# EQUILIBRIUM

## LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

## Law of Mass Action or Law of Chemical Equilibrium

The law of mass action is given by Guldberg and Waage.

According to them at a given temperature rate of reaction is proportional to product of active masses of reactants at that instant raised to the powers which are numerically equal to the number of their respective molecule in the stoichiometric equation describing the reaction.

## • Derivation of Equilibrium Constant

Consider a reversible homogeneous reaction which has attained equilibrium state at particular temperature:

$$A + B C + D$$

Let the active masses of A, B, C and D be [A] [B] [C] & [D] are respectively.

## • According to Law of Mass Action

rate of forward reaction  $\alpha$  [A] [B]

rate of backward reaction  $\alpha$  [C] [D]

$$R_{f} = K_{f} [A] [B] \qquad \qquad R_{b} = K_{b} [C] [D]$$

Where  $K_f$  and  $K_b$  are forward and backward rate constants respectively.

At equilibrium

$$R_{f} = R_{b}$$

$$K_{f} [A] [B] = K_{b} [C] [D]$$

$$\frac{K_{f}}{K_{b}} = \frac{[C][D]}{[A][B]}$$

$$K_{e} = \frac{[C][D]}{[A][B]}$$

$$K_{c} = \frac{K_{f}}{K_{b}}$$

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 $K_{C}$  is known as equilibrium constant  $K_{C}$  has a definite value for every chemical reaction at particular tempera true.

For a general reaction

$$\begin{split} m_1 A + m_2 B + m_3 C & n_1 M + n_2 N + n_3 O \\ r_f &\propto [A]^{m_1} [B]^{m_2} [C]^{m_3} \\ r_f &= K_f [A]^{m_1} [B]^{m_2} [C]^{m_3} & [K_f = \text{forward rate (velocity) constant}] \\ r_b &\propto [M^{p^1} [N]^2 [O]^{n_3} \\ r_b &= K_b [M]^{n_1} [N]^{n_2} [O]^{n_3} [K_b = \text{backward rate (velocity) constant}] \end{split}$$

At equilibrium  $r_f = r_b$ 

$$\begin{split} & K_{f}[A]^{m_{1}}[B]^{m_{2}}[C]^{m_{3}} = K_{b}[M^{m_{1}}[N]^{m_{2}}[O]^{m_{3}} \\ & K_{c} = \frac{K_{f}}{K_{b}} = \frac{[M]^{n_{1}}[N]^{n_{2}}[O]^{n_{3}}}{[A]^{m_{1}}[B]^{m_{2}}[C]^{m_{3}}} \end{split}$$

The equilibrium constant, at a given temperature, is the ratio of the rate constants of forward and backward reactions.

• Possible Value of K

$[0 < K < \infty]$	
When K = 1	[Product] = [Reactant]
When K > 1	[Product] > [Reactant]
When K < 1	[Product] < [Reactant]

As K  $\uparrow$  stability of products  $\uparrow$  stability of reactant  $\downarrow$  time to attain equilibrium  $\downarrow$ 

 $t \propto 1/K$ 

Stability of reactants and products

$$\begin{array}{rcl} 2\text{XO}(\text{g}) &\longrightarrow & \text{X}_2(\text{g}) + \text{O}_2(\text{g}) \; ; & \text{K}_1 = 1 \times \; 10^{24} \\ 2\text{XO}_2(\text{g}) &\longrightarrow & \text{X}_2(\text{g}) + 2\text{O}_2(\text{g}) \; ; & \text{K}_2 = 2.5 \times \; 10^{10} \\ \text{K}_1 > \text{K}_2 & \text{So the stability of} & \text{XO}_2 > \text{XO} \end{array}$$

For reactants, stability increases when value of K decreases.

For products, stability increases when value of K increases.

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(more is the value of equilibrium constant, more is the formation of product means more is the stability of product.)

Time taken to attain equilibrium increases when value of K decreases.

#### Forms of Equilibrium Constant

There are two forms.

