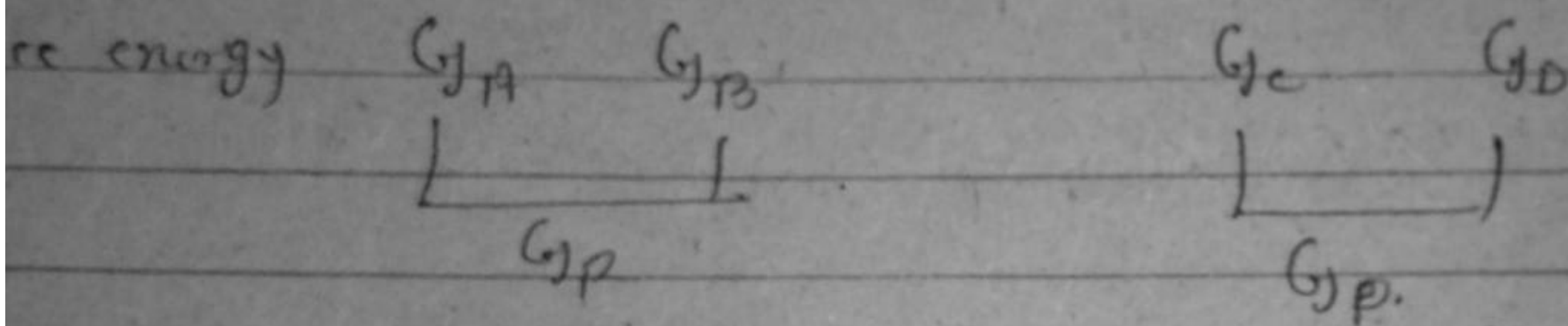
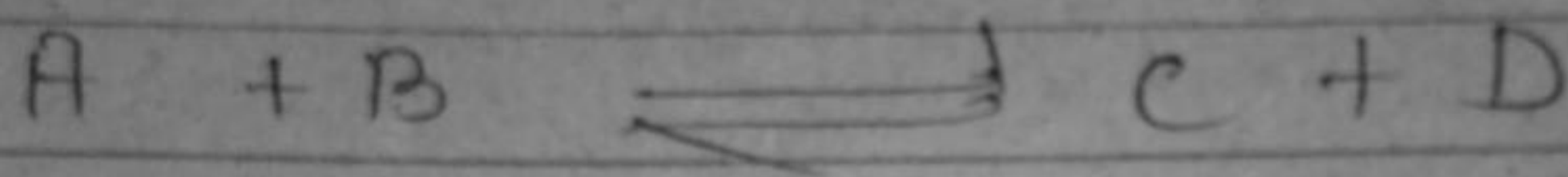


- Q. Write a note on Van't Hoff's reaction isotherm.  
 Q. Derive an expression for Van't Hoff's reaction isotherm.

Ans. Van't Hoff's reaction isotherm involves the calculation of change in free energy when a chemical reaction is carried out at const. temp. from <sup>some</sup> arbitrary concentrations of reactants to some other arbitrary concentrations.

Let us consider a gaseous reaction.



The free energy of reactants and products be given as below -

$$G_A = G_A^{\circ} + RT \ln P_A$$

where  $G_A^{\circ}$  = standard free energy of A

and  $P_A$  = pressure of A

similarly,

$$G_B = G_B^{\circ} + RT \ln P_B$$

$$G_C = G_C^{\circ} + RT \ln P_C$$

$$\text{and } G_D = G_D^{\circ} + RT \ln P_D$$



So for change in free energy of the reaction is given as

$$\Delta G = G_{\text{(products)}} - G_{\text{(reactants)}}$$

$$= (G_C + G_D) - (G_A + G_B)$$

$$= (G_C^\circ + RT \ln P_C + G_D^\circ + RT \ln P_D) - (G_A^\circ + RT \ln P_A + G_B^\circ + RT \ln P_B)$$

$$= \left\{ (G_C^\circ + G_D^\circ) - (G_A^\circ + G_B^\circ) \right\} + \left\{ (RT \ln P_C + RT \ln P_D) - (RT \ln P_A + RT \ln P_B) \right\}$$

$$= \Delta G^\circ + RT \left\{ (\ln P_C + \ln P_D) - (\ln P_A + \ln P_B) \right\}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{P_C \cdot P_D}{P_A \cdot P_B} \quad \text{--- (1)}$$

$$= \Delta G^\circ + 2.303 RT \log \frac{P_C \cdot P_D}{P_A \cdot P_B}$$

When  $\Delta G^\circ =$  Standard free energy change of the reaction

If the reaction is assumed to be equilibrium then

$$\Delta G = 0 \quad ; \quad \frac{P_C \cdot P_D}{P_A \cdot P_B} = K_P$$



Hence from equation (I)

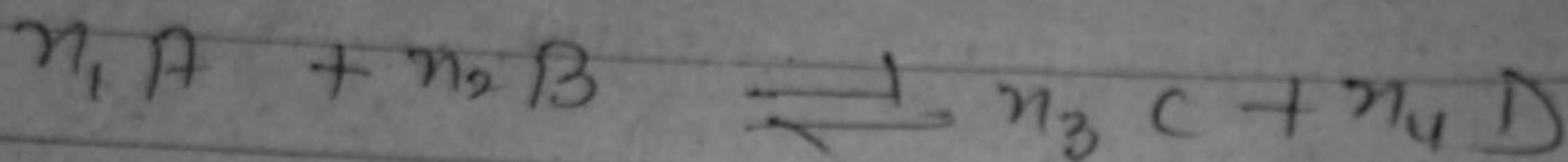
$$0 = \Delta G^{\circ} + RT \ln K_p$$

$$\text{or } \Delta G^{\circ} = -RT \ln K_p$$

Putting the value of  $\Delta G^{\circ}$  in equation (I) we get

$$\Delta G = -RT \ln K_p + RT \ln \frac{P_C \cdot P_D}{P_A \cdot P_B} \quad \text{--- (II)}$$

for a general reaction like



$$\Delta G = -RT \ln K_p + RT \ln \left( \frac{P_C^{n_3} \cdot P_D^{n_4}}{P_A^{n_1} \cdot P_B^{n_2}} \right)$$

$$-\Delta G = RT \ln K_p + RT \sum n \ln P \quad \text{--- (III)}$$

Equation (III) is one form of van't Hoff's ~~equation~~ reaction quotient.

$\therefore P \propto C$  in terms of concentration

The expression (III) may be written as

$$-\Delta G = RT \ln K_c - RT \sum n \ln C \quad \text{--- (IV)}$$

Eq. (IV) is another form of van't Hoff reaction quotient.