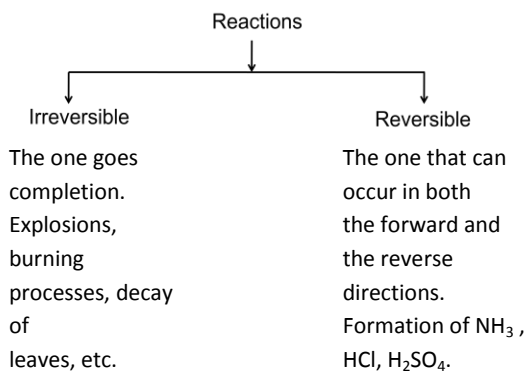
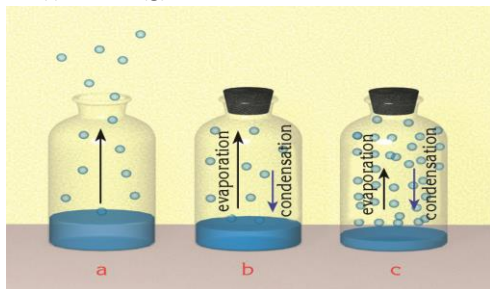


## CHEMICAL EQUILIBRIUM



### 1. Physical Equilibrium

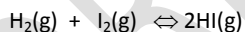
An equilibrium established by changing states of matter is called physical equilibrium.



- Vaporization and condensation of water in a closed container at constant temperature is a physical equilibrium.
- When rate of vaporization and rate of condensation become equal an equilibrium state is established.
- At equilibrium the amounts of water vapor and liquid water remain constant. But evaporation and condensation continues on microscopic scale. This is called dynamic equilibrium.

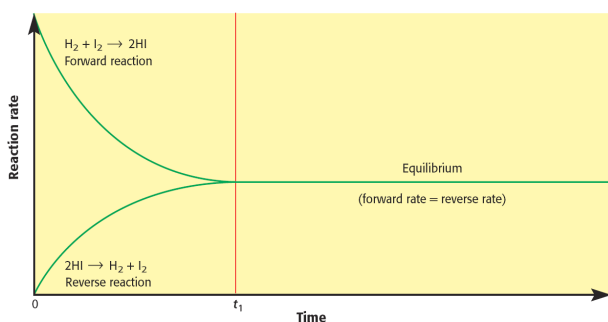
### 2. Chemical Equilibrium

• **Chemical equilibrium** is a state of balance in which the rate of a forward reaction equals the rate of the reverse reaction and the concentrations of products and reactants remain unchanged.

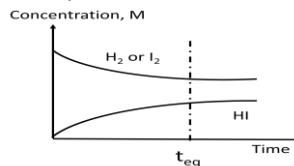


- Only a very small fraction of the collisions between  $\text{H}_2$  and  $\text{I}_2$  result in the formation of  $\text{HI}$ .
- As more  $\text{HI}$  molecules are made, they collide more often and form  $\text{H}_2$  and  $\text{I}_2$  by the reverse reaction.

- Rate Comparison for  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$



When the forward rate and the reverse rate are equal, the system is at chemical equilibrium.



When the reaction reaches equilibrium concentration of substances become constant

### Fundamentals of Dynamic Equilibrium

- It does not show any visible change.
- It reaches through spontaneous change.
- Forward and reverse reactions take place continuously.
- It must be in a closed system.
- Temperature must be kept constant through equilibrium.

### Example 1

- $\text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{HCl}(g)$  (homogeneous)
- $\text{Mg}(s) + 2\text{HCl}(aq) \rightleftharpoons \text{MgCl}_2(aq) + \text{H}_2(g)$  (heterogeneous)

### 3. Factors Causing Equilibrium

There are two opposing factors causing equilibrium in a chemical reaction;

#### 1. Tendency toward minimum energy

In nature matter tends to lose energy to reach a lower energy state.

- In exothermic reactions direction of minimum energy is in favor of products.
- In endothermic reactions direction of minimum energy is in favor of reactants.

#### Example 2

Find the direction of minimum energy in the following reactions.

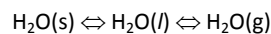
- $\text{N}_2\text{H}_4(g) \rightleftharpoons 2\text{NO}_2(g)$   $\Delta H = +14 \text{ kcal}$
- $2\text{O}_3(g) \rightleftharpoons 3\text{O}_2(g)$   $\Delta H = -68 \text{ kcal}$
- $2\text{NH}_3(g) + 22 \text{ kcal} \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$

**Solution**

- Reverse
- Forward
- Reverse

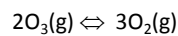
#### 2. Tendency toward maximum randomness (Entropy)

Randomness increases from solid state to gaseous state.



