

# E Content

**TOPIC: Chemical Equilibrium**

**Sub: Physical Chemistry**

**BSc. Part II**

By

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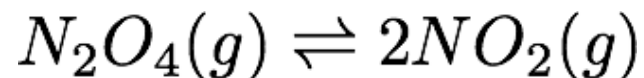
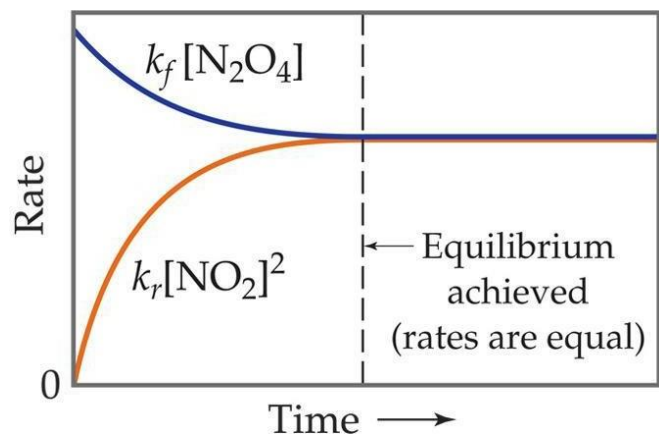
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# Introduction

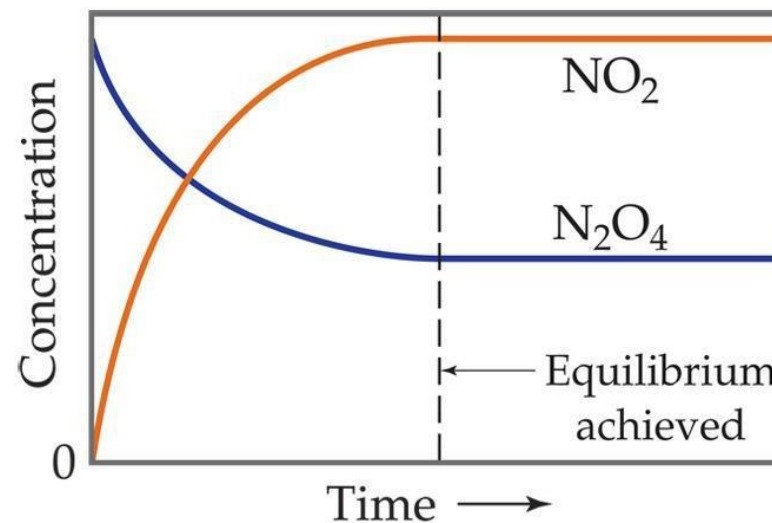
**Chemical equilibrium:** A state in which the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.

*For a system at Equilibrium,*

**Rates become equal**

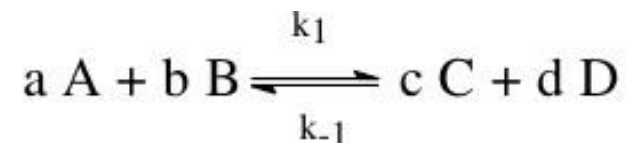


**Concentrations become constant**



# Law of mass action and Equilibrium Constant

- The rate of chemical reaction is directly proportional to the product of active masse of the reacting substances.



rate of the forward reaction =  $k_1 [A]^a [B]^b$

rate of the reverse reaction =  $k_{-1} [C]^c [D]^d$

At equilibrium:

rate of the forward reaction = rate of the reverse reaction

$$k_1 [A]^a [B]^b = k_{-1} [C]^c [D]^d$$

$$\frac{k_1}{k_{-1}} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

$K_{eq}$  is called *equilibrium constant*

**Equilibrium Constant** - A number equal to the ratio of the equilibrium concentrations of products to the equilibrium concentrations of reactants each raised to the power of its stoichiometric coefficient.

$$K_{\text{eq}} = \frac{[\text{products}]^n}{[\text{reactants}]^m}$$

- ◆ if  $K_{\text{eq}} > 1$  . . .  $[\text{products}] > [\text{reactants}]$   
equilibrium position favors products and equilibrium position lies to the right
- ◆ if  $K_{\text{eq}} < 1$  . . .  $[\text{reactants}] > [\text{products}]$   
equilibrium position favors reactants and equilibrium position lies to the left
- ◆ If the  $K_{\text{eq}}$  value is close to 1 ( $0.10 < K_{\text{c}} < 10$ ), the reaction mixture contains appreciable amounts of both reactants and products.

