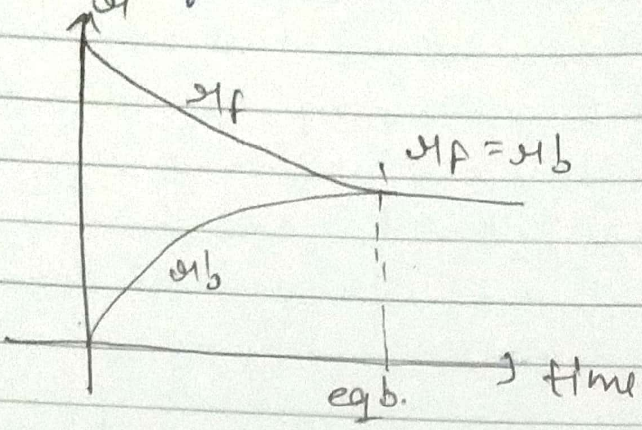
Chapter:

29/08/17

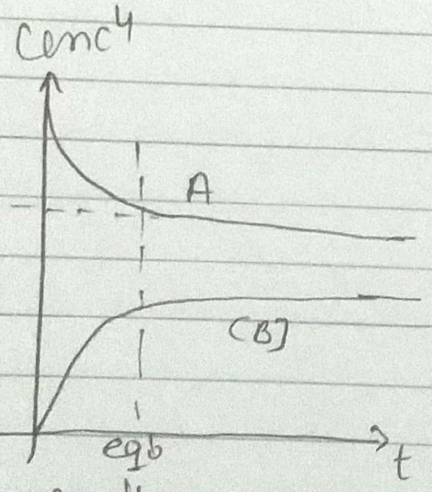
Chemical Equilibrium

* At chemical equ^{b} rate of forward rx^{n} will be equal to rate of backward rx^{n}.



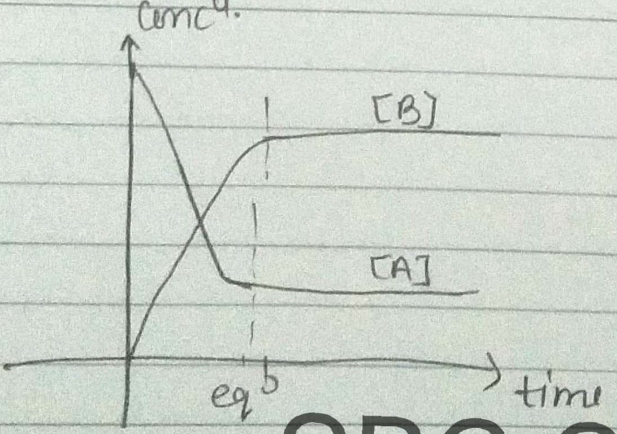
* Eq^{b} can be established both from forward and backward direction.

* At eqb conc^{n} of reactant and products becomes constant



$K_f < K_b$

$[A] > [B]$



$K_f > K_b$

$[B] > [A]$

* Law of Mass Action :-

$$aA + bB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

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

at equilibrium

$$r_f = r_b$$

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

$$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad K_c = \frac{K_f}{K_b}$$

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

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

$$\boxed{K_{eq} = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}}$$

a = active mass

* Calculation of Active mass :-

1. For gasous equilibrium :-

$a \Rightarrow P$ atm $\qquad K_{eq} = K_p$

$a \Rightarrow a$ [mole/L] $\qquad K_{eq} = K_c$

(ii) For liquid equilibrium:

$a \Rightarrow [\quad]$ $K_{eq} = K_c$

$a \Rightarrow P_{atm}$ ✗ K_P will not define for liquid equilibrium.

