

Relation Between K_p , K_c & K_x

(9)

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

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

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

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

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

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

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

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

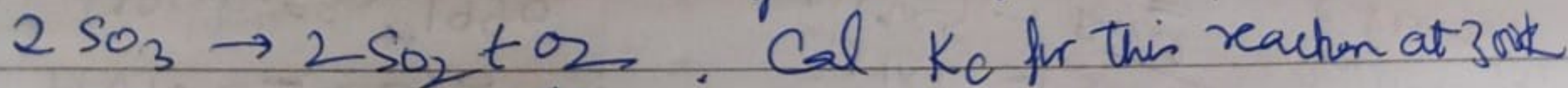
$\therefore C^\circ = 1 \text{ mole/dm}^3$, $P^\circ = 1 \text{ atm}$. $\therefore$ above relation

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

For any reaction when $\Delta \nu = 0$ i.e. $m+n=a+b$
then $K_p = K_c = K_x$

When $\Delta \nu \neq 0$, 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



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Cal K_c for this reaction at 300 K

Ans $\Delta D = (2+1)-2 = 1$ (18)
 $C^\circ = 1 \text{ mole/dm}^3$, $P^\circ = 1 \text{ atm}$

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

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

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

K_c is dimensionless quantity.

Q For the reaction $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$ at 300K & 1 atm .
 $K_p = 0.157$. Calculate K_c & K_n for this reaction
 under the given conditions

$$\Delta D = 2 - 1 = 1$$

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

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

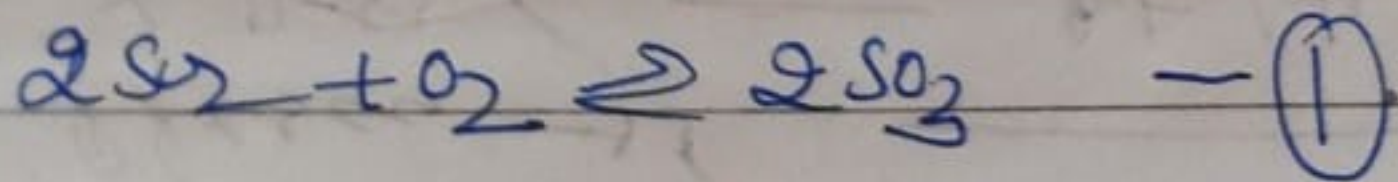
$$= 0.157 \left[\frac{1 \text{ atm}}{1 \text{ mole/dm}^3 \times 24.6 \text{ atm dm}^3 \text{ mole}^{-1}} \right]$$

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

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

$$= 0.157$$

change of K with the form of equation
 let us consider the reaction represented by



$$K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2 (P_{\text{O}_2})}$$

⑬ If the chemical eqⁿ is multiplied by a constant (11)
the eqⁿ const^t is raised to power n.

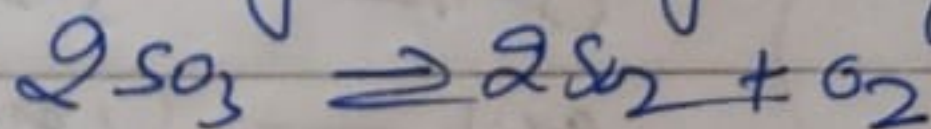
(a) Multiply above eq (1) by 2 to get new equation
 $4\text{SO}_2 + 2\text{O}_2 \rightleftharpoons 4\text{SO}_3$

$$K_p' = \frac{P_{\text{SO}_3}^4}{P_{\text{SO}_2}^4 P_{\text{O}_2}^2} = \left(\frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} \right)^2$$
$$= K_p^2.$$

(b) Multiply above eq (1) by $\frac{1}{2}$
 $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$

$$K_p'' = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}} = \left(\frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} \right)^{1/2} = \sqrt{K_p}$$

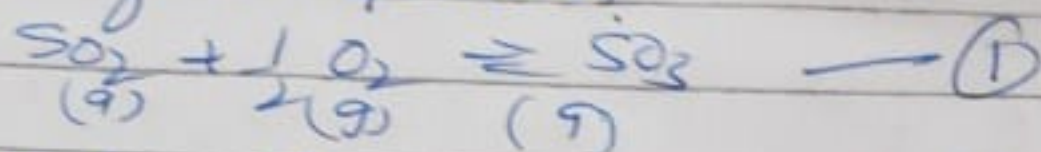
If reaction is written in reverse way, then new eqⁿ const^t of new equation is equal to the reciprocal of that of original chemical reaction



