The term irreversible applies that reaction preceeds to such a degree that the residual amounts of unchanged reactants are almost unmeasurably 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 eq^n bet^n solids & gases in which solids exists in pure form and don't form solid solutions. The free energy of mixing is limited to gaseous phase. For eg

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ At low P the free energy under given condition is $dG = dA = \mu_{CaCO_3} dn_{CaCO_3} + \mu_{CaO} dn_{CaO} + \mu_{CO_2} dn_{CO_2}$

If ξ is extent of reaction then change in the amts of various species are $d\xi = -dn_{CaCO_3} = dn_{CaO} = dn_{CO_2}$

$$dG = (\mu_{CaO} + \mu_{CO_2} - \mu_{CaCO_3})\, d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_{CaO} + \mu_{CO_2} - \mu_{CaCO_3} = \Delta G.$$

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

$$\mu_{CaO} + \mu_{CO_2} - \mu_{CaCO_3} = 0.$$

$$\mu_{CaCO_3} = \mu_{CaO} + \mu_{CO_2}$$

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

$\int d\mu = \int V dP$ where V is very small

$$\mu_i - \mu_i^{\circ} = \int V dP$$

$\therefore \mu_i = \mu_i^{\circ} = \mu_i^{*}$ when $P = P^{\circ} = 1\,atm$

Chemical potential of CO_2 $\mu_{CO_2} = \mu^{\circ}_{CO_2} + RT \ln P_{CO_2}/P^{\circ}$

At eq^n $\mu^{\circ}_{CaCO_3} = \mu^{\circ}_{CaO} + \mu^{\circ}_{CO_2} + RT \ln \frac{P_{CO_2}}{P^{\circ}}$

$$RT \ln \frac{P_{CO_2}}{P^{\circ}} = -[\mu^{\circ}_{CaO} + \mu^{\circ}_{CO_2} - \mu^{\circ}_{CaCO_3}]$$

$$= -\Delta G^{\circ} \quad \text{— ①}$$

$\because \Delta G^{\circ} = -RT \ln K_P$ — ②

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

$K_P = \frac{P_{CO_2}}{P^{\circ}}$ $\because P^{\circ} = 1\,atm,$ $K_P = P_{CO_2}$

free energy of reaction contains the standard energies of the R & P but at eq^n it contains

$= -\Delta G^0$ — ①

$\therefore \Delta G^\circ = -RT\ln K_p$ — ②

$-RT\ln \frac{P_{CO_2}}{P^0} = -RT\ln K_p$ ②

$K_p = \frac{P_{CO_2}}{P^0} \quad \because P^0 = 1atm, \quad K_p = P_{CO_2}$

standard free energy of reaction contains the standard free energies 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

$a\underset{(g)}{A} + b\underset{(s)}{B} \rightarrow m\underset{(l)}{M} + nN(g) \qquad K_p = \frac{(P_N)^n}{(P_A)^a}$

$\Delta G^0 = (m\mu_M^0 + n\mu_N^0) - (a\mu_A^0 + b\mu_B^0)$

eg $\underset{(s)}{ZnS} + \frac{3}{2}\underset{g}{O_2} \rightleftharpoons \underset{(s)}{ZnO} + \underset{(g)}{SO_2} \qquad K_p = \frac{P_{SO_2}}{P_{O_2}^{3/2}} \qquad \Delta G^\circ = \mu^\circ_{ZnO} + \mu^\circ_{SO_2} - \mu^\circ_{ZnO}$

$\underset{(s)}{PbS} + \frac{3}{2}O_2 \rightleftharpoons \underset{(s)}{PbO} + \underset{(g)}{SO_2} \qquad K_p = \frac{P_{SO_2}}{P_{O_2}^{3/2}} \qquad \Delta G^\circ = \mu^\circ_{PbO} + \mu^\circ_{SO_2} - \mu^\circ_{PbS}$