(iii) Value of active mass for Solvant:

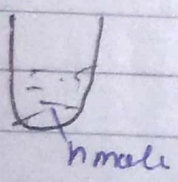
For Solvant $a = 1$

Generally Solvants are taken in large arei's excess amount of their Concentration
So, their concentration always constant during the reaction

(iv) For Solids and Pure liquids:

$a=1$

Because Concⁿ of solid are Pure liquid does not change during the Rxⁿ



$$\text{Concn} = \frac{n}{V}$$

mass of liquid = n × Molar mass

$$\text{Volume of liquid} = \frac{n \times \text{Molar mass}}{d}\ \text{ml}$$

$NaCl_{(s)}$ ✓ $NaCl_{(aq)}$.

$$\text{Concentration} = \frac{n}{\frac{\cancel{n} \times \text{molar mass}}{1000\,d}}$$

Conc^n = $\frac{1000d}{\text{molar mass}}$

Ex:- Pure water d = 1gm/ml

$= \frac{1000 \times 1}{18} = 55.55$ ~~mol~~

Que! Write down the expression eq of Kc and Kp for given equilibrium Rxn.

(1) $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$

$K_c = \frac{[CO]^2}{(CO_2)}$ $K_p = \frac{P_{CO}^2}{P_{CO_2}}$

(2) $CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$

$K_c = \frac{[CH_3COOH][C_2H_5OH]}{(CH_3COOC_2H_5)}$ $K_p = X$

(3) $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$

$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH] + C_2H_5OH)}$ $K_p \Rightarrow X$

(4) $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

$K_c = \frac{[H_2O_{(g)}]}{1}$ $K_p = \frac{P_{H_2O(g)}}{1}$

* Relation b/w kc and kp :

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

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

$$kp = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

$$\boxed{kp = kc (RT)^{\Delta ng}} \text{ — Imp.}$$

$\Delta ng = \Sigma$ s.c of Product − Σ s.c of reactant.

Note:

* Cofficient of substance which have active mass equal to one will not ~~Go~~ be considered in Δng

If $\Delta ng = 0$

$kp = kc$

if $RT = 1 \Rightarrow T = \frac{1}{R} = \frac{1}{0.0821} = 12.18$ k

$kp = kc$.

* If $RT > 1$ & $\Delta ng > 0$

then $kp > kc$.

If $RT > 1$ & $\Delta ng < 0$

then $kp < kc$.

* Unit of Kp and Kc :-

$$K_p = \frac{P_C^{c} \cdot P_D^{d}}{P_A^{a} \cdot P_B^{b}} = atm^{(c+d)-(a+b)}$$

$$\Rightarrow atm^{\Delta ng}.$$

$$K_c = \left(\frac{mol}{litre}\right)^{\Delta ng}.$$

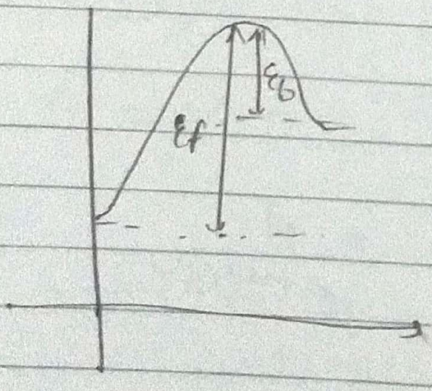
Que: for a Rxn $K_p = 2\ atm^{-1}$ at 300 Kelvin then calculate value of K_c for this rxn.

$$K_p = K_c(RT)^{\Delta ng}$$

$$2 = K_c(R(300))^{-1})$$

$$K_c = 600R = 600 \times 0.0821 \left(\frac{mol}{litre}\right)^{-1}.$$

* Dependence of equilibrium Constant on Temperature :-



$$k = A \cdot e^{-Ea/RT}$$

$$K_f = A_f\ e^{-Ea/RT}$$

$$K_b = A_b\ e^{-Eb/RT}$$

$$K_c = \frac{K_f}{K_b} = \frac{A_f\ e^{-Ef/RT}}{A_b\ e^{-Eb/RT}}$$

$$A \cdot e^{-(E_f - E_b)/RT}$$

$$\boxed{K_c = A \cdot e^{-\Delta H/RT}}$$

Vant half Equation..

Rate Constant

* Although value of both forward k_f and backward Rate constant k_b increase with Catalysist but value of K_c (eq^b const) will not depend on Catalysist.

* In presence of catalysist equilibrium will maintained in lesser time as compared to eq^b establised without cataylst.