Tendency toward maximum randomness

Randomness is in favor of the side which has more particles.



Tendency toward maximum randomness

If two tendencies (min. energy and max. randomness) are in opposite directions in a reaction, the reaction can reach equilibrium.

#### 4. Equilibrium Constant Expression



$$\text{Rate}_f = k_f[A]^a[B]^b \quad \text{Rate}_r = k_r[C]^c[D]^d$$

at equilibrium,

$$\text{Rate}_f = \text{Rate}_r \Rightarrow k_f[A]^a[B]^b = k_r[C]^c[D]^d$$

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

$$\text{In general, } K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

Solid and liquid substances are not included in  $K_c$  expressions.

#### Example 4

Write  $K_c$  expressions of the following equilibrium reactions.

- $N_2H_4(g) \rightleftharpoons 2NO_2(g)$
- $2Mg(s) + O_2(g) \rightleftharpoons 2MgO(s)$
- $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
- $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

*Solution*

$$K_c = \frac{[NO_2]^2}{[N_2H_4]} \quad K_c = \frac{1}{[O_2]} \quad K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} \quad K_c = \frac{1}{[Ag^+][Cl^-]}$$

#### Example 5

The following reaction is allowed to reach equilibrium.

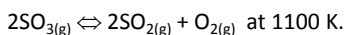
$X_2(g) + 2Y_2(g) \rightleftharpoons 2XY_2(g)$  The initial amounts of  $X_2$  and  $Y_2$  gas present in a 2-L container are 2 mol and 6 mol respectively. The amount of  $XY_2$  is 1 mol at equilibrium. What is the value of equilibrium constant  $K_c$ ?

	$X_2(g)$	$2Y_2(g)$	$2XY_2(g)$
Initial:	2 mol	6 mol	-
Change:	-0.5 mol	-1 mol	+1 mol
At equilibrium:	1.5 mol	5 mol	1 mol
Concentrations:	1.5/2 M	5/2 M	1/2 M
	0.75 M	2.5 M	0.5 M

$$K_c = \frac{[XY_2]^2}{[X_2][Y_2]^2} \Rightarrow K_c = \frac{(0.5)^2}{(0.75)(2.5)^2} = 0.053$$

#### Example 6

A 0.80 g sample of  $SO_3$  placed in a 1.00 liter container decomposes 80% to establish equilibrium represented by the equation



Calculate  $K_c$  for this reaction. (S:32, O:16)

*Solution*

$$n_i = 0.8/80 = 0.01 \text{ mol}$$

$$n_{eq} = 0.01 - 0.01 \times 0.80 \text{ (80\% decomposes)} = 0.002 \text{ mol}$$

	$2SO_3(g)$	$2SO_2(g)$	$O_2(g)$
Initial:	0.01 mol	-	-

Change:	-0.008 mol	+0.008 mol	+0.004 mol
At equilibrium	0.002 mol	0.008 mol	0.004 mol
Concentrations	0.002/1 M	0.008/1 M	0.004/1 M

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} \Rightarrow K_c = \frac{(0.008)^2(0.004)}{(0.002)^2} = 0.064$$

#### Example 7

For the equilibrium system described by:  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$   $K_{eq}$  equals 35 at 487°C. If the concentrations of the  $PCl_5$  and  $PCl_3$  at equilibrium are 0.015 M and 0.78 M, respectively, what is the concentration of the  $Cl_2$ ?

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} \quad K_c = \frac{(0.78)[Cl_2]}{(0.015)} = 35 \Rightarrow [Cl_2] = 0.67 \text{ M}$$

#### Example 8

A 3 mol sample of  $N_2O_5$  was placed and heated in a 1-L vessel. Some of  $N_2O_5$  decomposed according to the reaction,



At equilibrium the total mole number of gases was found to be 3.75

Calculate the value of  $K_c$  for this reaction.