(3) $\underset{(s)}{HgO} \rightleftharpoons Hg(l) + \frac{1}{2}\underset{(g)}{O_2} \qquad K_p = P_{O_2}^{1/2} \qquad \Delta G^\circ = -\mu^\circ_{HgO}$

(4) $H_2O(l) \rightleftharpoons \underset{(V)}{H_2O} \qquad K_p = P_{H_2O(v)} \qquad \Delta G^\circ = \mu^\circ_{H_2O(v)} - \mu^\circ_{H_2O(l)}$

(5) $2\underset{(s)}{CuO} \rightleftharpoons 2\underset{(s)}{Cu} + \underset{(g)}{O_2} \qquad K_p = P_{O_2}, \quad \Delta G^\circ = -2\mu^\circ_{CuO(s)}$

Equilibrium constt for Real Gases

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

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

Real Gas $\mu_i = \mu_i^\circ + RT\ln f_i$ where f_i is fugacity — ①

eq ① becomes $\Delta G^\circ = (m\mu_M^0 + RT\ln f_M^m + n\mu_N^0 RT\ln f_N^n) - (a\mu_A^0 + RT\ln f_A^a + b\mu_B^0 RT\ln f_B^b)$

$\Delta G = (m\mu_M^0 + n\mu_N^0 - a\mu_A^0 - b\mu_B^0) + RT\ln \frac{f_M^m f_N^n}{f_A^a f_B^b}$ — ②

Since at eqn $\Delta G = 0$

$0 = \Delta G^0 + RT\ln \left[\frac{f_M^m f_N^n}{f_A^a f_B^b}\right]_{eqn}$ — ③

$\Delta G^0 = -RT\ln \left[\frac{f_M^m f_N^n}{f_A^a f_B^b}\right]_{eqn}$

ΔG° is std. free energy of the reaction at a given T when R & P are in their std stat of unit fugacity i.e $f^\circ = 1$atm ∴ R.H.S. of eq of K

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

$$\Delta G^\circ = -RT\ln K_{therm} \quad — ⑬$$

$$-RT\ln K_{therm} = \ln \frac{f_M^m f_N^n}{f_A^a f_B^b} \quad \Rightarrow K_{therm} = \left[\frac{f_M^m f_N^n}{f_A^a f_B^b}\right]_{eq^n}$$

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

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

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

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

But γ can change with change of P of system or individual gas P change ∴ K_{therm} is constt for any change of change Pressure & term K_p is non constt eq^n constt." ∴ 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_{therm}
100	0.0072	0.88	0.0063
300	0.0088	0.69	0.0061
600	0.0129	0.50	0.0064
1000	0.0231	0.43	0.0099

K_{thermo} 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_{therm}.

Eq^n Constt of Reaction in solution ④

$aA + bB \rightarrow mM + nN$

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

y Albeurs -

Eq^n Constt of Reaction in solution

$aA + bB \rightarrow mN + nN$

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

$\mu_i = \mu_i^\circ + RT\ln a_i = \mu_i^\circ + RT\ln \gamma_i x_i$ where a_i is the activity of the substance when it is present at the concen of interest, γ_i is activity coefficent & x_i is mole fraction. $\Delta G^\circ = -RT\ln K_a$ 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 eq^n $\Delta G^\circ = 0$

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

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

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

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

$+RT\ln K_a = RT\ln K_\gamma K_x$ $\qquad K_\gamma = \frac{\gamma_m^m \gamma_N^n}{\gamma_A^a \gamma_B^b}$

$K_a = K_\gamma K_x.$

K_γ is not eq^n constt but ratio of activity coefficent $\qquad K_x = \frac{x_m^m x_N^n}{x_A^a x_B^b}$

In some case activity coefficents remain constt over a range of conc^n so K_γ may be taken as constt : then

$K' = \frac{x_m^M x_N^n}{x_A^a x_B^b}$ where K' is called apperent eq^n constt

For dilute solution, solvent follow Raoult's law & solute follow Henry 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 conc^n $a_i = \gamma_i' c_i$

The eq^n constt 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