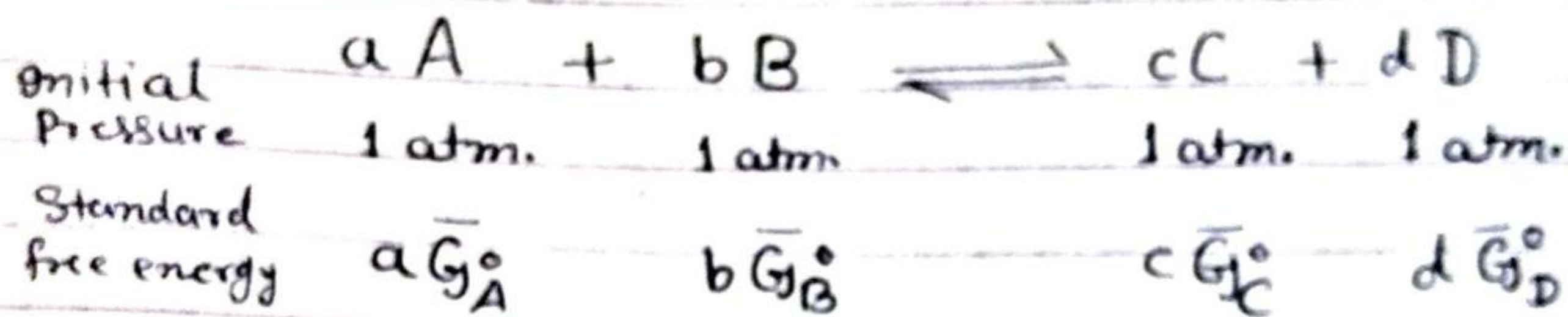


T. D. C. Part II ; Chem. (Hons.)
 Paper IV ; Gr. A (Phy. Chem.)
 Unit II chemical Equilibrium
Vant - Hoff reaction Isotherm

The equation gives the increase of free energy for the transfer of reactant at any concentration or partial pressure to products

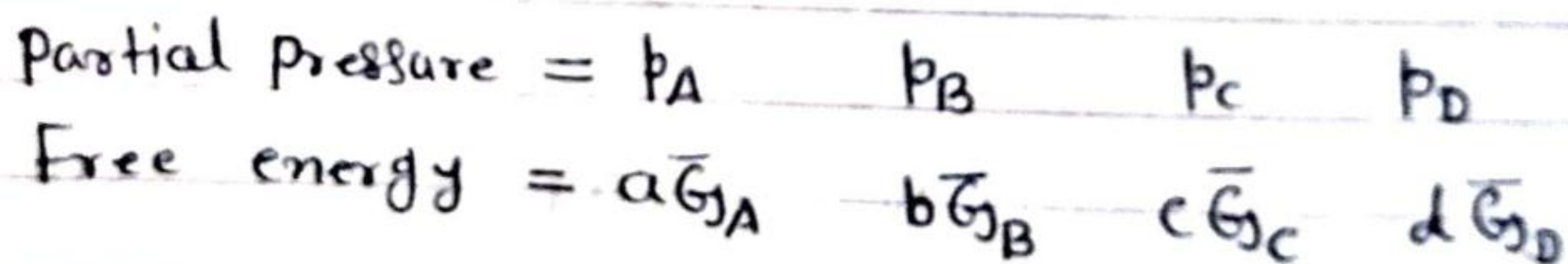
For the following reaction in the gas state, if all the reactants and the products be in the standard state i.e. at 1 atm. pressure and const. temp. T.



\therefore Standard free energy change,

$$\Delta G^\circ = c\bar{G}_C^\circ + d\bar{G}_D^\circ - a\bar{G}_A^\circ - b\bar{G}_B^\circ$$

if at any specified state, let



\therefore Free energy, (ΔG)

$$\Delta G = c\bar{G}_C + d\bar{G}_D - a\bar{G}_A - b\bar{G}_B$$

For an infinitesimal change in free energy and partial pressure of any component,

$$dG = vdp - SdT$$

$$= vdp \quad (\text{at const. } T)$$

$$= nRT \frac{dp}{p} \quad (\text{for 'n' moles of an ideal gas})$$

Thus, for A,

$$dG = aRT \frac{dp}{p}$$

For A, when pressure changes from 1 to p_A

Free energy changes from

$$a\bar{G}_A^0 \longrightarrow a\bar{G}_A$$

Integrating between the above limits,

$$\int_{a\bar{G}_A^0}^{a\bar{G}_A} dG = aRT \int_1^{p_A} \frac{dp}{p}$$

$$\text{or, } a\bar{G}_A - a\bar{G}_A^0 = aRT \ln \frac{p_A}{1}$$

Similarly,

$$b\bar{G}_B - b\bar{G}_B^0 = bRT \ln p_B$$

$$c\bar{G}_C - c\bar{G}_C^0 = cRT \ln p_C$$

$$d\bar{G}_D - d\bar{G}_D^0 = dRT \ln p_D$$

Subtracting ΔG^0 from ΔG

$$\Delta G - \Delta G^0 = (c\bar{G}_C - c\bar{G}_C^0) + (d\bar{G}_D - d\bar{G}_D^0) - (a\bar{G}_A - a\bar{G}_A^0) - (b\bar{G}_B - b\bar{G}_B^0)$$

$$= cRT \ln p_C + dRT \ln p_D$$

$$- aRT \ln p_A - bRT \ln p_B$$

$$= RT [c \ln p_C + d \ln p_D - a \ln p_A - b \ln p_B]$$

$$\text{or, } \Delta G_j = RT \ln \frac{p_c^c \cdot p_D^d}{p_A^a \cdot p_B^b} + \Delta G^{\circ} \quad \text{--- (1)}$$

$$= \Delta G^{\circ} + RT \sum v \ln p.$$

Where, \bar{G}_j = partial molar free energy.
 v = no. of molecules of space.

