

Unit - III Second law of

Application of Thermodynamics of

തമിഴ് ഭാഷയിൽ ഉള്ളിടങ്ങളിൽ പരാമർശിക്കുക.

Equilibrium constant: ഗുണിതം!

Forward & backward rxns are Equi

Special properties: characters

Temp, conc. ^{are} observable

can approach any side

* Catalyst did not change the equilib

change the time to go to reach 1st

equilibrium.

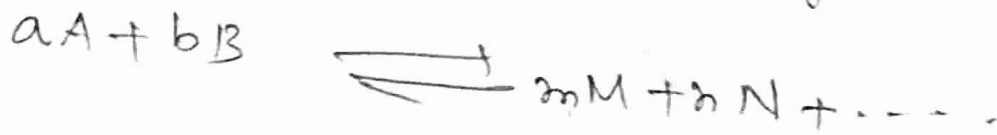
* chemical equil. is dynamic in nature

Le donder's principle.

Laws of Mass Action: $\text{Bloom} \text{ } \text{H} \text{ } \text{B} \text{ } \text{S}$

ഉണ്ടി:

Temp, Pressure in closed system attain Eq^{li}



$$dG_{(T,P)} = G_{\text{pdt}} - G_{\text{reactant}} \quad K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

$$= (M_m dn_m + N_n dn_n + \dots) - (M_a dn_a + N_b dn_b + \dots)$$

M - partial molar ~~Gibbs~~ ^{free} energy for reactants + pds.

$$dG_{(T,P)} = 0$$

$$\circ \circ (M_m dn_m + N_n dn_n + \dots) - (M_a dn_a + N_b dn_b + \dots) = 0$$

$$(M_m dn_m + N_n dn_n + \dots) = (M_a dn_a + N_b dn_b + \dots)$$

$$dn_a \propto a$$

$$dn_b \propto b$$

$$dn_m \propto m$$

$$dn_n \propto n$$

$\text{B} \text{ } \text{B} = \text{B} \text{ } \text{B}$

$$m(\mu_M d n_M + \mu_N d n_N + \dots) + (a \mu_A + b \mu_B + \dots)$$

$$(m \mu_M + n \mu_N + \dots) - (a \mu_A + b \mu_B) = 0 \quad \text{--- ①}$$

chemical pressure in liquid or gas

$$\mu = \mu^\circ + RT \ln a$$

This value substituted in equ ①

$$m(\mu_M^\circ + RT \ln a_M) + (n \mu_N^\circ + RT \ln a_N) + \dots$$

$$= (a \mu_A^\circ + RT \ln a_A) + (b \mu_B^\circ + RT \ln a_B) + \dots$$

$$RT \ln \frac{a_M^m \times a_N^n \times \dots}{a_A^a \times a_B^b \times \dots}$$

$$(a \mu_A^\circ + b \mu_B^\circ + \dots) - (m \mu_M^\circ + n \mu_N^\circ) = -\Delta G^\circ$$

$-\Delta G^\circ$ & $R.T.$ are constant

$$\frac{a_M^m \times a_N^n \times \dots}{a_A^a \times a_B^b \times \dots} = \text{constant } K$$

$$a_A^a \times a_B^b \times \dots$$

$K = \text{Equilibrium Constant}$

Equilibrium
Pressure & Concentration:

HS

* Equi. affected by con, pressure & Temp

* This is explained by ~~Le-chatlier~~
Le chatelier

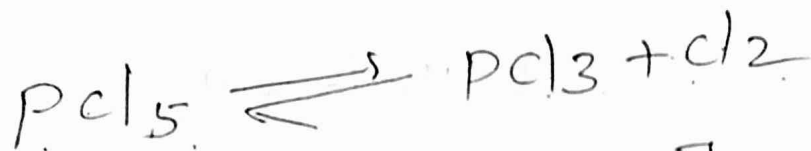
* This Le chatelier principle is called Le chatelier-Braun principle.

Statement:

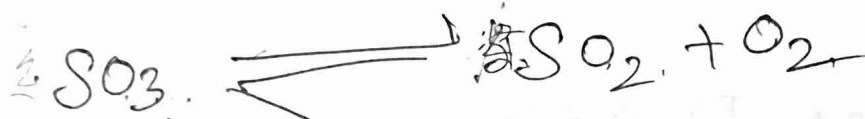
If an equil. is subjected to a stress the equil. shifts in such a way as to reduce the stress.

