}^2}{P_{(\text{N}_2\text{O}_4)}}$
- We get
- $K_P = P_T \times \frac{4f^2}{(1-f^2)}$       Here,  $P_T$  = total pressure of reactants and products;  
 $f$  = fraction of the original  $\text{N}_2\text{O}_4$  that dissociated.
- $K_p$  is constant that depends only on temperature. If total pressure,  **$P$  is varied**, the fraction of  **$\text{N}_2\text{O}_4$  dissociated must change** so as to keep the **right-hand side of constant**.
- **Q.** Let, volume of the system is increased so that ' $P$ ' decreases. Does ' $f$ ' increase or decrease?  
$$P_T = \frac{K_P}{4} \times \left( \frac{1}{f^2} - 1 \right)$$

## Some Numerical Problems

- **Q.N.1.** A mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  has at eqm. a total pressure of 1.5 atm. What fraction of  $\text{N}_2\text{O}_4$  has dissociated to  $\text{NO}_2$  at  $25^\circ\text{C}$ ? [ $K_p$  0.14] [Ans. 0.15]
- **Q.N. 2.** If the volume of the system is increased so that pressure falls to 1 atm. ,what fraction of original  $\text{N}_2\text{O}_4$  is dissociated? [Ans. 0.18]
- **Q.N. 3.** Suppose a reaction  $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$ 
  - (i)  $K_p = P_{\text{NH}_3}P_{\text{H}_2\text{S}} = 0.11$  Find the partial pressure of each  $\text{NH}_3$  and  $\text{H}_2\text{S}$  at equilibrium. [Ans.  $P_{\text{NH}_3} = 0.33 \text{ atm.} = P_{\text{H}_2\text{S}}$ ]
  - (ii) If ammonium hydrosulfide is placed in a flask containing 0.50 atm of  $\text{NH}_3$ . What are pressures of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  when equilibrium is reached. [ $P_{\text{NH}_3} = 0.50 + P_{\text{H}_2\text{S}}$ ] [Ans.  $P_{\text{H}_2\text{S}} = 0.17 \text{ atm.} ; P_{\text{NH}_3} = 0.67 \text{ atm}$ ]

contd....

- **Q.N. 4.** Suppose a reaction,  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- $K_p$  is 11.5 at  $300^\circ\text{C}$ . If  $P^0$  is (=1.5 atm) atm. then find equilibrium pressure of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$ , and fraction ( $f$ ) of  $\text{PCl}_5$  dissociated.
- The pure solid  $\text{PCl}_5$  is placed in a flask, on raising the temperature to  $300^\circ\text{C}$ , it would vaporize to give a pressure of  $P^0$  atm, if no  $\text{PCl}_5$  dissociated. If some of  $\text{PCl}_5$  undergoes dissociation as shown above equation.
- Here,  $P_{\text{PCl}_3} = P_{\text{Cl}_2}$ , and  $P_{\text{PCl}_5} = P^0 - P_{\text{Cl}_2}$
- Then
$$K_P = \frac{P_{(\text{Cl}_2)}^2}{P^0 - P_{(\text{Cl}_2)}} = 11.5$$
- $P_{\text{Cl}_2} = \mathbf{1.34 \text{ atm}}$  ( $= P_{\text{PCl}_3}$ ) and  $P_{\text{PCl}_5} = P^0 - P_{\text{Cl}_2} = \mathbf{1.5 - 1.34 = 0.16 \text{ atm}}$
- Fraction ( $f$ )  $\text{PCl}_5$  dissociated,  $f = \frac{P_{(\text{Cl}_2)}}{P^0} = \mathbf{1.34/1.5 = 0.89}$

contd....

- **Q.N. 5.** Suppose a reaction,  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- $K_p$  is 11.5 at  $300^\circ\text{C}$ . If  $P^0$  is 3 atm. then find equilibrium pressure of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$ , and fraction ( $f$ ) of  $\text{PCl}_5$  dissociated.
- [Ans.  $P_{\text{PCl}_3} = P_{\text{Cl}_2} = 2.47 \text{ atm}$ . and  $P_{\text{PCl}_5} = 0.53 \text{ atm}$ ,  $f = 0.82$ ]
  - Increasing the total amount of material at fixed volume, or increasing the total pressure, decreases the fraction of  $\text{PCl}_5$  that dissociates.
- **Q.N. 6.** What is the effect of adding  $\text{Cl}_2$  gas (1.5 atm) to reaction mixture of Q.N. 5?
- [Ans.  $P_{\text{PCl}_3} = 2.26 \text{ atm}$ ,  $P_{\text{Cl}_2} = 3.76 \text{ atm}$ . and  $P_{\text{PCl}_5} = 0.74 \text{ atm}$ ,  $f = 0.75$ ]
  - Addition of chlorine gas will diminish the amount of  $\text{PCl}_5$  that dissociates.

