Relation Between K_p, K_c & K_x

For a general reaction $aA + bB \rightleftharpoons mM + nN$

we know that $RT \ln K_p = -\Delta G^\circ$ — (1)

$RT \ln K_c \left(\frac{C^\circ RT}{p^\circ}\right)^{\Delta U} = -\Delta G^\circ$ — (2)

$RT \ln K_x \left(\frac{P}{p^\circ}\right)^{\Delta U} = -\Delta G^\circ$ — (3)

$\therefore$ on L.H.S. eq (1), (2) & (3) have ΔG° so we can compare their R.H.S

$RT \ln K_p = RT \ln K_c \left(\frac{C^\circ RT}{p^\circ}\right)^{\Delta U} = RT \ln K_x \left(\frac{P}{p^\circ}\right)^{\Delta U}$

$\ln K_p = \ln K_c \left(\frac{C^\circ RT}{p^\circ}\right)^{\Delta U} = \ln K_x \left(\frac{P}{p^\circ}\right)^{\Delta U}$

$K_p = K_c \left(\frac{C^\circ RT}{p^\circ}\right)^{\Delta U} = K_x \left(\frac{P}{p^\circ}\right)^{\Delta U}$

$\because C^\circ = 1 \text{ mole/dm}^3$ $P^\circ = 1 \text{ atm}$ $\therefore$ above relation

$\therefore K_p = K_c (RT)^{\Delta U} = K_x (P)^{\Delta U}$

For any reaction when $\Delta U = 0$ ie $m+n = a+b$

then $K_p = K_c = K_x$

when $\Delta U \neq 0$, the numerical value of the equilibrium const. depends upon the way, expression is written

$K_p = 0.35 \times 10^{-24}$ at 300 K for the following reaction

$2SO_3 \rightarrow 2SO_2 + O_2$. Cal K_c for this reaction at 300K

(9) (9) (9)

Ans $\Delta n = (2+1) - 2 = 1$. $2n_{SO_2} + n_{O_2} \rightarrow 2n_{SO_3}$

$C^\circ = 1 \text{ mole/dm}^3$, $P^\circ = 1 \text{ atm}$

$$K_C = K_P \left(\frac{P^\circ}{C^\circ RT}\right)^{\Delta n}$$

$$= 0.35 \times 10^{-24} \left[\frac{1 \text{ atm}}{1 \text{ mole/dm}^3 \times 0.082 \text{ atm dm}^3 \text{ mole}^{-1} K^{-1} \times 300 K}\right]$$

$$= 1.42 \times 10^{-26}$$

K_C is dimensionless quantity.

Q For the reaction $N_2O_4 \rightarrow 2NO_2$ at 300K & 1 atm. $K_P = 0.157$. Calculate K_C & K_n for this reaction under the given conditions

$\Delta n = 2 - 1 = 1$

$RT = 0.082 \times 300 = 24.6 \text{ atm dm}^3 \text{ mole}^{-1}$

$$K_C = K_P \left(\frac{P^\circ}{C^\circ RT}\right)^{\Delta n}$$

$$= 0.157 \left[\frac{1 \text{ atm}}{1 \text{ mole/dm}^3 \times 24.6 \text{ atm dm}^3 \text{ mole}^{-1}}\right]$$

$$= 6.38 \times 10^{-3}$$

$$K_n = K_P \left(\frac{P^\circ}{P}\right)^{\Delta n} = 0.157 \frac{1 \text{ atm}}{1 \text{ atm}}$$

$$= 0.157$$

change of K with the form of equation

Let us consider the reaction represented by

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad -(1)$$

$$K_P = \frac{(P_{SO_3})^2}{(P_{SO_2})^2 (P_{O_2})}$$

(11)

(i) If the chemical eqn is multiplied by a constt n / the eqn constt is raised to power n.

(a) Multiply above eq(1) by 2 to get new equation

$$4SO_2 + 2O_2 \rightleftharpoons 4SO_3$$

$$K_p' = \frac{P_{SO_3}^4}{P_{SO_2}^4 \; P_{O_2}^2} = \left(\frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}\right)^2$$

$$= K_p^2.$$

(b) Multiply above eq(1) by $\frac{1}{2}$

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$$

$$K_p'' = \frac{P_{SO_3}}{P_{SO_2} \; P_{O_2}^{\frac{1}{2}}} = \left(\frac{P_{SO_3}^2}{P_{SO_2}^2 \; P_{O_2}}\right)^{\frac{1}{2}} = \sqrt{K_p}$$

(ii) If reaction is written in reverse way & then new eqⁿ constt of new equation is equal to the reciprocal of that of original chemical reaction