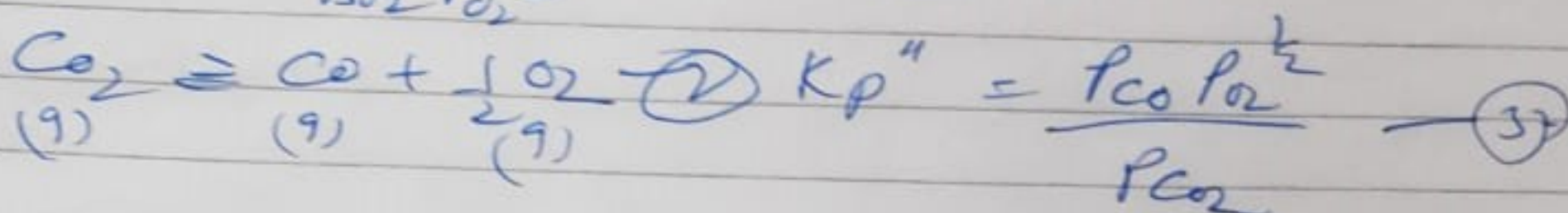
$$K_p''' = \frac{P_{\text{SO}_2}^2 P_{\text{O}_2}}{P_{\text{SO}_3}^2} = K_p^{-1}$$

If 2 chemical equations are added to get a new chemical equation, then its equilibrium const^t

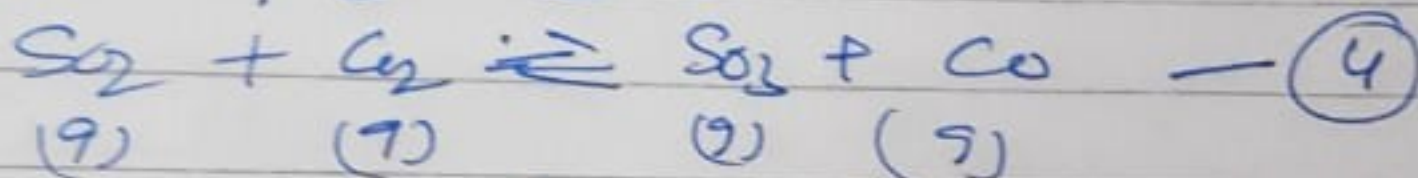
will be equal to the product of the equilibrium constants of the original equations. (12)



$$K_p' = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}} \quad \text{--- (1a)}$$



Add eq (1) & (2)



eq. (4) equilibrium constant

$$K_p''' = \frac{P_{\text{CO}} P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{CO}_2}}$$

Multiply

eq. (1a) & eq. (3) (their L.H.S & R.H.S)

$$K_p' K_p'' = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}} \times \frac{P_{\text{CO}} P_{\text{O}_2}^{1/2}}{P_{\text{CO}_2}} \quad \text{--- (5)}$$

$$= \frac{P_{\text{SO}_3} P_{\text{CO}}}{P_{\text{SO}_2} P_{\text{CO}_2}} \quad \text{--- (6)}$$

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

(13)

Thermodynamic Validity of various statements

Let the free energy for reaction $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO}_3$ as

ΔG_1° and for reaction $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2$ as ΔG_2°

then free energy ΔG_3° for reaction $\text{SO}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{SO}_3$

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

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

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

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

Subs (2) in (1)

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

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

The ab statements of above reactions can be so

If the coefficients in the chemical eq. are

Doubled -

Tripled

Halved

Multiplied by n

Chemical eq. written

in reverse way

of chemical eq. are added

Then K

Squared

Cubed

Replaced by squ

Raised to power n

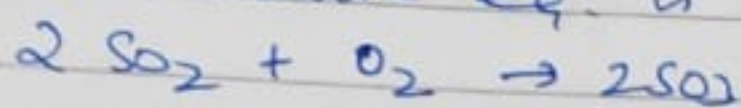
Inverted

Multiplied

Q1 For reaction $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3(g)$ $K_p = 1.7 \times 10^{12}$ (14)

at 300K. cal. K_p when (1) reaction is doubled,
 (2) reaction is reverse. (3) Reaction $2\text{SO}_3 \rightarrow 2\text{SO}_2 + \text{O}_2$

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



$$K_{p(1)} = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} = K_p^2 = 1.7 \times 10^{12} = 2.89 \times 10^{24}$$

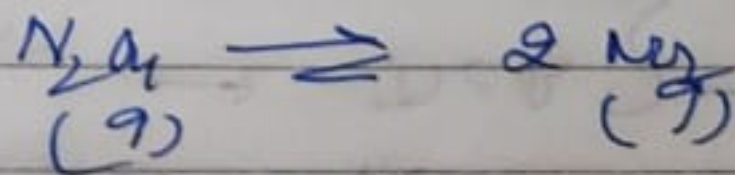


$$K_{p(2)} = \frac{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} = \frac{1}{K_p} = \frac{1}{1.7 \times 10^{12}} = 0.588 \times 10^{-12}$$

