r_f = rate of forward reaction
r_b = rate of backward reaction

Chemical Equilibrium

ISHITA KANODIA

1.

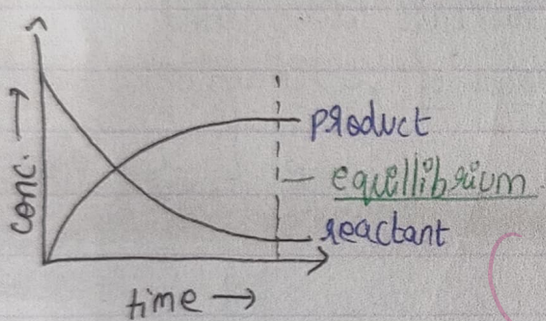
Irreversible reaction -
- proceeds in one direction
- no establishment of equilibrium
- generally, double displacements like strong neutralisation and precipitation.

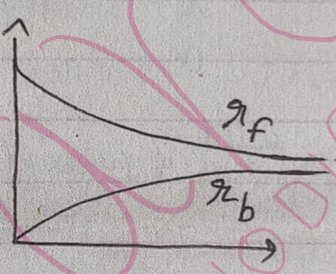
(Equilibrium is a dynamic process.)

Reversible reaction -
- proceeds in both directions
- establishment of equilibrium when $r_f = r_b$.
- generally molecular reactions.

Eg- $N_2 + 3H_2 \rightleftharpoons 2NH_3$
$N_2 + O_2 \rightleftharpoons 2NO$
$H_2 + Cl_2 \rightleftharpoons 2HCl$.

2. Rate of reaction = $\frac{|\text{change in concentration}|}{\text{time}}$.





3. $aA + bB \rightleftharpoons cC + dD$

$r_f = k_f [A]^a [B]^b$
$r_b = k_b [C]^c [D]^d$.

(At equilibrium - $r_f = r_b$)

$K_c = \frac{k_f}{k_b}$.

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

→ $K_p = \frac{[p_C]^c [p_D]^d}{[p_A]^a [p_B]^b}$.

$p_A = [A]RT$.

→ $K_p = K_c (RT)^{\Delta ng}$.

If $\Delta ng = 0$ or $RT = 1$
$\Rightarrow T = 1/R \approx 12K$

$\Rightarrow \underline{K_p = K_c}$.

ISHITA KANODIA

4. ① When two equations are added/subtracted, their equilibrium constants should be multiplied/divided.
② If reaction is reversed, the new equilibrium constant will be reciprocal of previous one.
③ If reaction is multiplied with n, the new equilibrium constant will be raised to the power n.
④ If pure solid or pure liquid is present in the reversible reaction, they will not be considered in the expression of K. ∵ their active mass is taken to be 1.
⑤ K_c and k_p depend only on temperature. (not on pressure, volume, concentration, moles, etc.)

5. $k_p = e^{-\Delta H/RT}$ $\qquad \log \frac{k_{p_2}}{k_{p_1}} = \frac{-\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$

6. $\alpha = \frac{x}{a}$ $\qquad x$ = moles of reactant dissociated.
a = no. of moles of reactant.

$\alpha \propto (V)^{\frac{\Delta n_g}{\text{moles of gaseous product}}}$

$\alpha \propto (\frac{1}{P})^{\frac{\Delta n_g}{\text{moles of gaseous product}}}$

7. **Calculation of K_c and k_p**

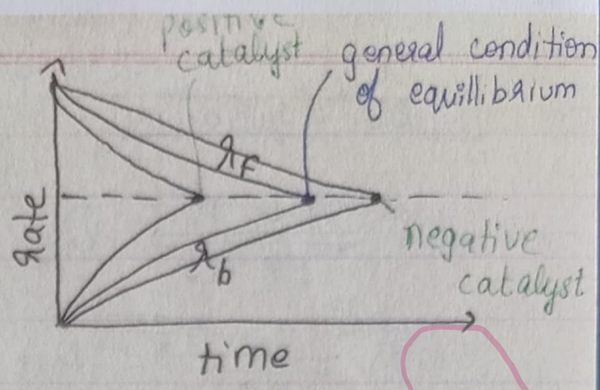
→ If $0 \le \alpha \le 5\%$ ⇒ $\alpha << 1$ ⇒ $1 - \alpha = 1$.

→ for conc. ⇒ $\frac{\text{moles}}{V}$ (where V = volume of container)

→ for partial pressure ⇒ $p_A = x_A P$ (where P = total pressure)

8. $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ for $aA + bB \rightleftharpoons cC + dD$
Q = reaction quotient (at any given time t)

→ If $Q < K_c$ ⇒ forward reaction
$Q > K_c$ ⇒ backward reaction
$Q = K_c$ ⇒ equilibrium



9. **Le Chatelier's Principle-** $aA + bB \rightleftharpoons cC + dD$.

