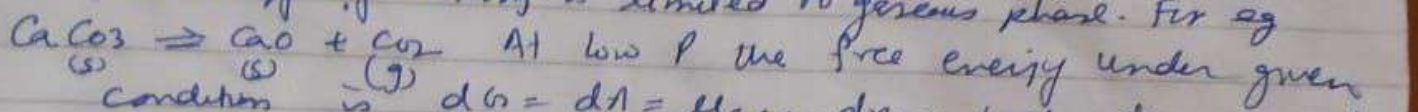


The term irreversible applies that reaction proceeds to such a degree that the residual amounts of unchanged reactants are almost immeasurably small. Therefore in such cases a min. value of G could not be represented on diagram.

Equilibrium between ideal gases and a pure condensed state / phase

Let us consider a reaction at eqⁿ betⁿ solids & gases in C which solids exists in pure form and don't form solid solutions. The free energy of mixing is limited to gaseous phase. For eg



At low P the free energy under given condition is $dG = dA = \mu_{\text{CaCO}_3} dn_{\text{CaCO}_3} + \mu_{\text{CaO}} dn_{\text{CaO}} + \mu_{\text{CO}_2} dn_{\text{CO}_2}$

If ξ is extent of reaction then change in the amts of various species are $d\xi = -dn_{\text{CaCO}_3} = dn_{\text{CaO}} = dn_{\text{CO}_2}$

$$dG = (\mu_{\text{CaO}} + \mu_{\text{CO}_2} - \mu_{\text{CaCO}_3}) d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_{\text{CaO}} + \mu_{\text{CO}_2} - \mu_{\text{CaCO}_3} = \Delta G$$

$$\text{At eq}^n \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \left(\frac{\partial A}{\partial \xi}\right)_{T,P} = 0$$

$$\mu_{\text{CaO}} + \mu_{\text{CO}_2} - \mu_{\text{CaCO}_3} = 0$$

$$\mu_{\text{CaCO}_3} = \mu_{\text{CaO}} + \mu_{\text{CO}_2}$$

under ordinary conditions the μ of solid components can be taken equal to their values of pure substance

$$d\mu = \int v dp \text{ where } v \text{ is very small}$$

$$\mu_i - \mu_i^0 = \int v dp$$

$$\therefore \mu_i = \mu_i^0 = \mu_i^* \text{ when } P = P^0 = 1 \text{ atm}$$

Chemical potential of CO_2 $\mu_{\text{CO}_2} = \mu_{\text{CO}_2}^0 + RT \ln \frac{P_{\text{CO}_2}}{P^0}$

$$\text{At eq}^n \mu_{\text{CaCO}_3}^0 = \mu_{\text{CaO}}^0 + \mu_{\text{CO}_2}^0 + RT \ln \frac{P_{\text{CO}_2}}{P^0}$$

$$RT \ln \frac{P_{\text{CO}_2}}{P^0} = -[\mu_{\text{CaO}}^0 + \mu_{\text{CO}_2}^0 - \mu_{\text{CaCO}_3}^0] = -\Delta G^0 \quad \text{--- (1)}$$

$$\Delta G^0 = -RT \ln K_p \quad \text{--- (2)}$$

$$RT \ln \frac{P_{\text{CO}_2}}{P^0} = -RT \ln K_p$$

$$K_p = \frac{P_{\text{CO}_2}}{P^0} \quad \therefore P^0 = 1 \text{ atm}, \quad K_p = P_{\text{CO}_2}$$