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

$$K_p''' = \frac{P_{SO_2}^2 \; P_{O_2}}{P_{SO_3}^2} = K_p^{-1}$$

(iii) If 2 chemical equation are added to get a new chemical equation, then its equilibrium constt

will be equal to the product of the equilibrium const of the original equations

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3 \quad \text{—— (1)}$$
(g) (g) (g)

$$K_p' = \frac{P_{SO_3}}{P_{SO_2} P_{O_2}^{1/2}} \quad \text{—— (19)}$$

$$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2 \quad \text{(2)} \quad K_p'' = \frac{P_{CO} P_{O_2}^{1/2}}{P_{CO_2}} \quad \text{—— (3)}$$
(g) (g) (g)

Add eq (1) & (2)

$$SO_2 + CO_2 \rightleftharpoons SO_3 + CO \quad \text{—— (4)}$$
(g) (g) (g) (g)

Eq. (4). equilibrium const

$$K_p''' = \frac{P_{CO} P_{SO_3}}{P_{SO_2} P_{CO_2}}$$

Multiply

Eq. 19) & eq. (3) (their L.HS & R.HS)

$$K_p' K_p'' = \frac{P_{SO_3}}{P_{SO_2} P_{O_2}^{1/2}} \times \frac{P_{CO} P_{O_2}^{1/2}}{P_{CO_2}} \quad \text{—— (5)}$$
(K_p' K_p'')

$$= \frac{P_{SO_3} P_{CO}}{P_{SO_2} P_{CO_2}} \quad \text{—— (6)}$$

$$K_p''' = K_p' K_p'' \quad \text{—— (7)}$$

Thermodynamic Validity of various statements.

Let the free energy for reaction $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ as ΔG_1° and for reaction $CO_{2(g)} \rightleftharpoons CO_{(g)} + \frac{1}{2}O_{2(g)}$ as ΔG_2°

then free energy ΔG_3° for reaction $SO_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + SO_{3(g)}$

ΔG_3° in should be equal to sum of free energies for SO_2 & CO_2 equations

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ = -RT \ln K_p' - RT \ln K_p''$$

$$-R = -RT \ln K_p' K_p'' \quad \text{---} (1)$$

For reaction $\Delta G_3^\circ = -RT \ln K_p'''$ ---(2)

Subs (2) in (1)

$$-RT \ln K_p''' = -RT \ln K_p' K_p''$$

$$K_p''' = K_p' K_p''$$

The abs statements of above equ reactions can be S

If the coefficients in the chemical eq. are

Doubled -

Tripled

Halved

Multiplied by n

chemical eq^n written in reverse way

s. of chemical eq^n are added

Then K

squared

Cubed

Replaced by squ

Raised to power n

Inverted

Multiplied

Q) For reaction $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3(g)$ $K_p = 1.7 \times 10^{12}$ (14)
at 300K. cal. K_p when (1) reaction is doubled, (2) reaction is reverse. (3) Reaction $2SO_3 \rightarrow 2SO_2 + O_2$

(1). The above eq. is multiplied by (2)

$2SO_2 + O_2 \rightarrow 2SO_3$

$K_{P(1)} = \frac{P^2_{SO_3}}{P^2_{SO_2} P_{O_2}} = K_p^2 = 1.7 \times 10^{12}$

$= 2.84 \times 10^{24}$.

(2) $SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$

$K_{P(2)} = \frac{P_{SO_3} P_{O_2}^{1/2}}{P_{SO_3}} = \frac{1}{K_p} = \frac{1}{1.7 \times 10^{12}} = 0.588 \times 10^{-12}$

(3) $K_{P(3)} = \frac{P^2_{SO_3} P_{O_2}}{P^2_{SO_3}} = K^2_{P(2)} = 0.588 \times 10^{-12}$

$= 0.334 \times 10^{-24}$.

Equilibrium constt & Degree of Dissociation (α)

Let us consider the dissociation of N_2O_4 to NO_2

$N_2O_4 \rightleftharpoons 2NO_2$

(g) (g)

Let the initial no of moles of N_2O_4 is 'a', Σ moles of N_2O_4 are dissociated at equilibrium

$N_2O_4 \rightleftharpoons 2NO_2$

(g) (g)

$\alpha = \frac{\text{Moles of reactant dissociated}}{\text{Initial Moles of the reactant}} = \frac{\Sigma}{a}$

No moles of reactant & product at equilibrium are

$n(N_2O_4) = a - z = a(1-\alpha)$ = moles of undissociated N_2O_4

$n(NO_2) = 2z = 2a\alpha$ = moles of NO_2 formed

Total moles of reaction mixture at equilibrium equal to sum of moles of N_2O_4 undissociated & the mole of NO_2 produced.

