Relation b/w α and vapour density:

- it is applicable for ~~only~~ gaseous reactions only.

$$\boxed{\alpha = \frac{D-d}{(n-1)d}}$$

here; D = initial vapour density of reactant $\left[\frac{\text{mol.wt}}{2}\right]$
d = vapour density at equilibrium $\left[\frac{\text{mol.wt}}{2}\right]_{mix}$
n = moles of product produced by 1 mole of reactant.

Q:16 Vapour density of PCl_5 is 104.16 (D); when PCl_5 decomposed then vapour density reduces upto 62(d) find α (degree of dissociation of PCl_5.

$\Rightarrow$ $PCl_5 \overset{\Delta}{\rightleftharpoons} PCl_3 + Cl_2$ $\quad n = 2$

$$\alpha = \frac{D-d}{(n-1)d} \Rightarrow \frac{104.16-62}{(2-1)\,62}$$

$$\Rightarrow \frac{42.16}{62} = 0.68 \text{ or } \boxed{68\%}$$

Le-Chatelier Principle:

- when the reaction is already at their equilibrium and if it is subjected to a charge of concentration, pressure and temperature, the equilibrium shifts to the direction which tends to undo the effects of the charge.

Concen↑↓ = no change.

(A.) Effects of concentration:

- adding of reactant : moved forward
- adding of product : moved backward
- removal of reactant : moved backward.

* it happens until the equilibrium completely establishes.

- concentration change of solid / liq doesn't affect equi^n

(B.) Effects of pressure:

- if pressure increases : reaction moves to less volume side.
  (P↑ V↓)
- if pressure decreases : reaction moves to more volume side.
  (P↓ V↑)

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

→ no pressure effect.

eg: $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

→ pressure increases then rxn moves to backward side.

(C.) Effects of temperature: ΔH constant = enthalpy

- Endothermic reaction (ΔH +ve)
  - → if temp↑ : forward
  - → if temp↓ : backward
- Exothermic reaction (ΔH -ve)
  - → if temp↑ : backward
  - → if temp↓ : forward.

$$R + \text{Heat} \underset{\text{exo.}}{\overset{\text{endo}}{\rightleftharpoons}} P.$$

(D.) Effects of inert gas:

- at constant volume and constant pressure, we can study about addition of inert gas during an equilibrium.

INERT GAS	$\Delta ng = 0$	$\Delta ng > 0$	$\Delta ng < 0$
at const. volume	no eff.	no eff.	no eff.
at const. pressure	no eff.	moves forward	moves backward.

Q: when we add any inert gas at constant volume, why does the equilibrium remains unaffected?

→ $aA \rightleftharpoons bB$ $\quad (\because K_p = K_c\, RT^{\Delta ng})$

- $K_p = \dfrac{[B]^b}{[A]^a} \cdot RT^{\Delta ng} \longrightarrow K_p = \dfrac{n_B^b / V_B^b}{n_A^a / V_A^a}\, RT^{\Delta ng}.$

- $K_p = \left(\dfrac{n_B^b}{n_A^a}\right) \dfrac{1}{V^{b-a}}\, RT^{\Delta ng} \longrightarrow K_p = \left(\dfrac{n_B^b}{n_A^a}\right)\left(\dfrac{RT}{V}\right)^{\Delta ng}.$

→ as $\dfrac{RT}{V}$ is a constant hence, reaction remains in equilibrium even though we add an inert gas to reaction.

Q: When we add an inert gas at constant pressure, why does chemical equilibrium's direction change?

$$\rightarrow K_p = \left(\frac{n_B^{\,b}}{n_A^{\,a}}\right)\left(\frac{RT}{V}\right)^{\Delta n_g} \qquad (\because PV = nRT)$$

