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$$\prod_i \left( \hat{f}_i / f_i^\circ \right)^{\nu_i} = \exp \left( \frac{-\Delta G^\circ(T)}{RT} \right)$$

The term  $\exp \left( \frac{-\Delta G^\circ}{RT} \right)$  is given the symbol  $K$ , and is called the

**equilibrium constant** for the rxn, and is function of temperature **ONLY**:

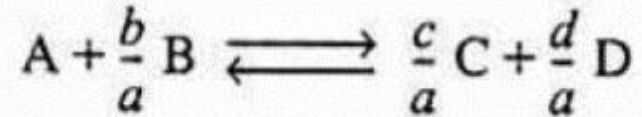
$$K \equiv \exp \left( \frac{-\Delta G^\circ(T)}{RT} \right)$$

□ Therefore,  $\prod_i \left( \hat{f}_i / f_i^\circ \right)^{\nu_i} = K$   $\because a_i \equiv \hat{f}_i / f_i^\circ$

$\therefore \prod_i (a_i)^{\nu_i} = K$  , where  $a_i$  is the activity (effective concentration)

of species  $i$  &  $\nu_i$  is its stoichiometric number.

For the reaction:



1. The true (dimensionless) equilibrium constant

$$K = \frac{a_C^{c/a} a_D^{d/a}}{a_A a_B^{b/a}}$$

$$K = \prod_i (a_i)^{\nu_i}$$

$K$  = True equilibrium constant

$K_p$  = Pressure equilibrium constant

$K_c$  = Concentration equilibrium constant

2. The pressure equilibrium constant  $K_p$  is

$$K_p = \frac{P_C^{c/a} P_D^{d/a}}{P_A P_B^{b/a}}$$

$$K_p = \prod_i (P_i)^{\nu_i}$$

3. The concentration equilibrium constant  $K_c$  is

$$K_c = \frac{C_C^{c/a} C_D^{d/a}}{C_A C_B^{b/a}}$$

$$K_c = \prod_i (C_i)^{\nu_i}$$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^0$$

## (A) Equilibrium Constant ( $K$ ) for Gas-Phase Reactions:

$f_i^0$  is the standard state fugacity.

The standard state for a gas is the ideal-gas state of the pure gas at the standard-state pressure  $P^0$  of 1 bar.

Because the fugacity of an ideal gas is equal to its  $P$ ,  $f_i^0 = P^0 = 1 \text{ bar}$ .

$\hat{f}_i$  is the fugacity of species  $i$  in the gas mixture.

The fugacity is related to the fugacity coefficient by:  $\hat{\phi}_i = \hat{f}_i / P_i$

or  $\hat{f}_i = \hat{\phi}_i P_i = \hat{\phi}_i y_i P$

Therefore, for gases:  $a_i = \hat{f}_i / f_i^0 = \hat{\phi}_i P_i / P^0$

$$K = \prod_i (a_i)^{\nu_i} = \prod_i (\hat{\phi}_i P_i / P^0)^{\nu_i}$$

$$K = \prod_i (\hat{\phi}_i)^{\nu_i} \prod_i (P_i)^{\nu_i} \prod_i (P^0)^{-\nu_i}$$

$\hat{\phi}_i$  is a measure of deviation from ideal-gas (ig) behavior for gaseous mixtures:

$$\hat{\phi}_i \equiv \hat{f}_i / P_i$$

$$\hat{\phi}_i = \hat{f}_i / \hat{f}_i^{ig}$$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^\circ$$