* Dependence of temp.
* for exothermic rxn:

if ΔH is = -ve :

$$K_c = A \cdot e^{-\Delta H/RT}$$

$$K_c = A \cdot e^{+ve/RT}$$

$$\boxed{T\uparrow \quad K_c\downarrow}$$

(ii) Endothermic Rxn:

$$\Delta H = +ve$$

$$K_c = A \cdot e^{-\Delta H/RT}$$

$$K_c = A \cdot e^{-ve/RT} = \frac{A}{e^{+ve/RT}}$$

$$\boxed{T\uparrow \quad K_c\uparrow}$$

Practally eq^b const. depend only on temp. but theorticaly it also depend on S.C. of reactant and product

$A \rightleftharpoons B \qquad K_c = \frac{[B]}{[A]}$

$2A \rightleftharpoons 2B = \qquad K'C = \frac{[B]^2}{[A]^2}$

$k'c = KC^2$

$\frac{1}{2}A \rightleftharpoons \frac{1}{2}B \qquad Kc' = \frac{[B]^{1/2}}{[A]^{1/2}}$

$Kc' = Kc^{1/2}$

$A \rightleftharpoons B \qquad K_{c_1} = \frac{[B]}{[A]}$

$C \rightleftharpoons D \qquad K_{c_2} = \frac{[D]}{[C]}$

$A + C \rightleftharpoons B + D \qquad Kc = \frac{[B][D]}{[A][C]} =$

$Kc = K_{c_1} \times K_{c_2}$

Que:- calculate eqb const. for the R_x^n

$A \rightleftharpoons D$

if

$2A \rightleftharpoons 2B \qquad K_c = 4$

$D \rightleftharpoons B \qquad K_c = 2$

$Kc = \frac{[B]^2}{[A]^2} =$

$4 =$

$A \rightleftharpoons \cancel{B} \qquad Kc' = 2$

$\cancel{B} \rightleftharpoons D \qquad Kc' = \frac{1}{2}$

$A \rightleftharpoons \qquad Kc = 2 \times \frac{1}{2} = 1$

$\Rightarrow HCl_{(g)} \rightleftharpoons H^{+}_{(aq)} + Cl^{\ominus}_{aq}$

$$K_{pc} = \frac{[H^{+}][Cl^{\ominus}]}{P_{HCl}}$$

* Type of equilibrium Constant :

By chemical kinetics

- * K_p
- * K_c
- * K_{pc}

By thermodynamics

- K_p°
- K_c°
- K_{pc}°

* In thermodynamics eqb constant will be a unit less quantity because in thermodynamics Active mass is defined as

$$\Rightarrow a = \frac{[\ \ ]}{1M}$$

$$\Rightarrow a = \frac{P\ atm}{1\ atm}.$$

* In chemical kinetic both K_p and K_c will be defined for gaseous eqb.

But in thermodynamics for gaseous eqb Only K_p will not defined.

* Application of eqb constant:

1. To find out direction of equilibrium direction of eqb can be find out with the help of reaction quotien (Q) expression of reaction quotent Q and eqb constant K. will be similar only difference is that

Radioactive   H.W ! S-1 + O-1 complete.
↓
1 to 15

equilibrium Constant can be measured only at the state when equilibrium has established but reaction Quotient can be measured at any time of Rx^n.

$$\Rightarrow aA + bB \rightleftharpoons cC + dD$$

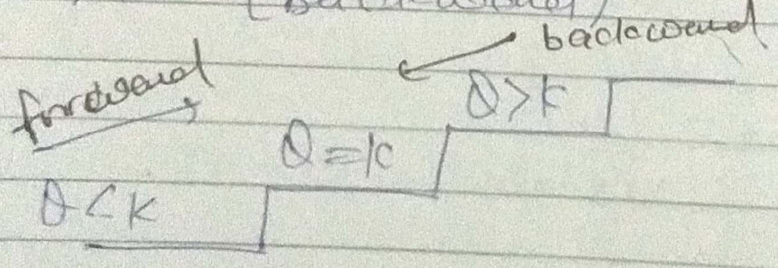
$$\boxed{K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}}$$

→ equilibrium

$$\boxed{Q_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}}$$

→ any instant

$Q = K$ [equilibrium)
$Q < K$ [forward)
$Q > K$ [backward)