### Chemical equilibrium (Numerical Problems).

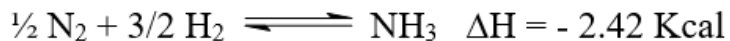
1. Write the equilibrium- constant expression for each of the following reactions.
  - a.  $2\text{NOCl(g)} = 2\text{NO(g)} + \text{Cl}_2\text{(g)}$
  - b.  $\text{Zn(s)} + \text{CO}_2\text{(g)} = \text{ZnO(s)} + \text{CO(g)}$
  - c.  $\text{MgSO}_4\text{(s)} = \text{MgO(s)} + \text{SO}_3\text{(g)}$
  - d.  $\text{Zn(s)} + 2\text{H}^+\text{(aq.)} = \text{Zn}^{++}\text{(aq)} + \text{H}_2\text{(g)}$
  - e.  $\text{NH}_4\text{Cl(s)} = \text{NH}_3\text{(g)} + \text{HCl(g)}$
2. For which of the following reactions does the equilibrium constant depend on the units of concentration?
  - a.  $\text{CO(g)} + \text{H}_2\text{O(g)} = \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$
  - b.  $\text{COCl}_2\text{(s)} = \text{CO(g)} + \text{Cl}_2\text{(g)}$
  - c.  $\text{NO(g)} = \frac{1}{2} \text{N}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)}$

**[Ans.  $\text{COCl}_2\text{(s)} = \text{CO(g)} + \text{Cl}_2\text{(g)}$ ]**

3. Of the metals Zn, Mg, and Fe, which removes cupric ion from the solution most completely? The following equilibrium constants hold at room temperature.
  - a.  $\text{Zn(s)} + \text{Cu}^{++}\text{(aq.)} = \text{Cu(s)} + \text{Zn}^{++}\text{(aq)} \quad K = 2 \times 10^{37}$
  - b.  $\text{Mg(s)} + \text{Cu}^{++}\text{(aq.)} = \text{Cu(s)} + \text{Mg}^{++}\text{(aq)} \quad K = 6 \times 10^{90}$
  - c.  $\text{Fe(s)} + \text{Cu}^{++}\text{(aq.)} = \text{Cu(s)} + \text{Fe}^{++}\text{(aq)} \quad K = 3 \times 10^{26}$

**[Ans.  $\text{Mg(s)} + \text{Cu}^{++}\text{(aq.)} = \text{Cu(s)} + \text{Mg}^{++}\text{(aq)}$ ]**

4. Nitrogen and hydrogen react to form ammonia by the reaction,



If a mixture of the three gases were in equilibrium, what would be the effect on the amount of  $\text{NH}_3$  if

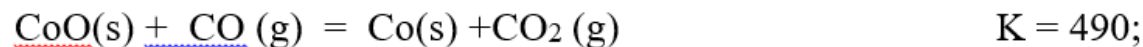
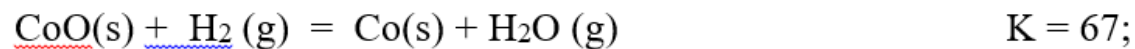
- (a) the mixture were compressed; (b) temperature were raised; (c) additional  $\text{H}_2$  were introduced?

**[Ans. (a) increased, (b) decreased, (c) increased,]**

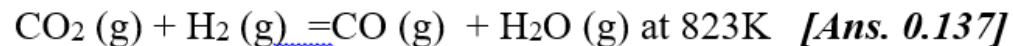
5. Would you expect the equilibrium constant for the reaction,  $I_2(g) \rightleftharpoons 2I(g)$  to increase or decrease as temperature increases? Why?

**[Ans. Equilibrium constant increases, Heat is used to cleavage  $I_2$  molecule producing more  $I$  atoms]  $K = [I]^2 / [I_2]$**

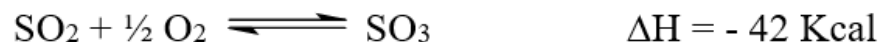
6. The equilibrium constants for the following reactions have been measured at 823K;



From these data, calculate the equilibrium constants of the reaction.