(i) Concentration form (K<sub>C</sub>) (ii) Partial pressure form (K<sub>P</sub>)

**Partial Pressure:** The individual pressure exerted by the gases substance of the total pressure is called partial pressure of the gases substance.

$$\begin{array}{c} \textbf{Closed vessel} \\ \textbf{Gaseous} & \textbf{A} & \textbf{B} & \textbf{C} & \textbf{D} \\ \textbf{moles} & \textbf{n_1mol} & \textbf{n_2mol} & \textbf{n_3mol} & \textbf{n_4mol} \end{array} \Rightarrow \textbf{P}_{total} \\ \end{array}$$

Partial pressure = 
$$\frac{Moles of substance}{Total moles} \times P_{total} \Rightarrow [\frac{Moles of substance}{Total moles} = Mole fraction]$$
  
= mole fraction × P<sub>total</sub>  
let n<sub>1</sub> + n<sub>2</sub> + n<sub>3</sub> + n<sub>4</sub> = N  
P<sub>A</sub> =  $\frac{n_1}{N}P_t$ , P<sub>B</sub> =  $\frac{n_2}{N}P_t$ , P<sub>C</sub> =  $\frac{n_3}{N}P_t$ , P<sub>D</sub> =  $\frac{n_4}{N}P_t$   
P<sub>A</sub> + P<sub>B</sub> + P<sub>C</sub> + P<sub>D</sub> = P<sub>total</sub>

When the reactants and products are in gaseous state then partial pressure can be used instead of concentration. At a definite temperature, as the partial pressure of a substance is proportional to its concentration in the gas phase.

$$m_1 A + m_2 B n_1 C + n_2 D$$

If partial pressure of A, B, C and D at equilibrium are  $P_{\mbox{A}},\,P_{\mbox{B}},\,P_{\mbox{C}}$  and  $P_{\mbox{D}}$  respectively, then

$$K_{P} = \frac{(P_{c})^{n_{1}} \times (P_{D})^{n_{2}}}{(P_{A})^{m_{1}} \times (P_{B})^{m_{2}}}$$

#### Relation Between Kp and KC

This relation can be established for reaction not involving liquids because kp is not defined for liquids.

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Consider a reversible reaction

$$\begin{split} m_1 A + m_2 B \quad n_1 C + n_2 D \\ K_C &= \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}} \\ K_P &= \frac{(P_C)^{n_1}(P_D)^{n_2}}{(P_A)^{m_1}(P_E)^{m_2}} \end{split}$$
 For an ideal gas  $\begin{aligned} PV &= nRT \\ P &= \frac{n}{V}RT = active \ mass \times RT \\ \ddots & n = number \ of \ mole \ and \ V = Volume \ in \ liter \\ So & \frac{n}{V} = molar \ concentration \ or \ active \ mass \\ P &= [] RT \end{split}$ 

at constant temperature P  $\propto$  [ ]

$$\begin{split} P_{A} &= [A] \text{ RT, } P_{B} = [B] \text{ RT, } P_{C} = [C] \text{ RT, } P_{D} = [D] \text{ RT} \\ K_{p} &= \frac{[C]^{n_{1}(RT)^{n_{1}}[D]^{n_{2}}(RT)^{n_{2}}}{[A]^{m_{1}(RT)^{m_{1}} \times [B]^{m_{2}}(RT)^{m_{2}}} \\ K_{p} &= \frac{[C]^{n_{1}}[D]^{n_{2}}}{[A]^{m_{1}}[B]^{m_{2}}} \times \frac{(RT)^{n_{1}+n_{2}}}{(RT)^{m_{1}+m_{2}}} \\ K_{P} &= K_{C}(RT)^{(n_{1}+n_{2})-(m_{1}+m_{2})} \\ \Delta n &= (n_{1}+n_{2}) - (m_{1}+m_{2}) \\ &= \text{total number of gaseous molecules of products - total number of gaseous molecules of reactants.} \end{split}$$

So

$$K_{\rm P} = K_{\rm C} ({\rm RT})^{\Delta n_{\rm g}}$$

### CALCULATION OF EQUILIBRIUM CONSTANT

(a)	H <sub>2</sub> (g) +	$I_2(g) \longrightarrow$	2HI (g)		
Initially	а	b	0		
At equilibrium	(a-x)	(b-x)	2x		
	$K_{C} = K_{C} = \frac{1}{2}$	$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(a-x)(b-x)^2}$	$\frac{4x^2}{(a-x)(b-x)}$		
	$K_{p} = \frac{\frac{(2x)^{2}}{(a+b)^{2}}P^{2}}{\frac{(p_{HI})^{2}}{p_{H_{2}} \times p_{I_{2}}} = (\frac{a-x}{a+b} \cdot P)(\frac{b-x}{a+b} \cdot P)} = \frac{4x^{2}}{(a-x)(b-x)}$				