① **Change in Concentration**

→ If $[A][B] \uparrow$ ⇒ forward ⇒ more product is obtained
→ If $[C][D] \uparrow$ ⇒ backward ⇒ more reactant / less product obtained.
→ If $[A][B] \downarrow$ ⇒ backward
→ If $[C][D] \downarrow$ ⇒ forward.

② **Change in Pressure**

→ If $\Delta ng > 0 \longrightarrow P \uparrow$ ⇒ backward
→ $\Delta ng < 0 \longrightarrow P \uparrow$ ⇒ forward
→ $\Delta ng = 0 \longrightarrow P \uparrow$ ⇒ no change.

③ **Change in Volume**

→ If $\Delta ng > 0 \rightarrow V \uparrow$ ⇒ forward
→ $\Delta ng < 0 \rightarrow V \uparrow$ ⇒ backward
→ $\Delta ng = 0 \rightarrow V \uparrow$ ⇒ no change.

④ **Change in Temperature**

→ exothermic ⇒ If $T \uparrow$ ⇒ backward
If $T \downarrow$ ⇒ forward
→ endothermic ⇒ If $T \uparrow$ ⇒ forward
If $T \downarrow$ ⇒ backward.

⑤ **Addition of Inert Gas**

→ at constant volume ⇒ inert gas ↑ ⇒ no change
→ at constant pressure ⇒ inert gas ↑ ⇒ If $\Delta ng > 0$ ⇒ forward
$\Delta ng < 0$ ⇒ backward
$\Delta ng = 0$ ⇒ no change.

10 Physical Equilibrium -

→ solid $\underset{P\uparrow\ T\downarrow}{\overset{P\downarrow\ T\uparrow}{\rightleftharpoons}}$ liquid liquid $\underset{P\uparrow\ T\downarrow}{\overset{P\downarrow\ T\uparrow}{\rightleftharpoons}}$ gas

solid $\underset{P\uparrow\ T\downarrow}{\overset{P\downarrow\ T\uparrow}{\rightleftharpoons}}$ gas Except Ice $\underset{P\downarrow\ T\downarrow}{\overset{P\uparrow\ T\uparrow}{\rightleftharpoons}}$ water

→ solubility of gases increases with increase in pressure for those gases which dissolve in a solvent with decrease in volume.

11. Relation Between α and V.D.

→ $(VD)_T = D_T = \frac{d_{gas}}{d_{H_2}} = \frac{M_{gas}}{2}$.

→ $\boxed{\alpha = \frac{n_1}{\Delta n_g}\left[\frac{D_T - D_o}{D_o}\right] = \frac{n_1}{\Delta n_g}\left[\frac{M_T - M_o}{M_o}\right]}$.

[D_T = VD theoretical
D_o = observed VD.]

Case I $\Delta n_g = 0$

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

	H_2	I_2	HI
$t=0$	a	b	0
$t=t'$	$a-x$	$b-x$	$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{4x^2}{(a-x)(b-x)}$$

If $a=b=1 \Rightarrow x=\alpha$

$$\Rightarrow K_c = \frac{4\alpha^2}{(1-\alpha)^2}$$

If $\alpha << 1$ $\quad (0 \le \alpha \le 5\%)$

$$\Rightarrow \boxed{K_c = 4\alpha^2}$$

$\Delta n_g = 0$

$\therefore K_c = K_p = 4\alpha^2$.

Case II $\Delta n_g < 0$.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

	N_2	H_2	NH_3
$t=0$	a	b	0
$t=t'$	$a-x$	$b-3x$	$2x$

[Total volume = V, Total pressure = P]

$$\rightarrow K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2}{(a-x)(b-3x)^3} \cdot V^2$$

If $a=1$, $b=3 \Rightarrow x=\alpha$

$$K_c = \frac{4\alpha^2 V^2}{(1-\alpha)(3-3\alpha)^3} = \frac{4\alpha^2 V^2}{3^3(1-\alpha)^4}$$

If $\alpha << 1 \Rightarrow \boxed{K_c = \frac{4\alpha^2 V^2}{27}}$.

$$\rightarrow K_p = \frac{\left(\frac{2x}{a-x+b-3x+2x}P\right)^2}{\left(\frac{(b-3x)}{a+b-2x}P\right)^3\left(\frac{(a-x)P}{a+b-2x}\right)} = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3 P^2}$$

If $a=1,\ b=3 \Rightarrow x=\alpha$

$$\Rightarrow k_p = \frac{4\alpha^2(4-2\alpha)^2}{(1-\alpha)^2(3-3\alpha)^3 p^2} = \frac{4\alpha^2 \times 4(2-\alpha)^2}{27(1-\alpha)^4 p^2}$$

$$= \frac{16\alpha^2}{27}\frac{(2-\alpha)^2}{(1-\alpha)^4 p^2}$$

If $\alpha << 1 \Rightarrow k_p = \frac{16\alpha^2 \times 2^2}{27 p^2} = \frac{64\alpha^2}{27 p^2}$.

Similarly for $\Delta n_g > 0$.