①

Q1 The equilibrium constant for the reaction $A \rightleftharpoons M$ is 0.10 at 300 K. Calculate (1) ΔG (2) ΔG° for the production of 1 mole of M at a Pressure of 1 atm from 'A' at a pressure of 20 atm. (3) Predict the nature of the reaction

Ans $A \rightleftharpoons M$, $K_p = 0.10$, $T = 300\,K$, $P_A = 20\,atm$, $P_M = 1.0\,atm$.

$$Q_p = \frac{1.0\,atm/1\,atm}{20\,atm/atm} = \frac{1}{20}$$

(a) $\Delta G = \Delta G^\circ + RT \ln Q_p$

$= -RT \ln K_p + RT \ln Q_p$

$= -2.303 \times 8.314\,J/K/mole\,[\log(-0.1) + \log \frac{1}{20}]$

$= -1729\,J/mole.$

(b) $\Delta G^\circ = -RT \ln K_p$

$= -2.303 \times 300\,K \times 8.314\,J/K/mole\,\log 0.1$

$= 5744\,J/mole$

(c) Since the free energy $\Delta G = -1729\,J$ is −ve for the given reaction, it should proceed spontaneously in the forward direction

Chemical Affinity Relation with other Thermodynamic function

The chemical Affinity is defined as rate of decrease of free energy G with the extent of reaction ξ) at Constt T & P

$$A_f = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = -\Delta G$$

For any chemical reaction the free energy function depends upon T, P, & concentration of the reacting species, which in turn are measure of the progress of the reaction

$$G = f(T, P, \xi)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\xi} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\xi} dP + \left(\frac{\partial G}{\partial \xi}\right)_{T,P} d\xi$$

$$= -SdT + VdP - A_f\, d\xi \quad \text{or}$$

$$dG = -SdT + VdP + \Delta G\, d\xi \quad — ①$$

(1) Work Function & Affinity

$$G = H - TS \Rightarrow E + PV - TS \Rightarrow (E - TS) + PV$$

$$G = A + PV. \Rightarrow dG = dA + PdV + VdP$$

$$dA = dG - PdV - VdP \quad — ②$$

Sub. value of dG ② in ①

$$dA = -SdT + VdP + \Delta G\, d\xi - PdV - VdP$$

$$dA = -SdT - PdV + \Delta G\, d\xi$$

At constt T & V, $dT = 0 = dV$

$$(dA)_{T,V} = \Delta G\, d\xi$$

$$\left(\frac{\partial A}{\partial \xi}\right)_{T,V} = \Delta G = -A_f \quad — ③$$

(2) Enthalpy & Affinity

$$H = G + TS \Rightarrow dG + TdS + SdT = dH$$

$$-S\cancel{dT} + VdP + \Delta G\, d\xi + TdS + \cancel{SdT} = dH$$

$$dH = VdP + TdS + \Delta G\, d\xi$$

At constt P & S $dP = dS = 0$

$$\left(\frac{\partial H}{\partial \xi}\right)_{S,P} = \Delta G = -A_f \quad — ④$$

(iii) Energy & Affinity:

$G = H - TS = E + PV - TS$

$E = G - PV + TS$

$dE = dG - PdV - VdP + TdS + SdT$

$= -SdT + VdP + \Delta G\, d\xi - PdV - VdP + TdS + SdT$

$dE = TdS - PdV + \Delta G\, d\xi$

At const S & V, $dS = dV = 0$

$(dE)_{S,V} = \Delta G\, d\xi \Rightarrow \left(\frac{\partial E}{\partial \xi}\right)_{S,V} = \Delta G$ — ⑤

From eq ③ & ⑤ shows that

$G = f(T, P, \xi)$, $A = f(T, V, \xi)$

$H = f(S, P, \xi)$, $E = f(S, V, \xi)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\xi} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\xi} dP + \left(\frac{\partial G}{\partial \xi}\right)_{T,P} d\xi \quad — ⑥$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,\xi} dT + \left(\frac{\partial A}{\partial V}\right)_{T,\xi} dV + \left(\frac{\partial A}{\partial \xi}\right)_{T,V} d\xi \quad — ⑦$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,\xi} dS + \left(\frac{\partial H}{\partial P}\right)_{S,\xi} dP + \left(\frac{\partial H}{\partial \xi}\right)_{S,P} d\xi \quad — ⑧$$

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,\xi} dS + \left(\frac{\partial E}{\partial V}\right)_{S,\xi} dV + \left(\frac{\partial E}{\partial \xi}\right)_{S,V} d\xi \quad — ⑨$$

These are called thermodynamic potentials to thermodynamic variables T, P ; T, V ; S, P ; S, V respectively.