	$2N_2O_5(g)$	$4NO_2(g)$	$O_2(g)$
Initial:	3 mol	-	-
Change:	-x mol	+2x mol	+0.5x mol
At equilibrium:	3-x mol	2x mol	0.5x mol

$$n_t = 3-x+2x+0.5x = 3.75 \text{ mol} \Rightarrow x = 0.5 \text{ mol}$$

Equilibrium concentrations:  $[N_2O_5] = 3-0.5 = 2.5 \text{ M}$ ,

$[NO_2] = 2 \cdot (0.5) = 1 \text{ M}$ ,  $[O_2] = (0.5) \cdot (0.5) = 0.25 \text{ M}$

$$K_c = \frac{[O_2][NO_2]^4}{[N_2O_5]^2} \Rightarrow K_c = \frac{(0.25)(1)^4}{(2.5)^2} = 0.04$$

#### The relation Between $K_p$ and $K_c$

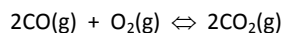


$$K_p = K_c (RT)^{\Delta n} \quad \text{Where } \Delta n = (c + d) - (a + b)$$

If  $\Delta n = 0$ , then  $K_p = K_c$

#### Example 9

Find  $K_p$  and  $K_c$  relationship for the reaction below.



*Solution*

$$K_p = K_c (RT)^{2-(2+1)} \Rightarrow K_p = K_c (RT)^{-1}$$

#### Example 10

Find  $K_p$  and  $K_c$  relationship for the reactions below.

- $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
- $CO(g) + H_2(g) \rightleftharpoons CH_3OH(g)$
- $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

#### Example 11

4 moles of  $NH_3$  in a 2-L vessel is allowed to come equilibrium at a total pressure of 3.6 atm. The number of mole of  $N_2(g)$  in the equilibrium mixture is measured to be 1 mol. What is the  $K_p$  for the following reaction below?  $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

*Solution*

	$2\text{NH}_3(\text{g}) \rightleftharpoons$	$\text{N}_2(\text{g})$	+	$3\text{H}_2(\text{g})$
Initial:	4 mol	-		-
Change:	-2 mol	+1 mol		+3 mol
At equilibrium:	2 mol	1 mol		3 mol
Concentrations:	2/2 M	1/2 M		3/2 M

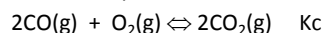
$$PV = n_r RT \Rightarrow 3.6 \times 2 = 6 \times RT \Rightarrow RT = 1.2$$

$$K_p = K_c(RT)^{\Delta n} \Rightarrow K_p = 1.6875(1.2)^{(1+3)-2} = 2.43$$

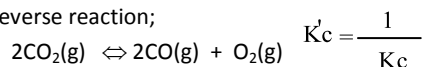
### Variation of Kc Expression

The value of Kc changes by altering the reaction in different ways.

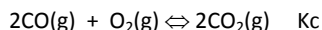
- The equilibrium constant for the forward and reverse reactions are the reciprocal of each other.



For the reverse reaction;

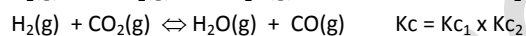
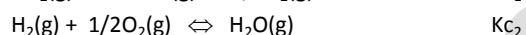
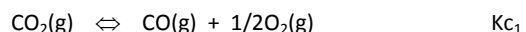


- If the coefficient of a reaction equation are multiplied by a number; the equilibrium constant is raised to the power of that number.



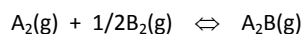
For the reaction;  $4\text{CO}(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons 4\text{CO}_2(\text{g}) \quad K'_c = K_c^2$

- If a reaction equation is expressed as a sum of two or more reaction equations, Kc for the overall reaction is the product of the equilibrium constants of individual reactions.



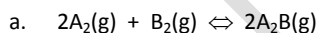
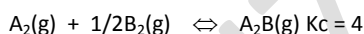
### Example 13

Suppose that the Kc for the reaction below is 4 at a certain temperature.



- $2\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons 2\text{A}_2\text{B}(\text{g})$
- $3\text{A}_2\text{B}(\text{g}) \rightleftharpoons 3\text{A}_2(\text{g}) + 3/2\text{B}_2(\text{g})$
- $1/2\text{A}_2\text{B}(\text{g}) \rightleftharpoons 1/2\text{A}_2(\text{g}) + 1/4\text{B}_2(\text{g})$

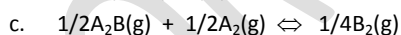
*Solution*



$$K_c' = (K_c)^2 = 4^2 = 16$$



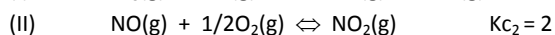
$$K_c' = (1/K_c)^3 = (1/4)^3 = 1/64 = 0.0156$$



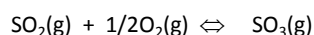
$$K_c' = (1/K_c)^{1/2} = (1/4)^{1/2} = 1/2 = 0.5$$

### Example 14

At a certain temperature:

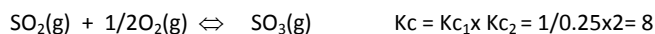
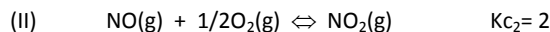
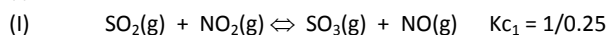


Find the value of Kc for the reaction below at the same temperature.