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So	$K_c = K_p$ (	$(\Delta n = 0)$					
(b)	$2NO(g) \longrightarrow$	N <sub>2</sub> (g)	+ 0 <sub>2</sub> (	(g)			
Initially	а	0	0				
At equilibrium	(a-x)	x/2	x/2				
	$K_{c} = \frac{[N_{2}][O_{2}]}{[NO]^{2}} =$	$\frac{x/2 \times x/2}{(a-x)^2} :$	$=\frac{x^2}{4(a-x)^2}$	$\frac{1}{2} = K_{p}($	$(\Delta n = 0)$		
(C)	$CH_3COOH_{(\ell)}$	+ C <sub>2</sub> H <sub>5</sub>	ОН <sub>(ℓ)</sub> -	$\rightarrow$ CH	I <sub>3</sub> COOC <sub>2</sub> I	$H_{5(\ell)} + H$	2 <sup>0</sup> (ℓ)
Initially	а	b		0	0		
At equilibrium	(a-x)	(b-x)		х	Х		
	$K_{c} = \frac{[CH_{3}COOC]}{[CH_{3}COOH]}$	<sub>2</sub> H <sub>5</sub> ][H <sub>2</sub> O] ][C <sub>2</sub> H <sub>5</sub> OH]	$=\frac{x^2}{(a-x)(a-x)}$	b-x)			
K <sub>p</sub> should not b	e given for this	reaction					
(d)	$PCl_5 (g) \longrightarrow$	PCl <sub>3</sub> (	g) + Cl	2 (g)			
Initially	а	0	0				
At equilibrium	(a-x)	Х	Х				
Active mass	$\frac{(a-x)}{v}$	$\frac{X}{V}$	$\frac{x}{v}$				
	$\mathbf{K}_{\mathbf{C}} = \frac{[\mathrm{PCl}_3][\mathrm{Cl}_2]}{[\mathrm{PCl}_5]} =$	$=\frac{\frac{x}{v}\times\frac{x}{v}}{\frac{(a-x)}{v}}=$	$\frac{x^2}{(a-x)v}$				
	$K_p = \frac{p_{PC_3} \times p_{Cl_2}}{p_{PCl_1}}$	$=\frac{(\frac{x}{a+x}\cdot P)}{(\frac{a}{a+x}\cdot P)}$	$\frac{\times (\frac{x}{a+x} \cdot P)}{(\frac{x}{x})P} :=$	$=\frac{x^2}{(a+x)}$	$\frac{e_P}{(a-x)} = \frac{x}{a^2}$	$\frac{2p}{-x^2}$	
(e)	N <sub>2</sub> (g) + 3	3H <sub>2</sub> (g) -	$\longrightarrow$	2NH3 (	(g)		
Initially	а	b	0				
At equilibrium	(a-x)	(b-3x)	2x	Ľ			
Active mass	$\frac{(a-x)}{V}$ (	$\left(\frac{b-3x}{V}\right)$	$\left(\frac{2\pi}{v}\right)$	$\left(\frac{x}{x}\right)$			
	$K_{C} = \frac{[NH_{3}]^{2}}{[N_{2}][H_{2}]^{3}} =$	$\frac{(\frac{2x}{v})^2}{(\frac{a-x}{v})(\frac{b-3x}{v})}$	$\frac{1}{(a-x)^3} = \frac{4}{(a-x)^3}$	$\frac{4x^2V^2}{(b-3x)}$	3		
	$K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3}$	$=\frac{[}{[\frac{(a-x)}{(a+b-x)}]}$	$\frac{2xP}{a+b-2x}^{2} \Big]^{2}$ $\frac{P}{2x} \Big] \Big[ \frac{(b-3x)}{(a+b-2x)} \Big] \Big[ \frac{(b-3x)}{(a+b-2x)} \Big] \Big] \Big[ \frac{(b-3x)}{(a+b-2x)} \Big] \Big] \Big[ \frac{(b-3x)}{(a+b-2x)} \Big] \Big] \Big] \Big[ \frac{(b-3x)}{(a+b-2x)} \Big] \Big] \Big[ \frac{(b-3x)}{(a+b-2x)} \Big] $	$\frac{\overline{(P)P}}{2x}]^3 = \frac{1}{(1+x)^2}$	$\frac{4x^2(a+b-2)}{(a-x)(b-3x)}$	$\frac{x)^2}{)^3 P^2}$	

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