Unit – IV

Application of Second law of Thermodynamics of

வெப்ப இயக்கவியல் விதிகளின் பயன்கள்.

Equilibrium constant: சமநிலை!

Forward & backward rxns are equ

Special ~~properties~~: characters

Temp, conc. are observable

* can approach any side
* Catalyst did not change the equilibr
change the time to go to reach t
quilibrium
* chemical equil. is dynamic in nature

Ledondee's principle:

laws of Mass Action: நிறைதாக்க

விதி:

Temp, Pressure in closed system attain equi

$$aA + bB \rightleftharpoons mM + nN + \cdots$$

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

$$= (\mu_M dn_M + \mu_N dn_N + \cdots) - \mu_A dn_A + \mu_B dn_B +)$$

μ - partial molar ~~gibbs~~ free energy for reactants + pdts.

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

$$\therefore (\mu_M dn_M + \mu_N dn_N + \cdots) - \mu_A dn_A + \mu_B dn_B + \cdots) = 0$$

$$(\mu_M dn_M + \mu_N dn_N + \cdots) = (\mu_A dn_A + \mu_B dn_B + \cdots)$$

$dn_A \propto a$

$dn_B \propto b$

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$dn_M \propto m$

$dn_N \propto n$

$\cancel{m}(\mu_M \, dn_M + \mu_N \, dn_N + \cdots) + (\mu_A \, dn_A + \mu_B \cdots)$

$(m\mu_M + n\mu_N + \cdots) - (a\mu_A + b\mu_B) = 0$ — ①

chemical pressure in liquid (or gas

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

This value substituted in equ ①

$$m(\mu^\circ_M + RT \ln a_M) + (n\mu^\circ_N + RT \ln a_N) + \cdots$$

$$= (a\mu^\circ_A + RT \ln a_A) + (b\mu^\circ_B + RT \ln a_B) + \cdots$$

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

$$(a\mu^\circ_A + b\mu^\circ_B + \cdots) - (m\mu^\circ_M + n\mu^\circ_N) = -\Delta G^\circ$$

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

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

K = equ. Constant

Equilibrium Con

Pressure & Concentration:

- Equi. affected by con, pressure & Temp
- This is Explained by ~~Le-chatlier~~ Le chatelier .
- This Lechatelier principle is called Lechatelier-Braun principle.

Statement:

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

Explaination:

If a system at equi. is subjected to change in P, T (or) Conc. the equi. shifts either to the pdt side (or) react side

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

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

$$CaCO_3 \underset{}{\overset{\Delta}{\rightleftharpoons}} CaO + CO_2$$

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

20.10.20

Lechatelier principle:

$$\left[\frac{\delta \varepsilon}{\delta T}\right]_p = \frac{\Delta H}{T G_e}$$

$$\left[\frac{\delta \varepsilon}{\delta P}\right]_T = \frac{\Delta V}{G_e}$$

ΔV = change of vol. in forward rxn

$+\Delta V$

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$(\delta \varepsilon / \delta P)_T = -ve$

increscaning pressure decr. ε ~~temp~~. ε.

$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftharpoons NH_3$

$+\Delta H, -\Delta V$

$$\left(\frac{\delta \varepsilon}{\delta P}\right)_T = +ve$$

increasing pressure ε - on increase

high pr

Dissociation of PCl_5

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

$\Delta n = n_p - n_r$

$\Delta n = 2 - 1 = 1$

$K_p = K_c(RT)$

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

* The conc. of ~~compoun~~ components can be given as

	$PCl_{5(g)}$	$PCl_{3(g)}$	$Cl_{2(g)}$
Initial no. of moles	1	0	0
no. of moles which react	x	–	[illegible]
no. of moles at equil.	1−x	x	x
equilibrium conc.	$1-x/V$	$\frac{x}{V}$	$\frac{x}{V}$

According to law of mass action.

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

Substituting the values of equil. con in the above equation

$$K_c = \frac{x/V \cdot x/V}{\frac{1-x}{V}} = \frac{x^2 V^{\cancel{2}}}{\frac{1-x}{\cancel{V}}}$$

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

	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

Total no. of moles $= 1-\cancel{x}+\cancel{x}+x$

$= 1+x$

$$P_{PCl_5} = \frac{(1-x)P}{1+x}, \quad P_{PCl_3} = \frac{xP}{(1+x)}$$

$$P_{Cl_2} = \frac{xP}{1+x}$$

$$K_p = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}} = \frac{\frac{\cancel{x}xP}{1+x} \cdot \frac{\text{[illegible]}}{1+x}}{\frac{1-x\,P}{1+x}}$$

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

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

$x << 1$ x = value can be neglected.

$$K_p \simeq x^2 P$$

Influence of Pressure:

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

Influence of conc.

- Increase the conc of PCl_5 favours th
forward rxn.
- Increase the conc of PCl_3 & Cl_2 favo
the backward rxn.