Shuvo
CSE-08

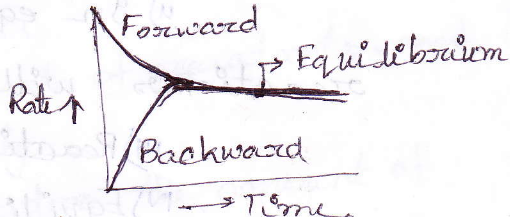
Chemical equilibrium

***Reversible reaction:** The chemical reaction which take place in both direction under the same conditions are called reversible reaction.

$$A+B \rightleftharpoons C+D.$$

$$N_2+3H_2 \rightleftharpoons 2NH_3$$

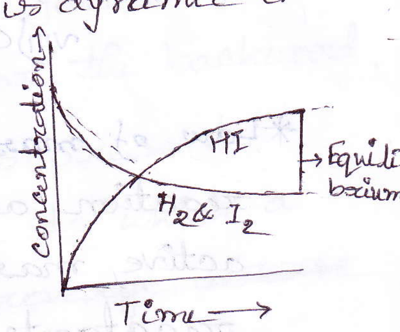
***Chemical equilibrium:** A state of reversible reaction at which the reactants form the products at the same rate by which the products react to form the reactants is called chemical equilibrium.



*** Dynamic nature of equilibrium:**

At equilibrium state if any reversible seems to be closed but in fact the reaction of both sides keep continuing at the same speed. If apparently I seen then it will be in motion. That is why equilibrium is dynamic in nature

Proof: If the mixture of H_2 and I_2 are kept at definite temperature for a long time then it will be seen that H_2 and I_2 reacts so fast and produce HI. But at times reaction will be slower. Actually, then problem created in equilibrim. But, reaction will be occuring at same ~~sppe~~ speed on both sides.



$$H_{2(g)} + I_{2(g)} \xrightleftharpoons{\Delta} 2HI_{(g)}.$$

After gaining of equilibrium if an treasure little amount of radioactive iodine $^{128}_{53}I_2$ is exerted then there occur no change, they remain unchanged. From it, is, understood that, after gaining of equilibrium the reaction of following is continuing, $H_2 + I_2^* \longrightarrow 2HI^*$

As, the total amount of hydrogen iodide is unchang therefore, when radioactive HI^* is produced at that time non radioactive HI is decomposed.

$$2HI \longrightarrow H_2 + I_2$$

*Characteristics of chemical equilibrium:

i) Chemical equilibrium is related with reversible reaction.

ii) In equilibrium rate of forward and backward reactions will be equal.

iii) Reaction never completes at equilibrium.

iv) Equilibrium can be initiated from any side

v) Equilibrium is established ~~at any~~ only in closed system

vi) Equilibrium continues forever it never ends

vii) Equilibrium is dynamic not static.

viii) Catalyst has no effect on equilibrium.

***Law of mass action**: At a definite temperature, the rate of a reaction at any instant is directly proportional to the active mass (molar concentration or partial pressure) of the reactants at that instant taking part in the reaction.

$$A + B \rightleftharpoons C + D.$$

Rate of forward reaction, $R_f \propto [A][B] \Rightarrow R_f = k_1[A][B]$

Rate of backward reaction, $R_b \propto [C][D] \Rightarrow R_b = k_2[C][D]$

As the rate of forward and backward reaction are equal at equilibrium so, $R_f = R_b$

$$\Rightarrow k_1[A][B] = k_2[C][D]$$

$$\Rightarrow \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} = k$$

When $aA + bB \rightleftharpoons cC + dD$ then equilibrium constant in terms of concentration is

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

that in terms of partial pressure is

$$k_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}.$$

Equilibribum constant: The ratio of the constant k_1 and k_2 at a definite temperature is called equilibrium constant

*** Characteristics of equilibrium constant:**

i) k is independent of the amount of reactants. ~~and~~

ii) k depends on temperature only.

Greater the value of k, greater the amount of product.

iii) Small the ~~amou~~ value of k, smaller is the amount of product.

iv) The equilibrium constand for the forward reaction is inverse of the equilibrium constant for the backword.

v) k is independent of catalyst's present.

vi) The value of k tells the extent to which a reaction proceeds in the forward or reverge ~~diverse~~ ~~direc~~ direction

*** Relation between kp and kc:** Let us consider a reversible reaction $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$ then,

$$k_c = \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$$

and

$$k_p = \frac{(P_C)^\gamma (P_D)^\delta}{(P_A)^\alpha (P_B)^\beta}$$

For ideal gas, we know, $Pv = nRT$

$$\Rightarrow P = \frac{n}{v} RT \quad \text{But } \frac{n}{v} = c = \text{concen}$$

$$\Rightarrow P = cRT$$

Therefore,

$$P_A = [A]RT \; ; \; P_B = [B]RT \; ; \; P_C = [C]RT \; ; \; P_D = [D]RT$$

so,

$$K_P = \frac{[C]^{\gamma}[RT]^{\gamma} \cdot [D]^{\delta}[RT]^{\delta}}{[A]^{\alpha}[RT]^{\alpha}[B]^{\beta}[RT]^{\beta}}$$

$$= \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}} \times \frac{[RT]^{\gamma+\delta}}{[RT]^{\alpha+\beta}}$$

$$= K_c [RT]^{(\gamma+\delta)-(\alpha+\beta)}$$

$$\therefore K_P = K_c [RT]^{\Delta n} \quad \left[\Delta n = (\gamma+\delta)-(\alpha+\beta)\right]$$

***Application of law of mass action:**

i) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Mole No. at ini. state: $a \quad b \quad 0$

" " at final " $\quad a-x \quad b-x \quad 2x$

$\therefore$ Mole number at equilibrium state $= (a-x)+(b-x)+2x$

$= a+b$.