Qu! What will be direction of given eq. Rx^n

$\Rightarrow A_{(g)} + 2B_{(s)} \rightleftharpoons 2C_{(g)} + D_{(g)}$ $K_c = 10$
1 mol   5mol   3mol   2mol

in a 10 litre Conc.

$$Q = \frac{[C]^2[D]}{[A]} = \frac{(3/10)^2\,(2/10)}{(1/10)} = \frac{18}{100} = 0.18 < K_c$$

forward

Q. $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$ $K_P = 100$

$t=0$ — 20 atm 20 atm

$t=eq$ — $20-x$ $20-x$

$Q_P = \frac{(20)(20)}{1} = 400 > K_P$ [backward].

$$100 = \frac{(20-x)(20-x)}{1}$$

(14)* To find Out Amount of Reactant and Products at equilibrium:

Que: Calculate eqb conc

Que: Calculate eq^b $conc^n$ of each Reactant and Product in given reaction.

$A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)} + D_{(solid)}$ $K_C = 100$

$t=0$ 2M 2M —

$t=eq$ = $2-x$ $2-x$ $2x$

$$100 = \frac{(2x)^2}{(2-x)^2}$$

$$10 = \frac{2x}{2-x}$$

$20 - 10x = 2x \Rightarrow x = \frac{20}{12} = \frac{10}{6}$

Degree of Dissociation α = $\frac{\text{dissociated amount of reactant}}{\text{initial amount of reactant}}$

Q. For Rx^{n} Calculate mol of $A_{(g)}$, $B_{(g)}$ at eq^{b} and also Calculate Degree of dissociation

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)} \qquad K_c = 100$$

$t=0$	1 mol	1 mol	1 mol	1 mol
$t=eq$	$1-n$	$1-n$	$1+n$	$1+n$.

$$Q : \frac{\left(\frac{1}{V}\right)\left(\frac{1}{V}\right)}{\left(\frac{1}{V}\right)\left(\frac{1}{V}\right)} = 1 < 100 \text{ [forward].}$$

$$100 = \frac{\left(\frac{1+n}{V}\right)\left(\frac{1+n}{V}\right)}{\left(\frac{1-n}{V}\right)\left(\frac{1-n}{V}\right)} = \left(\frac{1+n}{1-n}\right)^2$$

$$10 = \frac{1+n}{1-n} \Rightarrow n = \frac{9}{11} \qquad \alpha_A = \frac{9/11}{1}$$

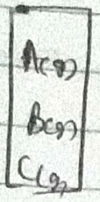
For a Rea^{n} if Δn_g = zero

$$K_p = K_c = K_{mol}$$

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

$$K_p = K_c = \frac{n_{H_2} + n_{I_2}}{N_{hr}}$$

* Partial pressure of different gaseous comp!



$P_T V = n_T RT$ —(i)

$P_A V = n_A RT$ —(ii)

(ii) — (i)

$$\frac{P_A}{P_T} = \frac{n_A}{n_T}$$

Partial Pressure of A → $\boxed{P_A = X_A P_T}$

$\boxed{P_B = X_B P_T}$

In Calculation of total mole (n_T) moles of all gaseous component which are present in the container will be consider wheather they are participating or not participate in the reaction

But moles and liquid will not be considered

Q. In a rigid close container 1 mole Nitrogen (g) 3 mol PCl_5 (g) taken initially
After some time PCl_5 (g) achieve equilibrium at 227°C according to the reaction.

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

If degree of dissociation of PCl_5 gas is $1/3$ or 33.33% and total pressure in the container is 2.05 atm then calculate value of K_P and K_C for eqb reaction of PCl_5

$$PCl_{5(g)} \xrightleftharpoons[]{\substack{N_{2}(g) \\ 1\,mol \\ +}} PCl_{3}(g) + Cl_{2}(g)$$

$t = 0$ 3mol — —

$t = t_{eq}$ $3 - x$ x x $x = 1$

$\Rightarrow$ 2 mol 1 mol 1 mol

$$K_P = \frac{P_{PCl_2} \, P_{Cl_2}}{P_{PCl_5}}$$

$$P_{PCl_5} = \frac{2}{5} \times 2.05$$

$$P_{PCl_3} = \frac{1}{5} \times 2.05$$

$$P_{PCl_2} = \frac{1}{5} \times 2.05$$

$$K_p = K_c [RT]^1$$

Imp

~~Question~~ if Initial amount of Reactant is not Provided.