Comparing the coefficents of dT in the ⑥ & ⑦

$$\left(\frac{\partial G}{\partial T}\right)_{P,\xi} = \left(\frac{\partial A}{\partial T}\right)_{V,\xi} = -S \quad \text{— ⑩}$$

Compare the coefficients of dP in ⑥ & ⑧

$$\left(\frac{\partial G}{\partial P}\right)_{\xi,T} = \left(\frac{\partial H}{\partial P}\right)_{S,\xi} = V \quad \text{— ⑪}$$

Compare the coefficents of dV · ⑦ & ⑨ eq.

$$\left(\frac{\partial A}{\partial V}\right)_{T,\xi} = \left(\frac{\partial E}{\partial V}\right)_{S,\xi} = -P \quad \text{— ⑫}$$

Compare the coefficients of dS in eq ⑧ ⑨

$$\left(\frac{\partial H}{\partial S}\right)_{P,\xi} = \left(\frac{\partial E}{\partial S}\right)_{V,\xi} = T \quad \text{— (13)}$$

Compare the coefficents of dξ

$$\Delta G = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \left(\frac{\partial A}{\partial \xi}\right)_{T,V} = \left(\frac{\partial H}{\partial \xi}\right)_{S,P} = \left(\frac{\partial E}{\partial \xi}\right)_{S,V} = -A_f \quad \text{— ⑭}$$

Conclusion

(1) Partial ~~differentiation~~ derivative of G or A w.r.t. intensive variable (T) gives an extensive variable S with sign change: eq(10)

2) Partial derivative of H or E w r t S extensive variable given an intensive variable T eq.(13)

⑤

(3) The rate of change of thermodynamic functions with degree of advancement under appropriate experimental conditions is equal to reaction potential ΔG.

Other forms of Equilibrium constt for Ideal Gases Reactions

For an ideal gas the partial Pressure P_i

$$P_i V = n_i RT \cdot \quad = \left(\frac{n_i}{V}\right) RT = C_i RT$$

where C_i is called molarity

$$\mu_i = \mu_i^0(T) + RT\ln\left(\frac{C_i RT}{p^0}\right)$$

For reaction $aA + bB \rightleftharpoons mM + nN$ at equilibrium

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

$$= \left(m\mu_M^0 + mRT\ln\frac{C_M RT}{p^0} + n\mu_N^0 + nRT\ln\frac{C_N RT}{p^0}\right)$$

$$-\left(a\mu_A^0 + aRT\ln\frac{C_A RT}{p^0} + b\mu_B^0 + bRT\ln\frac{C_B RT}{p^0}\right.$$

$$= \left(m\mu_M^0 + n\mu_N^0 - a\mu_A^0 - b\mu_B^0\right) + RT\ln\frac{\left[\left(\frac{C_M RT}{p^0}\right)^m\left(\frac{C_N RT}{p^0}\right.\right.}{\left(\frac{C_A RT}{p^0}\right]^a\left[\frac{C_B R}{p}\right.}$$

$$0 = \Delta G^0 + RT\ln\frac{\left(\frac{C_M RT}{p^0}\right)^m\left(\frac{C_N RT}{p^0}\right)^n}{\left(\frac{C_A RT}{p^0}\right)^a\left[\frac{C_B RT}{p^0}\right]^b}$$

$$-\frac{\Delta G^0}{RT} = \ln\left[\quad ,, \quad\right]$$

C.

$$\frac{-\Delta G^o}{RT} = \ln\left[\frac{(C_M)^m (C_N)^n}{(C_A)^a (C_B)^b}\left(\frac{RT}{P^o}\right)^{m+n-a-b}\right]$$

Taking Antilog

$$\exp\left(-\frac{\Delta G^o}{RT}\right) = \frac{C_M^m\, C_N^n}{C_A^a\, C_B^b} \times \left(\frac{RT}{P^o}\right)^{\Delta\nu}$$

$$\exp\left(-\frac{\Delta G^o}{RT}\right)\left(\frac{P^o}{RT}\right)^{\Delta\nu} = \frac{C_M^m\, C_N^n}{C_A^a\, C_B^b}$$