$$= -\Delta G^{\circ}$$

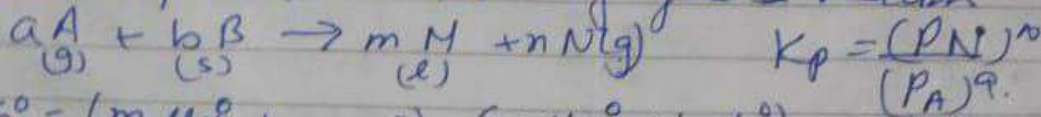
①

$$\Delta G^{\circ} = -RT \ln K_p \quad \text{--- (2)}$$

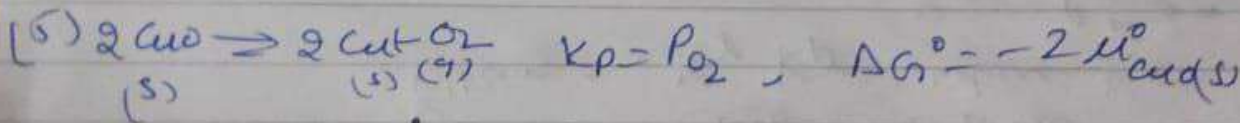
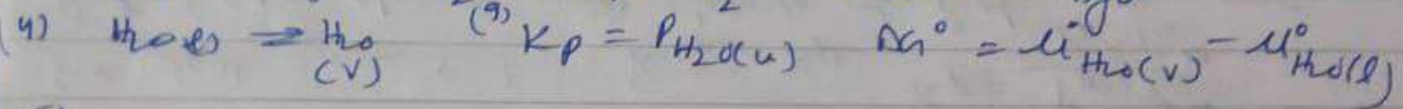
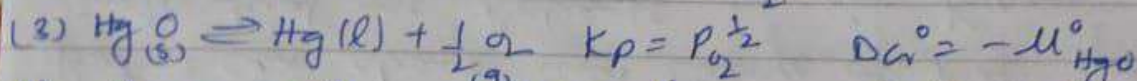
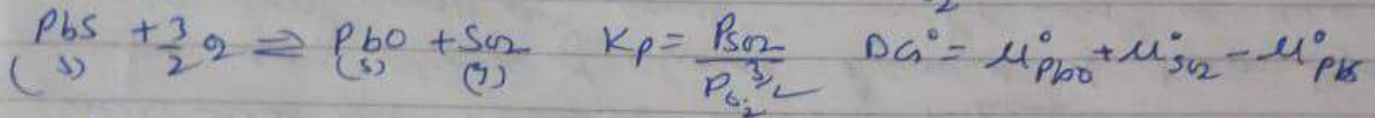
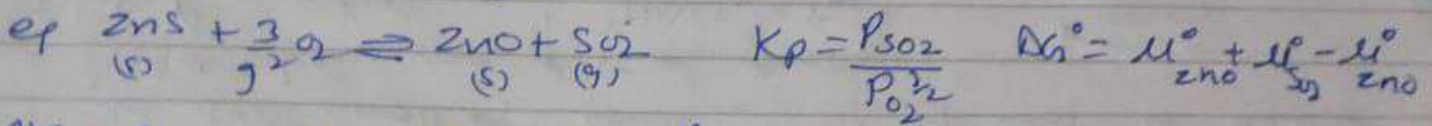
$$-RT \ln \frac{P_{CO_2}}{P^{\circ}} = -RT \ln K_p$$

$$K_p = \frac{P_{CO_2}}{P^{\circ}} \quad \because P^{\circ} = 1 \text{ atm}, \quad K_p = P_{CO_2}$$

standard free energy of reaction contains the standard free energy of the R & P but at eqⁿ it contains only P of the gaseous component this eqⁿ is called partial eqⁿ constt. For any general reaction



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



Equilibrium constt for Real Gases

Let us consider a general reaction $aA + bB \rightarrow mM + nN$

All are real gases $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0$

Let $\mu_i = \mu_i^{\circ} + RT \ln f_i$ where f_i is fugacity

eq ① becomes $\Delta G = (m\mu_M^{\circ} + RT \ln f_M^m + n\mu_N^{\circ} + RT \ln f_N^n) - (a\mu_A^{\circ} + RT \ln f_A^a + b\mu_B^{\circ} + RT \ln f_B^b)$

$$\Delta G = (m\mu_M^{\circ} + n\mu_N^{\circ} - a\mu_A^{\circ} - b\mu_B^{\circ}) + RT \ln \frac{f_M^m f_N^n}{f_A^a f_B^b} \quad \text{--- (2)}$$

Since at eqⁿ $\Delta G = 0$

$$0 = \Delta G^{\circ} + RT \ln \left[\frac{f_M^m f_N^n}{f_A^a f_B^b} \right]_{eq^n} \quad \text{--- (3)}$$

$$\Delta G^{\circ} = -RT \ln \left[\frac{f_M^m f_N^n}{f_A^a f_B^b} \right]_{eq^n}$$

ΔG° is std. free energy of the reaction at a given (3)
 T when R & P are in their std. state of unit
 fugacity is $f^\circ = 1 \text{ atm}$ \therefore R.H.S. of eq. K

$$\Delta G^\circ = -RT \ln K_p \text{ so here we use}$$

$$\Delta G^\circ = -RT \ln K_{chem} \quad \text{--- (3)}$$

$$-RT \ln K_{chem} = \ln \frac{f_M^m f_N^n}{f_A^a f_B^b} \quad \therefore K_{chem} = \left(\frac{f_M^m f_N^n}{f_A^a f_B^b} \right) e^{\frac{\Delta G^\circ}{RT}}$$