If Initial amount of Reactant is not Provided that it will be assume as P_0, x or C_0 according to the Question.

Que! For Rxn.

$$PCl_{5}(g) \rightleftharpoons PCl_{3}(g) + Cl_{2}(g) \qquad K_p = 3\,atm.$$

$t = 0$ P_0 — —

$t = t_{eq}$ $P_0 - P'$ P' P'

eq^b total Pressure of Rxn is 9 Atm. then calculate degree of dissociation of PCl_5 (g).

$3 = \frac{p'^2}{p^0 - p'}$ $\quad p^0 - p' + p' + p' = 9$

$p^0 + p' = 9$

2nd Method:

$PCl_{5(g)} \rightleftharpoons PCl_3 + Cl_2 \quad Kp = 3$

$t = 0 \quad p^0$

$t = t_{eq} \quad p^0 - p^0\alpha \quad p^0\alpha \quad p^0\alpha$

$$3 = \frac{(p^0\alpha)(p^0\alpha)}{(p^0 - p^0\alpha)}$$

$$3 = \frac{p^0\alpha^2}{1-\alpha}$$

$$p^0 - p^0\alpha + p^0\alpha + p^0\alpha = 9$$

$$p^0 + p^0\alpha = 9$$

$$p^0 = \frac{9}{1+\alpha}$$

$$3 = \frac{9\alpha^2}{(1+\alpha)(1-\alpha)}$$

$$1 = \frac{3\alpha^2}{1-\alpha^2}$$

$$1 - \alpha^2 = 3\alpha^2$$

$$1 = 4\alpha^2$$

$$\alpha = 1/2$$

* Relation b/w degree of dissociation and average molar mass/

$$\begin{array}{lll} & m_1 A \rightleftharpoons & m_2 B \\ t=0 & n\ \text{mol} & - \\ t=t_{eq} & n-n\alpha & \frac{m_2}{m_1}(n\alpha) \end{array}$$

initial total mol = n mol

total mol at eqb $= n - n\alpha + \frac{m_2}{m_1}(n\alpha)$

$$= n\left(1-\alpha+\frac{m_2}{m_1}\alpha\right)$$

$$= n\left(1+\left(\frac{m_2}{m_1}-1\right)\alpha\right)$$

$$\text{mol} \propto \frac{1}{\text{Molar mass}}$$

$$n \propto \frac{1}{M_T} \quad \text{— (i)}$$

$$n\left[1+\left(\frac{m_2}{m_1}-1\right)\alpha\right] \propto \frac{1}{M_{avg}} \quad \text{— (ii)}$$

$$\boxed{1+\left(\frac{m_2}{m_1}-1\right)\alpha = \frac{M_T}{M_{avg}}}$$

$$\boxed{1+(n-1)\alpha = \frac{M_T}{M_{avg}}}$$

$$n = \frac{\text{S.C of Product}}{\text{S.C of reactant.}}$$

Here M_T = is called Theortical Molar mass or molar mass of Reactant

Radio ⇒ J-Advance
Kc ⇒ 8-2

Mavg: It is called average molar mass at eq^b or observe molar mass

Que: Initally 1 mole NH_3 is taken in a Container after equilibrium observed molar mass of reaction is 16g/mol then Calculate Value of eqb Constant K_c. If reaction occur in a 10 litre Container.

v = 10

	$2NH_3 \rightleftharpoons$	N_2	$+ 3H_2$
t = 0	1 mol.	–	–
t = t_{eq}	$1 - 1/16$	$1/32$	$\frac{3}{2}(1/6)$

* Le- [illegible]

$$1 + (n-1)\alpha = \frac{M_T}{M_{avg}}$$

$$1 + \left(\frac{4}{2} - 1\right)\alpha = \frac{17}{16}$$

$$\alpha = \frac{1}{16}$$

* Le-chatelier principle :

In this principle we will study effect of change in conc^n, volume, pressure, temp. etc. at equilibrium reaction

* **Effect on Concentration:** $R \rightleftharpoons P$
  - # add R
    $Q < K$ (forward)
  - # add P
    $Q > K$ (backward)

Exothermic = ΔH −ve   V → Q change.
Endothermic = ΔH +ve

Remove R
$Q > K$ [backward]
Remove P
$Q < K$ [forward].