Explanation:

If a system at equi. is subjected to change in P, T con Conc. the equi. shifts either to the prod side con react side



$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$



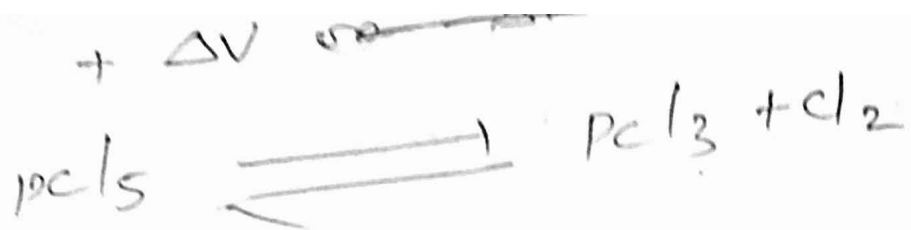
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Lechatelier principle:

$$\left[\frac{\partial \varepsilon}{\partial T} \right]_P = \frac{\Delta H}{T \Delta n}$$

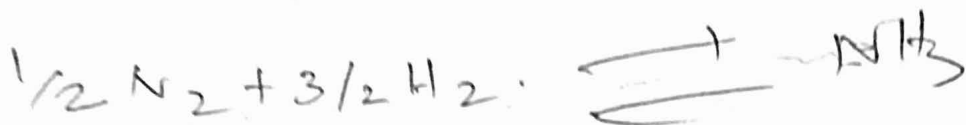
$$\left[\frac{\partial \varepsilon}{\partial P} \right]_T = \frac{\Delta V}{\Delta n}$$

ΔV = change of vol. in forward rxn



$$\left(\frac{\partial \xi}{\partial P} \right)_T = -ve$$

increasing pressure deqs. ξ



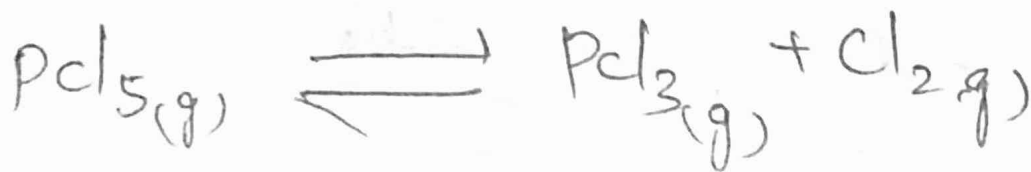
$$+ \Delta H, -\Delta V$$

$$\left(\frac{\partial \xi}{\partial P} \right)_T = +ve$$

increasing pressure ξ increases

high pr

Dissociation of PCl_5



$$\Delta n = n_p - n_r$$

$$\Delta n = 2 - 1 = 1$$

$$K_p = K_c(RT)$$

* 'v' moles of PCl_5 dissociates - 'x' mole gives PCl_3 & Cl_2

* The conc. of components can be given as

	$\text{PCl}_5(g)$	$\text{PCl}_3(g)$	$\text{Cl}_2(g)$
Initial no. of moles	ϕ	0	0
no. of moles react	x	-	x
no. of moles at equil.	$1-x$	x	x
equilibrium conc.	$\frac{1-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

According to law of mass action

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

Substituting the values of equilibrium in the above equation

$$K_c = \frac{\frac{x}{v} \cdot \frac{x}{v}}{\frac{1-x}{v}} = \frac{x^2 v^2}{(1-x)v}$$

$$\frac{x^2}{(1-x)V}$$

	PCl_5	PCl_3	Cl_2
Initial no. of moles	1	0	0
no. of moles reacted	x	-	-
no. of moles at equil.	$1-x$	x	x

$$\begin{aligned} \text{Total no. of moles} &= 1-x + x + x \\ &= 1+x \end{aligned}$$

$$P_{\text{PCl}_5} = \frac{(1-x)P}{1+x}, \quad P_{\text{PCl}_3} = \frac{xP}{(1+x)}$$

$$P_{\text{Cl}_2} = \frac{xP}{1+x}$$

$$K_p = \frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{\frac{x^2 P}{1+x} \cdot \frac{1-x}{1+x}}{\frac{1-x P}{1+x}}$$

$$= \frac{x^2 P^2}{(1+x)^2} \cdot \frac{1-x}{1+x P} = \frac{x^2 P^2}{(1+x)^2} \cdot \frac{1+x}{(1-x) P}$$

$$= \frac{x^2 P}{1-x^2}$$

* $x \ll 1$ x = value can be neglected.

$$K_p \approx x^2 P$$

Influence of Pressure:

- * K_c contains volume term
- * K_p " " pressure term
- * equil. affected by total pressure
- * Increase the value of P increase K_p .
- * K_p constant at constant temp.
- * Increase the pressure favours the reverse rxn. and increase the value of x .

Influence of conc.

- * Increase the conc. of HCl favours the forward rxn.
- * Increase the conc. of FeCl_3 & Cl_2 favours the backward rxn.