*The Equilibrium Constant is,*

- ◆ typically unitless
- ◆ concentrations used are relative to a standard molar concentration of 1M
- ◆ dependent on specific reaction
- ◆ dependent on temperature
- ◆ dependent on equilibrium composition
- ◆ independent of initial concentrations



# Le Chatelier's Principle

*'When a stress is applied to a system at equilibrium, the equilibrium position will shift in the direction that relieves the applied stress'*

Stresses include:

- changes in concentration or pressure of reactants or products by the addition or removal
- changes in pressure as a result of changes in volume of container
- changes in temperature (value of  $K$  will change)
- addition of a catalyst



**Henry Louis Le Chatelier**  
French Scientist

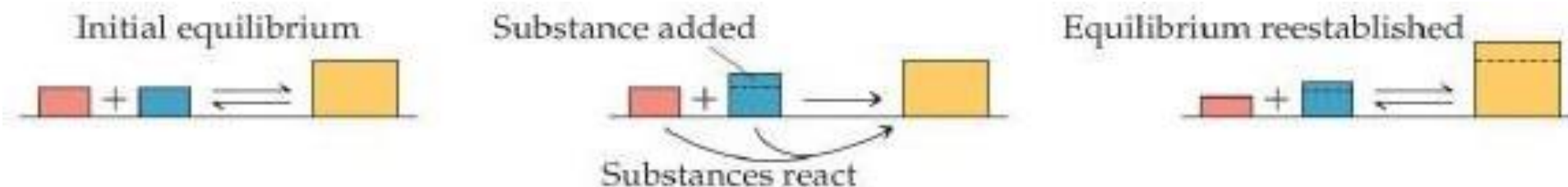
## Effect of concentration on Equilibrium Position

- If the concentration of a substance is increased by the addition of more reactant or product . . .

- the equilibrium position will shift in the direction that consumes the added substance OR the equilibrium position will shift away from the increased concentration

- If the concentration or pressure of a substance is decreased by the removal of reactant or product .

- the equilibrium position will shift in the direction that replenishes the removed substance OR the equilibrium position will shift toward the decreased concentration



## Effect of Changing Pressure on Equilibrium Position

- An increase in pressure will bring about net reaction in the direction that decreases the number of moles of gas phase species (i.e. the volume of the chemical system will decrease)
- A decrease in will bring about net reaction in the direction that increases the number of moles of gas phase species (i.e. the volume of the chemical system will increase).



# Effect of Changing Temperature on Equilibrium Position

The temperature dependence of the equilibrium position is determined by whether the reaction is endothermic or exothermic.

*If the reaction is exothermic, ( $\Delta H < 0$ )*

- An increase in temperature shifts the equilibrium toward the reactants.
- A decrease in temperature shifts the reaction toward the products.

*If the reaction is endothermic, ( $\Delta H > 0$ )*

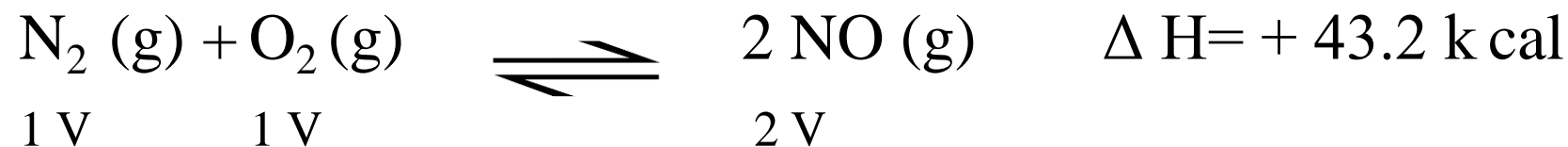
- an increase in temperature shifts the equilibrium toward the products.
- A decrease in temperature shifts the reaction toward the reactants.

## *Effect of a Catalyst on the Equilibrium Position*

◆ The addition of a catalyst does not effect the equilibrium position of a reaction – only the rate at which the system reaches equilibrium.

*Example:*

Formation of nitric oxide:



- (i) **Effect of pressure:** As no change of volume occurs during the formation of nitric oxide, there will be no effect of pressure on the equilibrium.
- (ii) **Effect of temperature:** if the temperature is increased then the equilibrium will shift in that direction in which heat is absorbed, i.e., in the forward direction. So, high temperature favours the formation of nitric oxide.
- (iii) **Effect of concentration:** If to the system in equilibrium  $\text{N}_2$  is added, the equilibrium will shift in that direction so as to reduce the concentration of  $\text{N}_2$ . So, more nitric oxide will be formed. Similar is the effect of adding oxygen. So, the formation of nitric oxide is favoured by (i) High temperature and (ii) High concentrations of  $\text{N}_2$  or  $\text{O}_2$ .