* If Solid Substances are added or subtracted at equilibrium then their will be no effect on eqb because active mass of Solid Substances will be equal to 1.

* Effect of temperature:

$Q = K$ $Q = \frac{[P]}{[R]}$

$R \rightleftharpoons P$

Exothermic ($\Delta H = -ve$)
T↑   K↓
$Q > K$ [backward]

Endothermic ($\Delta H = +ve$)
T↑ K↑
$Q < K$ [forward].

* Effect of Volume:

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

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b}\left(\frac{1}{V}\right)^{\Delta ng}$$

$\Delta ng > 0$
V↑ $Q < K$ (forward)

$\Delta ng < 0$
V↑ $Q > K$ [backward]

$\Delta ng = 0$ V↑   no effect at Eq^b.

Ang° ba° - f

Leamy

Q. K_C T } not change not disturb eq^b.

Note: <u>On increasing</u> Volume at eq^b. eq^b will procedd in the direction where gasious no. of moles are increasing.

* On decreasing Volume eq^b. will shift in backward direction.

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)} \qquad \Delta n = -ve$$

* On decreasing temperature ⇒ forward.

* Effect of pressure:

By default in Question Pressure is changes by either decreasing or increasing Volume

$\boxed{P\uparrow \quad V\downarrow}$ $\boxed{P\downarrow \quad V\uparrow}$

* ON increasing pressure eq^b will shift in the direction where gasious no. of moles are decreasing

* Effect of mixing Inert gas at equlibrium:

(1) mixing of inert gas at constant Pressure:

* If inert gas is mixed at const. Pressure then Volume of container will increase so eq^b will shift in the direction where gasious no. of moles are increasing.

* Mixing of Inert gas at const. Volume :

There will be no effect on eqb. because both Value of Reaction quitent Q and eqb constant K remain unchanged

Q — n, V depend

K — T depend.

* Effect of temp. and pressure on physical equilibrium :

* effect of temp. will be chacked like in Chemical equilibrium

* on Increasing Pressure eqb will shift in the direction where Vol. is decreasing or density will increasing.

$P\uparrow \; V\downarrow \quad d\uparrow$

$P\downarrow \; V\uparrow \quad d\downarrow$

$A_{(s)} \rightleftharpoons A_{(l)} \quad \Delta n = +ve$

$P\uparrow$ = backward

$T\uparrow \Rightarrow$ forward.

Ex: $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$

$P\uparrow \Rightarrow$ forward — $V_{H_2O_{(s)}} > V_{H_2O_{(l)}}$

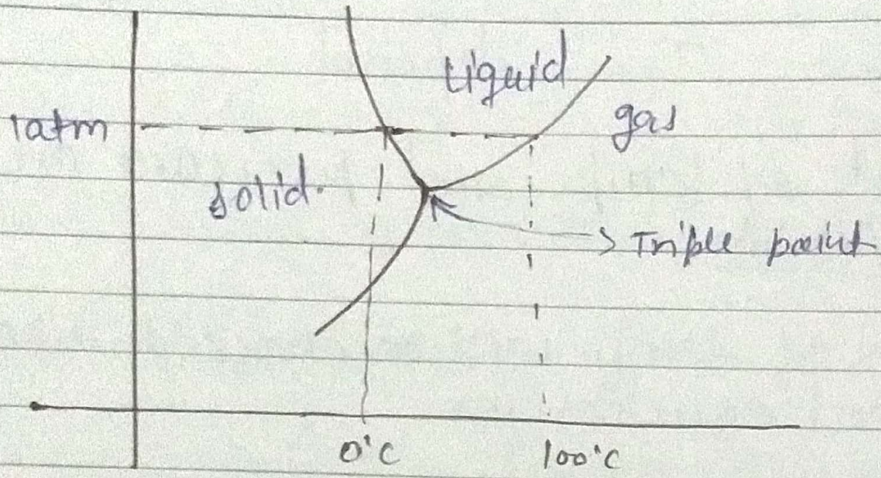
1 atm

($C_{graphite}$) $\rightleftharpoons$ $C_{diamond}$)

P↑ forward.