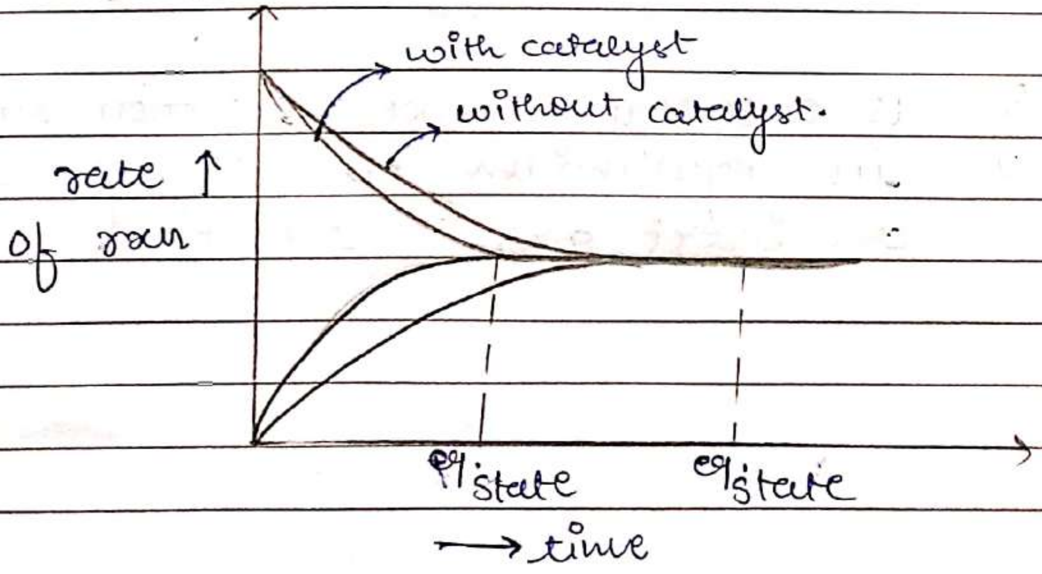
$$\frac{RT}{V} = \frac{P}{n} \longrightarrow K_p = \left(\frac{n_B^{\,b}}{n_A^{\,a}}\right)\left(\frac{P}{n}\right)^{\Delta n_g}$$

CASE: 1 if Δn_g +ve then $K_p \propto \frac{1}{n}$ (moves forward)

CASE: 2 if Δn_g −ve then $K_p \propto n$ (moves backward)

(E) Effect of catalyst:

- The catalyst merely increases the rates of both forward and backward reaction to the same extent so, that equilibrium is reached more rapidly.
- Overall, effect of catalyst on equilibrium is nothing.



Relation between equilibrium constant & Temperature:
(Van't Hoff equation)

→ $\boxed{\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)}$

→ here,

- K_1 and K_2 are equilibrium constant at temperature T_1 and T_2 respectively.
- ΔH is change in enthalpy
- R = universal gaseous constant
  ⟶ 8.314 J/mole/K.

CASE:I if $\Delta H = 0$ then $\log \frac{K_2}{K_1} = 0$.

∴, $\log K_2 = \log K_1 \longrightarrow \underline{K_2 = K_1}$

(hypothetical situation) (not possible in real)

CASE:II if $\Delta H > 0$ then $\log \frac{K_2}{K_1} > 0$ $(T_2 > T_1)$

∴, $\log K_2 > \log K_1 \longrightarrow \underline{K_2 > K_1}$

CASE:III if $\Delta H < 0$ then $\log \frac{K_2}{K_1} < 0$ $(T_1 > T_2)$

∴, $\log K_2 < \log K_1 \longrightarrow \underline{K_1 > K_2}$

Physical equilibrium:

- the equilibrium established between different phases of a particular substance.

eg: $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$
$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$
$H_2O_{(g)} \rightleftharpoons H_2O_{(s)}$

- this phase equilibrium are established at particular fixed combination of temperature and pressure.

- for a substance;
  - (A.) temperature at which its solid and liquid state are in equilibrium is known as melting point or freezing point.
  - (B.) temperature at which its liquid and gaseous state are in equilibrium is known as boiling point or condensation poi
  - (C.) temperature at which its solid and gaseous state are in equilibrium is known as sublimation point.

- in general, this temperatures are known as transition temperature and for a particular substances these depends upon pressure.

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