If the total pressure at equilibrium state is P then according to Dalton's partial pressure law -

$$P_{H_2} = \frac{a-x}{a+b} \times P \; ; \; P_{I_2} = \frac{b-x}{a+b} \times P \text{ and } P_{HI} = \frac{2x}{a+b} \times P.$$

Now,

$$K_P = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}} = \frac{\left[\frac{2x}{a+b} \times P\right]^2}{\frac{(a-x)(b-x)}{(a+b)^2} \times P^2}$$

$=$

$$\Rightarrow K_p = \frac{4x^2P^2}{(a+b)^2} \times \frac{(a+b)^2}{(a-x)(b-x)P^2}$$

$$= \frac{4x^2}{(a-x)(b-x)}$$

For K_c:

$$[H_2] = \frac{a-x}{v} ; \ I_2 = \frac{b-x}{v}$$

$$[HI] = \frac{2x}{v}$$

$$\therefore K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{4x^2}{v^2} \times \frac{v^2}{(a-x)(b-x)}$$

$$= \frac{4x^2}{(a-x)(b-x)}$$

(ii) $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

At initial state: n $\quad 0 \quad 0$

At equilibrium: $n(1-\alpha)$ $\quad n\alpha \quad n\alpha$

$$\therefore [PCl_5] = \frac{n(1-\alpha)}{v} ; \ [PCl_3] = \frac{n\alpha}{v} ; \ [Cl_2] = \frac{n\alpha}{v}$$

Therefore,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{\frac{n\alpha}{v} \times \frac{n\alpha}{v}}{\frac{n(1-\alpha)}{v}}$$

$$= \frac{n^2\alpha^2}{v^2} \times \frac{v}{n(1-\alpha)}$$

$$= \frac{n\alpha^2}{v(1-\alpha)}$$

Again,

Mole number at equilibrium state.

$$n(1-\alpha) + n\alpha + n\alpha$$

$$= n(1+\alpha)$$

$$\therefore P_{PCl_5} = \frac{n(1-\alpha)}{n(1+\alpha)} \times P = \frac{1-\alpha}{1+\alpha} P.$$

$$P_{Cl_2} = \frac{n\alpha}{n(1+\alpha)} P = \frac{\alpha}{1+\alpha} P.$$

$$P_{PCl_3} = \frac{\alpha}{1+\alpha} P$$

Therefore,

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

$$= \frac{\frac{\alpha P}{1+\alpha} \times \frac{\alpha P}{1+\alpha}}{\frac{1-\alpha}{1+\alpha} \times P}$$

$$= \frac{\alpha^2 P^2}{(1+\alpha)^2} \times \frac{1+\alpha}{(1-\alpha) P}$$

$$= \frac{\alpha^2 P}{(1+\alpha)(1-\alpha)} = \left(\frac{\alpha^2}{1-\alpha^2}\right) P.$$

iii) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Initial state: $1 \quad 3 \quad 0$

Equilibrium n ; $1-x \quad 3-3x \quad 2x$

$$\therefore [N_2] = \frac{1-x}{v} ; \quad [H_2] = \frac{3(1-x)}{v}.$$

$$[NH_3] = \frac{2x}{v}.$$

Therefore,

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{4x^2}{v^2} \times \frac{v \times v^3}{(1-x)(1-x)^3 \times 27}$$

$$= \frac{4x^2}{27(1-x)^4} v^2$$

Total mole number at equilibrium state

$$1-x+3-3x+2x$$
$$=4-2x$$

$$P_{N_2}=\frac{1-x}{4-2x}\times P\ ;\ P_{H_2}=\frac{3(1-x)}{4-2x}\times P$$

$$P_{NH_3}=\frac{2x}{4-2x}\times P.$$

$$\therefore k_P=\frac{(P_{NH_3})^2}{P_{N_2}\times(P_{H_2})^3}$$

$$=\frac{\frac{4x^2}{(4-2x)^2}\times P^2}{\frac{1-x}{4-2x}\times P\times\frac{27(1-x)}{(4-2x)^3}\times P^3}$$

$$=\frac{4x^2P^2}{(4-2x)^2}\times\frac{(4-2x)^4}{27(1-x)^2\times P^4}$$

$$=\frac{4x^2(4-2x)^2}{27P^2(1-x)^2}$$

*Le-Chatelier's principle: If a system in equilibrium is disturbed by the change of any one of the factors like temperature, pressure and concentration, the equilibrium will shift so as to reduce the effect of that change.

i) Effect of temperature

ii) Effect of pressure

iii) Effect of concentration

i) Effect of change of temperature: In endothermic reaction, ~~o~~ ie where heat is absorbed, an increase of temperature increase the yeild of product.

Example: $N_2 + O_2 \rightleftharpoons 2NO - 180.75 \, kJ$.

On the otherhand, in exothermic reaction ~~o~~ is where heat is evolved, an increase of temperature decrease the yeild of product. Example

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 92.38 \, kJ.$$

ii) Effect of pressure: If the mole number of reactants and products are equal then there will be no effect of pressure $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$.

If the number of moles of product is more than that of reactant then due to increase of pressure, the yeild of product will decrease.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

And if the no. of moles of product is less than that of reactant then increase of pressure will increase the yeild of product.

~~iv) Effect of concentration;~~

~~iii) Effect of equilibrium constant!~~

iii) Effect of concentration: When the concentration of reactant is more equilibrium shifts to the right ie production increase. And when the concentration of product is more equilibrium shifts to the ~~right~~ left ie production decreases.