The fugacity term is related $f = \gamma P$ where γ is fugacity coefficient

$$\therefore K_{chem} = \frac{(\gamma_M P_M)^m (\gamma_N P_N)^n}{(\gamma_A P_A)^a (\gamma_B P_B)^b}$$

$$K_{chem} = K_\gamma K_p \quad \text{where } K_\gamma = \frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b}$$

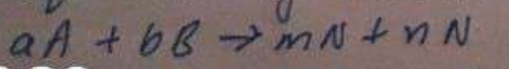
For ideal gas $\gamma = 1$, $K_{chem} = K_p$ $K_p = \frac{P_M^m P_N^n}{P_A^a P_B^b}$

But γ can change with change of P of system or individual gas P change $\therefore K_{chem}$ is constt. for any change of pressure & term K_p is not constt. $\therefore K_p$ can't be used to a behaviour of real gases

Total P	K_p	$\gamma_{NH_3} / \gamma_{N_2}^{1/2} \gamma_{H_2}^{3/2}$	K_{chem}
100	0.0072	0.88	0.0063
300	0.0088	0.69	0.0061
600	0.0129	0.50	0.0064
1000	0.0237	0.43	0.0099

K_{chem} is found to be constt. as compare to K_p over a wide range of P, only at 1000 atm there is marked change in the value of K_{chem} .

Eqⁿ Constt of Reaction in solution



(4)

$$\Delta G^\circ = -RT \ln K = -RT \ln \left(\frac{[M]^m [N]^n}{[A]^a [B]^b} \right) = -RT \ln \left(\frac{mM + nN}{aA + bB} \right) = 0$$

Eqⁿ Constⁿ of Reaction in solution
 $aA + bB \rightarrow mM + nN$

$$\Delta G = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0 \quad (4)$$

$\mu_i = \mu_i^\circ + RT \ln a_i = \mu_i^\circ + RT \ln \gamma_i x_i$ where a_i is the activity of the substance when it is present at the concⁿ of interest, γ_i is activity coefficient & x_i is mole fraction.

$$\Delta G^\circ = -RT \ln K_a \quad \text{where } K_a = \frac{a_M^m a_N^n}{a_A^a a_B^b}$$

$$K_a = \frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b} \cdot \frac{x_M^m x_N^n}{x_A^a x_B^b}$$

For eqⁿ $\Delta G^\circ = 0$

$$0 = (m\mu_M^\circ + n\mu_N^\circ - a\mu_A^\circ - b\mu_B^\circ) + RT \ln \frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b} \cdot \frac{x_M^m x_N^n}{x_A^a x_B^b}$$

$$= \Delta G^\circ + RT \ln \frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b} \cdot \frac{x_M^m x_N^n}{x_A^a x_B^b}$$

$$0 = \Delta G^\circ + RT \ln K_\gamma K_x$$

$$\Delta G^\circ = -RT \ln K_a = \text{where } K_a = \frac{a_M^m a_N^n}{a_A^a a_B^b}$$

$$+ RT \ln K_a = RT \ln K_\gamma K_x$$

$$K_a = K_\gamma K_x$$

$$K_\gamma = \frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b}$$

$$K_x = \frac{x_M^m x_N^n}{x_A^a x_B^b}$$

K_γ is not eqⁿ constⁿ but ratio of activity coefficient

In some case activity coefficients remain constⁿ over a range of concⁿ so K_γ may be taken as constⁿ: then

$$K' = \frac{x_M^m x_N^n}{x_A^a x_B^b} \quad \text{where } K' \text{ is called apparent eqⁿ constⁿ}$$

For dilute solutions, solvent follow Raoult's law & solute follow Henry's law
 $\gamma \rightarrow 1, x \rightarrow 1, K_a \rightarrow K_x, \Delta G^\circ \rightarrow -RT \ln K_x$

$\gamma' \rightarrow 1, K_a \rightarrow K_c$ if it is consider std. state of unit concⁿ $a_i = \frac{\gamma_i}{\gamma_i^\circ} x_i$

The eqⁿ constⁿ in solution is affected by solvent to great extent, although it is not directly participating in the reaction because solvent may affect the activity coefficients of reactants & products to different extent