On L.H.S ie exp side all terms are constt because it ~~takes~~ have all constt values at particular temp R, T, P°, etc

$\therefore$ R.H.S has to be constt

When $\Delta\nu \neq 0$, R.H.S. terms will not be dimensionless hence all terms are divided by C°

$$\exp\left(-\frac{\Delta G^o}{RT}\right)\left(\frac{P^o}{RT}\right)^{\Delta\nu} = \frac{\left(\frac{C_M}{C^o}\right)^m\left(\frac{C_N}{C^o}\right)^n}{\left(\frac{C_A}{C^o}\right)^a\left(\frac{C_B}{C^o}\right)^b} \times (C^o)^{\Delta\nu}$$

$$\exp\left(-\frac{\Delta G^o}{RT}\right)\left(\frac{P^o}{C^oRT}\right)^{\Delta\nu} = K_c$$

$$\text{where } K_c = \frac{\left(\frac{C_M}{C^o}\right)^m\left(\frac{C_N}{C^o}\right)^n}{\left(\frac{C_A}{C^o}\right)^a\left(\frac{C_B}{C^o}\right)^b}$$

K_c is called equilibrium constt & is function of temp only it is dimensionless quantity & ratio of molarites of P & Reactants

$$\exp\left(-\frac{\Delta G^\circ}{RT}\right)\left(\frac{p^\circ}{c^\circ RT}\right)^{\Delta\nu} = K_C$$

$$-\Delta G^\circ = RT\ln\left[K_C\left(\frac{C^\circ RT}{p^\circ}\right)^{\Delta\nu}\right]$$

Equlbrim constl can be also exprered as ratio of mole fraction of P & R

The partial Pressure of an ideal gas is given by Dalton law of Partial Pressure $P_i = x_i P$ where x_i is mole fraction of gas i & P is total P

$$\mu_i = \mu_i^\circ(T) + RT\ln\left(\frac{x_i P}{p^\circ}\right)$$

$$aA + bB \rightleftharpoons mM + nN$$

$$\left(\frac{\partial G}{\partial \xi}\right)_T = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B)$$

$$= (m\mu_M^\circ + n\mu_N^\circ - a\mu_A^\circ - b\mu_B^\circ) + RT\ln \frac{\left(\frac{x_M P}{p^\circ}\right)^m\left(\frac{x_N P}{p^\circ}\right)^n}{\left(\frac{x_A P}{p^\circ}\right)^a\left(\frac{x_B P}{p^\circ}\right)^b}$$

$$0 = \Delta G^\circ + RT\ln\frac{\left(\frac{x_M P}{p^\circ}\right)^m\left(\frac{x_N P}{p^\circ}\right)^n}{\left(\frac{x_A P}{p^\circ}\right)^a\left(\frac{x_B P}{p^\circ}\right)^b}$$

$$\frac{\Delta G^\circ}{-RT} = \ln\left[\left(\frac{P}{p^\circ}\right)^{m+n-a-b}\frac{x_M^m x_N^n}{x_A^a x_B^b}\right]$$

$$\exp\left(-\frac{\Delta G^0}{RT}\right) = \left(\frac{P}{P^0}\right)^{\Delta\nu} \frac{x_M^m \, x_N^n}{x_A^a \, x_B^b}$$

$$\exp\left(-\frac{\Delta G^0}{RT}\right)\left(\frac{P^0}{P}\right)^{\Delta\nu} = \text{Constt.}$$

$$\exp\left(-\frac{\Delta G^0}{RT}\right)\left(\frac{P^0}{P}\right)^{\Delta\nu} = K_x.$$

where $K_x = \dfrac{x_M^m \, x_N^n}{x_A^a \, x_B^b}$

$$\Delta G^0 = RT\left[\ln K_x \left(\frac{P}{P^0}\right)^{\Delta\nu}\right]$$

K_x is function of T & P. hence K_x is less useful than K_p for application to gas reaction.

But for liquids & solid mixtures, K_x is best eq^n constt. since for small molar volume of the condensed phase their equilibria is very insensitive to change to change of Pressure.