7. Suggest four ways in which the equilibrium concentration of  $\text{SO}_3$  can be increased in a closed vessel if the only reaction is :



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**[Ans: i. decrease in 'T', ii. increase in pressure, iii. increase in conc. of  $\text{SO}_2$  or  $\text{O}_2$  iv. increase in conc. of both reactants]**



8. Solid ammonium carbamate,  $\text{NH}_4\text{CO}_2\text{NH}_2$ , dissociates completely into ammonia and carbon dioxide when it evaporates, as shown by  $\text{NH}_4\text{CO}_2\text{NH}_2 \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$ . At  $25^\circ\text{C}$ , the total pressure of the gases in the equilibrium with solid is 0.116 atm. What is the equilibrium constant of the reaction? If 0.1 atm of  $\text{CO}_2$  is introduced after eqm. is reached, will the final pressure of  $\text{CO}_2$  be greater or less than 0.1 atm.? Will the pressure of  $\text{NH}_3$  increase or decrease?

[Ans:  $K_p = [2P]^2 \cdot [P]$ ;  $P_t = 2P + P$ ; Ans.  $K_p = 2.31 \times 10^{-4}$ ; Greater; Decrease]

9. For the reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ ;  $K = 55.3$  at 699 K.  $K_p = [\text{HI}]^2 / [\text{H}_2] \cdot [\text{I}_2]$  In a mixture that consists of 0.70 atm. of HI and 0.02 atm. each of  $\text{H}_2$  and  $\text{I}_2$  at 699 K, will there be any net reaction? If so, will HI be consumed or formed?

[Ans. Yes, backward; Consumed,  $Q_c = 1225$ ]

10. Hydrogen and iodine react at 699 K according to,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  If 1.00 mole of  $\text{H}_2$  and 1.00 mole of  $\text{I}_2$  are placed in a 1.00 litre vessel and allowed to react, what weight of HI will be present at equilibrium? At 699 K,  $K = 55.3$

**Solution:**  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

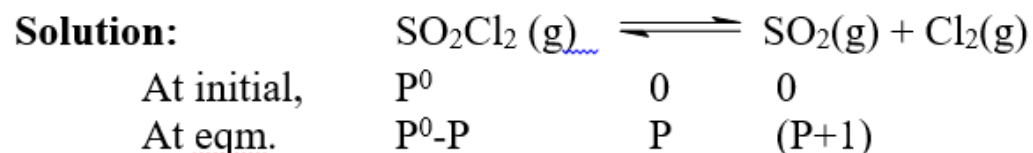
At initial, 1 0  
At eqm. 1-x 1-x 2x (Conc. in M.)

$[55.3 = (2x)^2 / (1-x)^2]$  or  $x = 0.787$ ;  $I = 127$ ; Wt. of HI =  $2x \cdot 0.787 \times \text{Mol. wt. of HI} = \text{ca. } 202 \text{ gm}$  Ans. 202 gm]

11. At 375 K, equilibrium constant  $K_p$  of the reaction,  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$  is 2.4 when pressure are expressed in atm. Assume that 6.7 gm of  $\text{SO}_2\text{Cl}_2$  (mol. wt. = 135) are placed into 1-litre bulb and the temperature is raised to 375 K. What would the pressure of  $\text{SO}_2\text{Cl}_2$  be if none of it dissociated. What are the pressures of  $\text{SO}_2$ ,  $\text{Cl}_2$  and  $\text{SO}_2\text{Cl}_2$  at equilibrium?

[Ans.  $\text{SO}_2\text{Cl}_2 \text{ eqm} = 1.526 - 1.06 (P) = 0.466 \text{ atm}$  and  $\text{SO}_2\text{Cl}_2 \text{ eqm} = 0.466 \text{ atm}$ ]

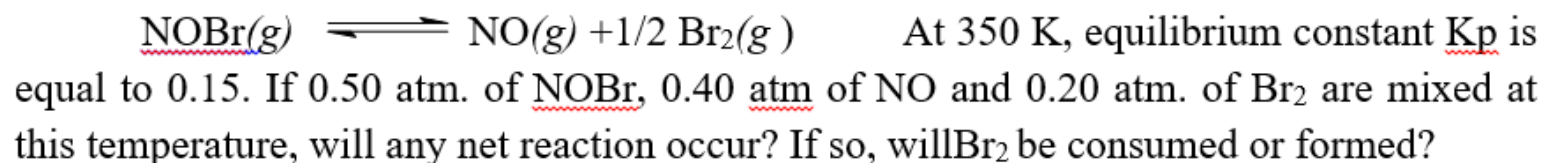
12. Compute the pressure of  $\text{SO}_2$ ,  $\text{Cl}_2$  and  $\text{SO}_2\text{Cl}_2$  in 1-litre bulb (at 375 K) to which 6.7gm of  $\text{SO}_2\text{Cl}_2$  and 1.0 atm. of  $\text{Cl}_2$  (at 375 K) have been added. Use the data supplied in problem 11. Compare your answer with that obtained for problem 11. and decide whether they are consistent with LP.