The above equation is known as,
 Vant-Hoff reaction isotherm.

Uses of reaction isotherm \Rightarrow

1. Equilibrium constant of a reaction \Rightarrow

At equilibrium at const. T & P ,

Since,

$$dG_j = v dp - s dT$$

$$= 0 \quad (dp=0, dT=0)$$

$\therefore \Delta G_j = 0$ for ~~a~~ finite change

Hence,

Vant-Hoff reaction isotherm

$$\Delta G_j = \Delta G^{\circ} + RT \sum v \ln p$$

becomes,

$$0 = \Delta G^{\circ} + RT \sum v \ln p$$

$$\text{or, } -\Delta G^{\circ} = +RT \sum v \ln p.$$

$$= RT \left(c \ln p_c + d \ln p_D - a \ln p_A - b \ln p_B \right)$$

$$\text{or } -\Delta G^\circ = RT \ln \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

ΔG° is a constant as it corresponds to standard state and therefore its $T = \text{const.}$

$$\frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} = \text{const.} = K_p \text{ is constant called equilibrium const.}$$

K_p is a constant at constant T .

② ΔG° from equilibrium constant \rightleftharpoons

At equilibrium constant at constant T & P .

$$\Delta G = 0$$

So that, by V-H reaction isotherm

$$\Delta G = \Delta G^\circ + RT \sum \nu \ln p$$

We have,

$$-\Delta G^\circ = RT \sum \nu \ln p$$

$$= RT \ln p \quad (\text{at equilibrium})$$

$$= 2.303 \log p$$

$$= 2.303 \log_{10} K_p$$

③ $\Delta G \rightarrow$

By V-H reaction isotherm

$$\Delta G = \Delta G^\circ + RT \sum \nu \ln p$$

$$= -RT \ln K_p + RT \sum \nu \ln p$$

Having determined, ΔG can be calculated at partial pressure p_A — of the reactants and products of the reaction.

Thermodynamic Equilibrium constant \rightarrow

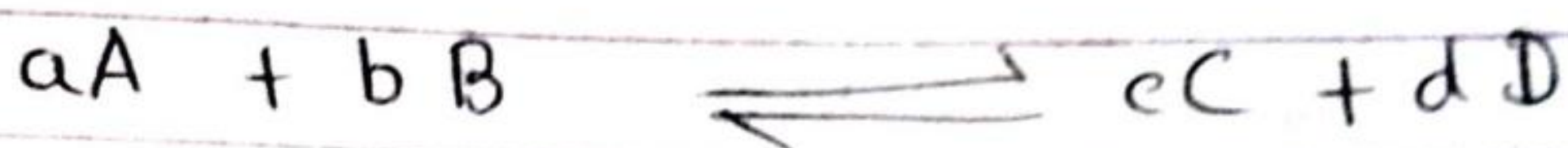
If activity 'a' is used for concentration.

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

Where, K_a is called thermodynamic equilibrium constant.

Relation between K_a , K_c and K_f \rightarrow

For the reaction,



Equilibrium constant

$$K_a = \frac{C_c^c \cdot C_D^d}{C_A^a \cdot C_B^b}$$

$$\text{As, } a = f \cdot C$$

Where, f = activity co-efficient
 a = activity.

$$\therefore K_c = \frac{(a_C/f_C)^c \cdot (a_D/f_D)^d}{(a_A/f_A)^a \cdot (a_B/f_B)^b}$$

$$= \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} \cdot \frac{f_A^a \cdot f_B^b}{f_C^c \cdot f_D^d}$$

$$= K_a \times \frac{f_A^a \cdot f_B^b}{f_C^c \cdot f_D^d}$$

$$= K_a \quad \left(\text{in infinite dilute solution } f=1 \right)$$

In a gas reaction,

activity, 'a' = fugacity 'f'

gf γ = activity coefficient

$$f = a = p\gamma$$

where, p = partial pressure.

$$\therefore K_f = \frac{f_c^c \cdot f_D^d}{f_A^a \cdot f_B^b}$$

Equilibrium
constant
using fugacity.

$$= \frac{p_c^c \gamma_c^c \cdot p_D^d \gamma_D^d}{p_A^a \gamma_A^a \cdot p_B^b \gamma_B^b}$$

$$= \frac{p_c^c \cdot p_D^d}{p_A^a \cdot p_B^b} \cdot \frac{\gamma_c^c \cdot \gamma_D^d}{\gamma_A^a \cdot \gamma_B^b}$$

$$= K_p \cdot \left(\frac{\gamma_c^c \cdot \gamma_D^d}{\gamma_A^a \cdot \gamma_B^b} \right)$$