(3) $K_{p(3)} = \frac{P_{\text{SO}_3}^2 P_{\text{O}_2}}{P_{\text{SO}_2}^2} = K_{p(2)}^2 = 0.588 \times 10^{-12} = 0.334 \times 10^{-24}$

Equilibrium constt & Degree of Dissociation (α)

Let us consider the dissociation of N_2O_4 to NO_2



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



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

The mole of reactant & product are equilibrium are
 $n(\text{N}_2\text{O}_4) = a - x = a(1-\alpha) = \text{mole of undissociated } \text{N}_2\text{O}_4$
 $n(\text{NO}_2) = 2x = 2a\alpha = \text{mole of NO}_2 \text{ formed}$
 Total mole of reaction mixture at equilibrium
 equal to sum of moles of N_2O_4 undissociated &
 the mole of NO_2 produced

$$\begin{aligned}
 a(1-\alpha) + 2a\alpha &= a - a\alpha + 2a\alpha \\
 &= a + a\alpha = a(1+\alpha) \\
 &= n(\text{N}_2\text{O}_4) + n(\text{NO}_2)
 \end{aligned}$$

Mole fractions of N_2O_4 & NO_2 are

$$x(\text{N}_2\text{O}_4) = \frac{a(1-\alpha)}{a(1+\alpha)} = \frac{1-\alpha}{1+\alpha}$$

$$x(\text{NO}_2) = \frac{2a\alpha}{a(1+\alpha)} = \frac{2\alpha}{1+\alpha}$$

Partial Pressure of N_2O_4 & NO_2 are given by Dalton Law

$$P_i = x_i P$$

$$P(\text{N}_2\text{O}_4) = \left(\frac{1-\alpha}{1+\alpha} \right) P \quad \text{total pressure}$$

$$P(\text{NO}_2) = \left(\frac{2\alpha}{1+\alpha} \right) P \quad P$$

$$K_p = \frac{(P_{\text{NO}_2}/P^0)^2}{(P_{\text{N}_2\text{O}_4}/P^0)} \quad P^0 = 1 \text{ atm}$$

$$\begin{aligned}
 &\left(\frac{P_{\text{NO}_2}}{P^0} \right)^2 \\
 &= \frac{\left(\frac{2\alpha}{1+\alpha} \right)^2 P^2}{\frac{1-\alpha}{1+\alpha} P} = \frac{2\alpha^2 P}{1-\alpha^2}
 \end{aligned}$$

$$\alpha K_p \rightarrow K_p \alpha^2 = 4\alpha^2 P$$

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

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

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

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

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

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

$$\sqrt{\frac{K_p}{K_p + 4P}} = \alpha$$

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

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

If α is known then K_p can be calculated

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

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, $N_2O_4 \rightleftharpoons 2NO_2$

$$= \frac{\ell_1}{\ell_2} = \frac{\text{total moles of after dissociation}}{\text{moles before dissociation}} = \frac{1-\alpha}{1+\alpha}$$

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

POCO

SHOT ON POCO F1

Since density is directly proportional to the molar mass M of the gas. (17)

$$\frac{P_1}{P_2} = \frac{M_1}{M_2} = 1 + \alpha$$

$$\alpha = \frac{P_1 - P_2}{P_2} = \frac{M_1 - M_2}{M_2}$$

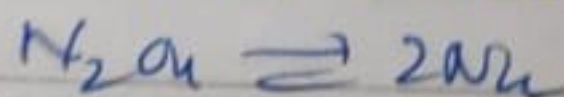
M_1 = Molar Mass of gas before dissociation

M_2 = Av. Molar Mass of gaseous mixture at equilibrium

When a molecule dissociates to produce α molecules

$$\alpha = \frac{M_1 - M_2}{M_2(\alpha - 1)}$$

Q 3.176g of N_2O_4 when taken in 1L vessel at $25^\circ C$ 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



$$\alpha = \frac{M_1 - M_2}{M_2(\alpha - 1)} = 0 = \alpha, P = 760 \text{ torr} = 1 \text{ atm}$$

$$V = 1 \text{ litres}, M_1 = 2 \times 14 + 4 \times 16 = 92$$

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

$$M_2 = \frac{WRT}{PV} = \frac{3.176g \times 0.082 \text{ atm L K}^{-1} \text{ mole}^{-1} \times 298 \text{ K}}{1 \text{ atm} \times 1 \text{ L}}$$

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

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

(18)

Cal. of K from ΔG°

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

1) From 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) From ΔH° obtain calorimetrically or from Hess' law ΔS° from third law entropies

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

using statistical mechanics & certain information about g . molecules obtained from spectroscopic data

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