* Phase diagram for Water (H_2O) :-

(1. ~~Boiling point~~



L ⇌ g

L ⇌ s

Phase diagram for H_2O

$$V_{H_2O_{(s)}} > V_{H_2O_{(l)}}.$$

(1) Boiling point.
At Boiling point liquid remain with eq^b with gas

on increasing pressure P↑ B.P ↑

* Boiling point at one 1 atm pressure called normal Boiling point

* Boiling point at 1 bar pressure called standard boiling point.

$1 \text{ atm} = 10^5$

- At fezing point solid will be in ~~eq~~ eq^b with liquid.

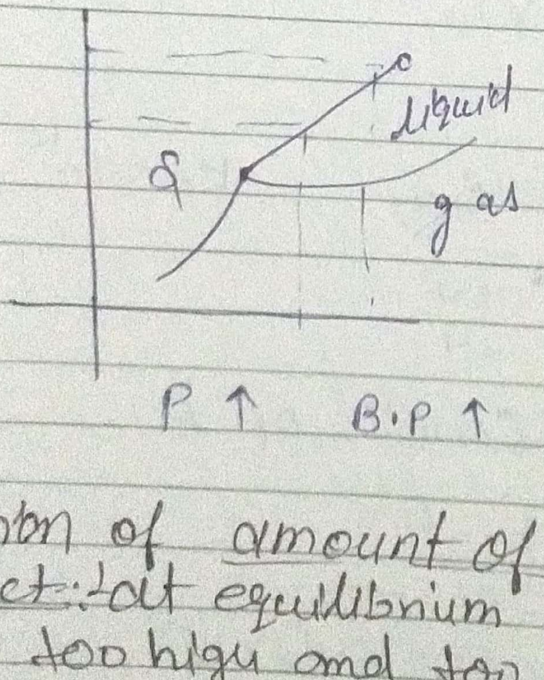
- for water on increasing pressure fezing point will decrease

- Tripple point:

  It is a unike point in phase diagram for which solid liquid and gas all three state of substance will remain in eqb.

for a substance in which

$V_{H_2O(l)} > V_{H_2O(g)}$



$l > s$.

P ↑ B.P ↑ m.P ↑

- Calculation of amount of Reactant and Product: at equilibrium if value of K_{eq} is too high and too low.

1) If value of K_{eq} too low like $10^{-5}, 10^{-3}, 10^{-7}$ negligible amount of Reactant will convert in product.

2) If value of k_{eq} is quite high like
Ex: $10^5, 10^3, 10^7$ almost Complete Reactant will convert in Product.

Ex! $A \rightleftharpoons 2B$ $\quad K_c = 10^{-8}$

$t=0$ $\quad 2M \quad -$

$t = t_{eq}$ $\quad \approx 2 \;\; (2-x) \quad 2x$ $\qquad x \approx 0$

then calculate eq^b concentration of A and B.

Ans x will be almost to zero

$$K_c = \frac{[B]^2}{[A]}$$

$$10^{-8} = \frac{(2x)^2}{2} \Rightarrow 2x = \sqrt{2} \times 10^{-4}$$

$$[B] = \sqrt{2} \times 10^{-4}$$

(ii) $A_{(g)} \rightleftharpoons 2B_{(g)}$ $\quad K_c = 10^{12}$

$t=0$ $\quad 2M \quad -$

$t = t_{eq}$ $\quad 2-x \quad 2x$ $\qquad x \approx 2$

$\qquad \approx 0 \quad = 4$

Calculate eq Conc^n of A

$$10^{12} = \frac{4^2}{(2-x)}$$

$$[A] = (2-x) = 16 \times 10^{-12}$$