$$a(1-\alpha) + 2a\alpha = a - a\alpha + 2a\alpha$$
$$= a + a\alpha = a(1+\alpha)$$
$$= n(N_2O_4) + n(NO_2)$$

Mole fractions of N_2O_4 & NO_2 are

$$x(N_2O_4) = \frac{a(1-\alpha)}{a(1+\alpha)} = \frac{1-\alpha}{1+\alpha}$$

$$x(NO_2) = \frac{2a\alpha}{a(1+\alpha)} = \frac{2\alpha}{1+\alpha}$$

Partial Pressure of N_2O_4 & NO_2 are given by Dalton law

$P_i = x_i P$

$$P(N_2O_4) = \left(\frac{1-\alpha}{1+\alpha}\right) P$$ total Pressure

$$P(NO_2) = \left(\frac{2\alpha}{1+\alpha}\right) P$$ P

$$K_p = \frac{(P_{NO_2}/p^0)^2}{\left(\frac{P_{N_2O_4}}{p^0}\right)} \qquad p^0 = 1\ atm$$

$$= \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 P}{\frac{1-\alpha}{1+\alpha}} = \frac{2\alpha P}{1-\alpha^2}$$

$\propto K_p \rightarrow K_p\alpha^2 = 4\alpha^2 p$

$K_p(1-\alpha^2) = 4\alpha^2 p$

$K_p + 4\alpha^2 p = K_p\alpha^2$

$K_p = K_p\alpha^2 +$

$K_p - K_p\alpha^2 = 4\alpha^2 p$

$K_p = K_p\alpha^2 + 4\alpha^2 p$

$K_p = (K_p + 4p)\alpha^2$

$\sqrt{\frac{K_p}{K_p+4p}} = \alpha.$

As Pressure rises towards ∞, $\alpha \rightarrow 0$

At $P \rightarrow 0$, $\alpha \rightarrow 1$

If α is known then K_p can be calculated

$\ell \propto \frac{1}{\text{no. of moles of a given mass of gas}}$

As gas dissociates, more molecules of lower mass are formed, ℓ decreases.

If ℓ_1 is density of gas before dissociation

ℓ_2 is " of gaseous mixture at eqⁿ

after dissociation, $N_2O_4 \rightleftharpoons 2NO_2$

$\frac{\ell_1}{\ell_2} = \frac{\text{total moles of after dissociation}}{\text{moles before dissociation}} = a($

$\frac{\ell_1}{\ell_2} = 1+\alpha$

Gas density is directly proportional to the molar mean M of the gas

$$\frac{\rho_1}{\rho_2} = \frac{M_1}{M_2} = 1+\alpha$$

$$\alpha = \frac{\rho_1 - \rho_2}{\rho_2} = \frac{M_1 - M_2}{M_2}$$

M_1 = Molar Mean of gas before dissociation

M_2 = Av. Molar Mean of gaseous mixture at equilibrium

When a molecule dissociates to produce D molecules $\alpha = \frac{M_1 - M_2}{M_2(D-1)}$

Q 3.176g of N_2O_4 when taken in 1 l vessel at 25°C gives a total P of 760 torr on dissociation. Calculate α, K_p what would be value of α if total P is 0.5 atm

$$N_2O_4 \rightleftharpoons 2NO_2$$

$\alpha = \frac{M_1 - M_2}{M_2(D-1)}$ = $D = 2$, $P = 760 \text{ torr} = 1 \text{ atm}$

$V = 1$ litres, $M_1 = 2\times14 + 4\times16 = 92$

For an ideal gas $PV = nR = \frac{w}{M_2}RT$.

$$M_2 = \frac{wRT}{PV} = \frac{3.176\text{g} \times 0.082 \text{ atm l K}^{-1}\text{mole}^{-1} \times}{1 \text{ atm} \times 1 \text{ l}}$$

$= 77.65 \text{ g/mole}$.

$$\alpha = \frac{92 - 77.65}{77.65} = 0.185$$

Cal. of K frm ΔG°

$\therefore \Delta G^\circ = -RT \ln K$ given is a way to evaluate the value of K (eqn consth) frm std-free energy ΔG° data

1) Frm std. free energy calculations ΔG_f° of the reactants & Products $\Delta G^\circ = \sum \Delta G_f^\circ(P) - \sum \Delta G_f^\circ(R)$ where ΔG_f° for elements in their std state is taken as zero

2) Frm ΔH° obtain calorimetrically or frm Hess' law ΔS° frm third law entropies

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

using statistical mechanics & certain information about of molecules obtained frm spectroscopic data

Frm emf data using $\Delta G^\circ = -nFE^\circ$