*Solution*

(I) reaction must be reversed.



### The Reaction Quotient, Qc

Qc helps us predict the direction in which a reaction mixture will proceed to reach equilibrium. Kc is determined when the reaction is at equilibrium at constant temperature. Qc is determined when the reaction is at non equilibrium conditions.

- $Q_c = K_c$ , then the reaction is at equilibrium.
- $Q_c > K_c$ , then the reverse reaction takes place to establish equilibrium.
- $Q_c < K_c$ , then the forward reaction takes place to establish equilibrium.

### Example 15

1 mol of  $\text{H}_2$ , 1 mol of  $\text{I}_2$  and 2 mol of HI are placed into a one liter container at a certain temperature to establish the equilibrium



What will be the equilibrium concentration of each species, if Kc is 64 at this temperature?

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \Rightarrow Q_c = \frac{2^2}{1.1} = 4 < K_c, \text{ then } \text{The reaction will proceed to forward}$$

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
Initial:	1 mol		1 mol		2 mol
Change:	-x mol		-x mol		+2x mol
At equilibrium	1-x mol		1-x mol		2+2x mol
Concentrations	1-x M		1-x M		2+2x M

$$K_c = \frac{(2+2x)^2}{(1-x)(1-x)} = 64 \Rightarrow \frac{2+2x}{1-x} = 8 \Rightarrow x = 0.6 \text{ mol}$$

$$[\text{HI}] = 2 - 2(0.6) = 0.8 \text{ M}, [\text{H}_2] = [\text{I}_2] = 1 - 0.6 = 0.4 \text{ M}$$

### Example 16

The equilibrium constant, Kc, is 36 at a certain temperature for the reaction,  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ .

Predict the direction in which the reaction will proceed to reach equilibrium if it is started with 0.5 mol of CO, 0.5 mol of  $\text{H}_2\text{O}$ , 5 mol of  $\text{CO}_2$  and 5 mol of  $\text{H}_2$  in a 5-L vessel.

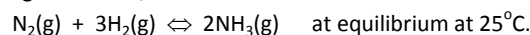
### 5. Factors Affecting Equilibrium

#### (Le Chatelier's Principle)

If a chemical system at equilibrium is disturbed by a change of concentration, pressure, or temperature, system tends to counteract this change in order to reestablish a new equilibrium. This principle is called **Le Chatelier's principle**, suggested by Henry Le Chatelier, French Scientist, professor of Chemistry at University of Paris.

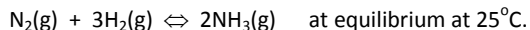
#### 1. The Effect of Concentration

For the effect of concentration there are four cases: Following reaction is given below;



a. If some  $N_2$  or  $H_2$  is added to reaction container, the system is disturbed and it will try to decrease this effect by moving forward, then the reaction will reestablish a new equilibrium. As a result of this, concentration of  $NH_3$  will increase.

b. If some  $NH_3$  is added the reaction will try to minimize this effect by moving backward. As a result concentration of both  $N_2$  and  $H_2$  will increase.



c. If some  $N_2$  or  $H_2$  is removed, decreasing concentration, from reaction container, the system is disturbed and it will try to decrease this effect by moving backward, then the reaction will reestablish a new equilibrium. As a result of this, concentration of  $NH_3$  will decrease.

d. If some  $NH_3$  is removed from the reaction container the reaction will try to minimize this effect by moving forward. As a result concentration of both  $N_2$  and  $H_2$  will decrease.

### Example 17

The following reaction at equilibrium is given, at  $25^\circ\text{C}$ .



Following changes are applied. Try to predict how the reaction respond to the these effects.

- Addition of CO gas,
- Addition of  $H_2$  gas,
- Removal of  $H_2O$  gas,
- Removal of  $CO_2$  gas.