**Quadratic equation:**  $x = [-b \pm \sqrt{b^2 - 4ac}] / 2a$

[Ans.  $\text{SO}_2\text{Cl}_2 = 0.67 \text{ atm.}$  ;  $\text{SO}_2 = 0.86 \text{ atm.}$  ;  $\text{Cl}_2 = 1.86 \text{ atm.}$ ]

13. The gaseous compound  $\text{NOBr}$  decomposes according to the reaction,



**Solution:**

$Q_p = \frac{[P_{\text{NO}}] \cdot [P_{\text{Br}_2}]^{1/2}}{[P_{\text{NOBr}}]}$  then,  $Q_p = 0.357$ . Since,  $Q_p > K_p$ , there will occur the net reaction ( i.e. backward side ). So,  **$\text{Br}_2$  will be consumed.** [Ans. 0.357 ]

14. The equilibrium constant for the reaction,  $[x=0.12]$



is 0.10 at 690 K. What is the equilibrium pressure of each substance in a mixture prepared by mixing 0.50 mole of  $\text{CO}_2$  and 0.50 mole of  $\text{H}_2$  in a 5-litre flask at 690 K

[ $PV = nRT$  ( $n = 1$ );  $P_t = 11.32 \text{ atm}$  ; Ans.  $\text{CO} = \text{H}_2\text{O} = 1.36 \text{ atm.}$  ;  $\text{CO}_2 = \text{H}_2 = 4.3 \text{ atm.}$  ]

15. At 1000 K, the pressure of  $\text{CO}_2$  in equilibrium with  $\text{CaCO}_3$  and  $\text{CaO}$  is equal to  $3.9 \times 10^{-2}$  atm. The equilibrium constant for the reaction  $\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2 \text{CO(g)}$  is 1.9 at the same temperature when the pressure are in atm. Solid carbon,  $\text{CaO}$  and  $\text{CaCO}_3$  are mixed and allowed to come to eqm. at 1000 K in a closed vessel. What is the pressure of CO at eqm.? [Ans. 0.27 atm. or  $2.7 \times 10^{-1}$ ]

**Solution:** For,  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO(s)} + \text{CO}_2$  ;  $K_1 = [\text{CO}_2] = 3.9 \times 10^{-2}$

For,  $\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2 \text{CO(g)}$  ;  $K_2 = [\text{CO}]^2 / [\text{CO}_2] = 1.9$

Now, from 2<sup>nd</sup> part,  $1.9 = [\text{CO}]^2 / [\text{CO}_2]$

or  $1.9 \times [\text{CO}_2] = [\text{CO}]^2$  or  $[\text{CO}] = \sqrt{(1.9 \times 3.9 \times 10^{-2})} = 0.272$  or  $2.7 \times 10^{-1}$  atm

16. A mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  has at eqm. a total pressure of 1.5 atm. What fraction of  $\text{N}_2\text{O}_4$  has dissociated to  $\text{NO}_2$  at  $25^\circ\text{C}$ ? [ $K_p$  0.14] [Ans. 0.15]
17. If the volume of the system is increased so that pressure falls to 1 atm., what fraction of original  $\text{N}_2\text{O}_4$  is dissociated? [Ans. 0.18]
18.  $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$   
Here,  $K_p = P_{\text{NH}_3} P_{\text{H}_2\text{S}} = 0.11$  Find the partial pressure of each  $\text{NH}_3$  and  $\text{H}_2\text{S}$  at equilibrium. [Ans.  $P_{\text{NH}_3} = 0.33$  atm. =  $P_{\text{H}_2\text{S}}$ ]
19.  $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$  If ammonium hydrosulfide is placed in a flask containing 0.50 atm of  $\text{NH}_3$ . What are pressures of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  when equilibrium is reached. [ $P_{\text{NH}_3} = 0.50 + P_{\text{H}_2\text{S}}$ ] [Ans.  $P_{\text{H}_2\text{S}} = 0.17$  atm. ;  $P_{\text{NH}_3} = 0.67$  atm]