# CLAUSIUS–CLAPEYRON EQUATION

- It relates the latent heat (heat of transformation) of vaporization or condensation to the rate of change of vapor pressure with temperature or, in the case of a solid-liquid transformation, it relates the latent heat of fusion or solidification to the rate of change of melting point with pressure



**Rudolf Clausius**  
1822-1888  
German  
Mathematician / Physicist

"Discovered" the Second Law  
Introduced the concept of entropy



**Benoit Paul Emile Clapeyron**  
1799-1864  
French  
Engineer / Physicist

Expanded on Carnot's work

# DERIVATION

For a system at equilibrium  $\Delta G = \Delta H - T\Delta S$   
 where  $H$  is the latent heat of vaporization,  $T$  the temperature and  $S$  the entropy of the system

Since  $G$  of the said system remains constant,

$$G_2 - G_1 = \Delta G = \Delta H - T\Delta S = 0$$

Thus,

$$\Delta H = T\Delta S$$

However, for gases,  $\Delta H = \Delta U + P\Delta V$ , where  $L$  is the latent heat of vaporization, making the previous equation

$$\Delta H = T\Delta S = \Delta U + P\Delta V$$

Given two states in the transition, the changes in entropy ( $\Delta S$ ), internal energy ( $\Delta U$ ) and volume ( $\Delta V$ ) would become constant.

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T(V_2 - V_1)}$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T(V_2 - V_1)}$$

However, the change in entropy  $\Delta S$  is given by

$$\Delta S = L / T$$

where  $L$  is the latent heat of vaporization

Thus, we arrive at the Clausius — Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T(V_2 - V_1)}$$

When the transition is to a gas phase, the final volume can be many times the size of the initial volume  $\Delta V$  thus  $\Delta V \approx V_2$  can be approximated as  $V_2$ . Furthermore, at low pressures, the gas phase may be approximated by the ideal gas law  $PV = nRT$ , changing the previous equation to:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{nRT^2}$$

Since  $\Delta H_{\text{vap}} = L / n$ ,

$$\frac{dP}{P} = \frac{dT}{T^2} \frac{\Delta H_{\text{vap}}}{R}$$

Also since  $\Delta H_{\text{vap}}$  is independent of pressure and temperature and  $R$  is a constant, integrating both sides, we get

$$\ln P = -\frac{1}{T} \frac{\Delta H_{\text{vap}}}{R} + C$$

If the vapor pressure was measured at two separate temperatures, we have two points on the same line.

$$\ln P_1 = -\frac{1}{T_1} \frac{\Delta H_{\text{vap}}}{R} + C$$

$$\ln P_2 = -\frac{1}{T_2} \frac{\Delta H_{\text{vap}}}{R} + C$$

Subtracting these two, we get

$$\ln P_2 - \ln P_1 = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

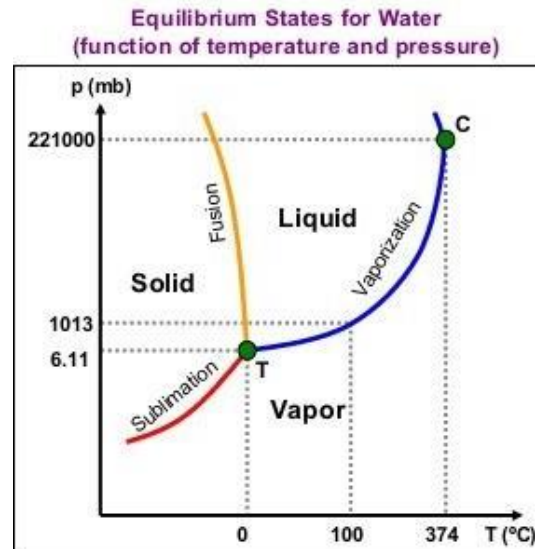
Finally, we get

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

the more commonly known form of the Clausius – Clapeyron equation

## Applications:

- To determine the vapor pressure of a substance.
- To estimate the effect of temperature on vapor pressure
- To calculate the heat of a phase change
- To calculate the boiling point of a liquid at a nonstandard pressure
- To reconstruct a phase diagram
- To determine if a phase change will occur under certain circumstances



An example of a phase diagram

## Referred Books:

- P. Atkins and J. de Paula, *Physical Chemistry*, 9th Edition, W. H. Freeman, 2009
- K.L. Kapoor, *A Textbook of Physical Chemistry*, 2nd Edition, Macmillan, 2011
- G.W. Castellan, *Physical Chemistry*, 3rd Edition, Addison Wesley, 1983
- Puri, Sharma, Pathania, *Principle of Physical chemistry*, 44<sup>th</sup> edition, 2010
- I.N. Levine, *Physical Chemistry*, 6th Edition, McGraw-Hill, 2008.