*Solution*



- The reaction shifts forward, and concentration of  $CO_2$  and  $H_2$  will increase and concentration of  $H_2O$  will decrease.
- The reaction shifts backward, and concentration of  $H_2O$  and CO will increase and concentration of  $CO_2$  will decrease.
- The reaction shifts backward, and concentration of  $CO_2$  and  $H_2$  will decrease and concentration of CO will increase.
- The reaction shifts forward, and concentration of CO and  $H_2O$  will decrease and concentration of  $H_2$  will increase.

### Example 18

Consider the reaction:  $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

An equilibrium mixture was found to contain 2 mol of HI, 1 mol of  $H_2$  and 1 mol of  $I_2$  in a 2-L vessel. At the same temperature 1 mol of HI is added to the vessel. Calculate the concentration of each substance when new equilibrium is established.

*Solution*

$[HI] = 2/2 = 1 \text{ M}$ ,  $[H_2] = [I_2] = 1/2 = 0.5$  at equilibrium.

$$K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.5)(0.5)}{1^2} = 0.25$$

	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
1 <sup>st</sup> Eq:	1 M		0.5 M		0.5 M
Effect :	+0.5 M		-		-
Change:	-2x		+x		+x
At 2 <sup>nd</sup> Eq:	1.5 - 2x		0.5 + x		0.5 + x

$$K_C = 0.25 = \frac{(0.5+x)(0.5+x)}{(1.5-2x)^2} \Rightarrow x = 0.125 \text{ M}$$

$$[HI] = 1.5 - 2(0.125) = 1.25 \text{ M}, [H_2] = [I_2] = 0.5 + 0.125 = 0.625 \text{ M}$$

## 2. Volume Changes or Effect of Pressure

\* Change in volume alters the concentrations of gas reactants and gas products.

\* According to Le Chatelier's principle, when the volume of the system is decreased; the reaction shifts to the side having the smaller number of coefficients of gases to decrease this effect.

\* When the volume of the system is increased; the reaction shifts to the side having the greater number of coefficients of gases to decrease this effect.

\* For heterogeneous equilibrium the effect of volume is predicted by counting the number of moles of gas indicated on each side of an equation.

Change in pressure affects the equilibrium reaction conversely with respect to volume change

### Example 19

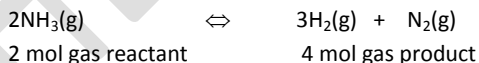
Consider the reaction:



Following changes are applied. Try to predict how the reaction respond to the these effects.

- Increasing volume,
- Decreasing volume,
- Increasing pressure.

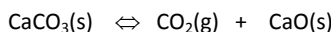
*Solution*



- The reaction shifts forward, and concentration of  $H_2$  and  $N_2$  will increase and that of  $NH_3$  will decrease.
- The reaction shifts backward, and concentration of  $H_2$  and  $N_2$  will decrease and that of  $NH_3$  will increase.
- Increasing pressure means decreasing volume. Thus it will have same effect in b.

### Example 20

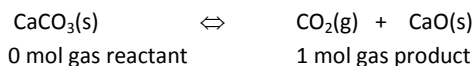
Consider the reaction:



Following changes are applied. How the reaction will the reaction shift to reestablish equilibrium.

- Increasing pressure,
- Decreasing volume,
- Increasing volume

*Solution*



- Increasing pressure means decreasing volume. The reaction shifts backward.
- The reaction shifts backward.
- The reaction shifts forward.

## 3. Effect of Temperature

\* Effect of temperature can be understood by knowing whether the reaction is exothermic or endothermic.

\* In endothermic reactions when temperature is increased the reaction will proceed to forward to eliminate effect.

\* In exothermic reactions when temperature is increased the reaction will move backward to minimize effect.



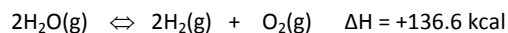
### Example 21

Consider the reaction:  $2\text{H}_2\text{O}(g) \rightleftharpoons 2\text{H}_2(g) + \text{O}_2(g)$   $\Delta H = +136.6\text{kcal}$

Following changes are applied. How the reaction will the reaction shift to reestablish equilibrium.

- Increasing temperature,
- Decreasing temperature.

*Solution*



The reaction is endothermic.

- Forward reaction needs energy to take place, if temperature is increased it will be in favor of forward reaction. The reaction will shift forward.
- Reverse reaction is exothermic. If temperature is decreased it will be in favor of reverse reaction. The reaction will shift backward.

### 4. Effect of Catalyst

- Catalyst does not affect equilibrium reactions and  $K_c$ .
- They effect both forward and reverse reactions equally; therefore they cause the reactions to reach equilibrium in a shorter time.