### (A) Equilibrium Constant ( $K$ ) for Gas-Phase Reactions:

$$K = \prod_i (\hat{\phi}_i)^{\nu_i} \prod_i (P_i)^{\nu_i} \prod_i (P^\circ)^{-\nu_i}$$

$$K = K_\phi \cdot K_p \cdot (P^\circ)^{-\delta}$$

For ideal gases (high  $T$ , low  $P$ ):

$$1. \hat{\phi}_i = 1 \quad \therefore K_\phi = 1 \quad \& \quad K = K_p \cdot (P^\circ)^{-\delta}$$

$$2. P_i = C_i RT$$

$$\therefore K_p = \prod_i (C_i RT)^{\nu_i} = (RT)^\delta \cdot \prod_i (C_i)^{\nu_i}$$

$$K_p = (RT)^\delta \cdot K_c \quad \Longleftrightarrow \quad K = K_c \cdot (RT / P^\circ)^\delta$$

where,

$$K_\phi \equiv \prod_i (\hat{\phi}_i)^{\nu_i}$$

$$K_p \equiv \prod_i (P_i)^{\nu_i}$$

$$\delta \equiv \sum_i \nu_i$$

where,

$$K_c \equiv \prod_i (C_i)^{\nu_i}$$

For reactions between ideal gases with no change in the total number of moles ( $\delta=0$ ):  $K = K_p = K_c$

$$\ln K = -\Delta G^\circ(T) / RT \quad K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^\circ$$

### (A) Equilibrium Constant (K) for Gas-Phase Reactions:

$$K = \prod_i (a_i)^{\nu_i} = \prod_i \left( \hat{\phi}_i P_i / P^\circ \right)^{\nu_i}$$

$$K = \prod_i \left( \hat{\phi}_i \right)^{\nu_i} \prod_i \left( P_i \right)^{\nu_i} \prod_i \left( P^\circ \right)^{-\nu_i}$$

$$K = K_\phi \cdot K_p \cdot \left( P^\circ \right)^{-\delta}$$

$$K = \prod_i \left( \hat{f}_i / f_i^\circ \right)^{\nu_i}$$

$$K = \prod_i \left( \hat{f}_i \right)^{\nu_i} \prod_i \left( f_i^\circ \right)^{-\nu_i}$$

$$K = K_f \cdot \left( P^\circ \right)^{-\delta}$$

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$$\therefore K_\phi \cdot K_p \cdot \left( P^\circ \right)^{-\delta} = K_f \cdot \left( P^\circ \right)^{-\delta}$$

$$\text{or } K_f = K_\phi \cdot K_p$$

At 1 bar (ideal gas),  $K_f = K_p^\circ$ , since

$K_f = K_f^\circ$  as  $K_f$  is  $f(T)$  only

For ideal gas  $K = K_p^\circ \cdot \left( P^\circ \right)^{-\delta}$

$$\therefore K_p^\circ = K_\phi \cdot K_p$$

Notes:

1.  $K = K_f$  in magnitude, not units
2.  $K$  &  $K_f$  are  $f(T)$  ONLY
3. But  $\hat{f}_i$ ,  $\hat{\phi}_i$ ,  $K_\phi$  are  $f(T, P, y_i)$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^\circ$$

## (B) Equilibrium Constant ( $K$ ) for Liquid-Phase Reactions:

$f_i^\circ$  is the standard state fugacity.

For liquids,  $f_i^\circ$  is the fugacity of pure liquid  $i$  at the system  $T$  and 1 bar.

$\hat{f}_i$  is the fugacity of species  $i$  in the solution.

The fugacity is related to the activity coefficient by:  $\hat{f}_i = \gamma_i x_i f_i$

where  $f_i$  is fugacity of pure liquid  $i$  at system  $T$  &  $P$ .

Therefore, for liquid solution:

$$a_i = \hat{f}_i / f_i^\circ = \gamma_i x_i f_i / f_i^\circ = \gamma_i x_i (f_i / f_i^\circ)$$

Because the fugacities of liquids are weak

functions of  $P$ , the ratio  $f_i / f_i^\circ$  is often taken as unity.

$$\therefore a_i = \hat{f}_i / f_i^\circ \cong \gamma_i x_i$$

$\gamma_i$  is a measure of deviation from ideal-solution (id) behavior for liquid solutions:

$$\gamma_i \equiv \hat{f}_i / x_i f_i$$

$$\gamma_i = \hat{f}_i / \hat{f}_i^{\text{id}}$$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^0 = \gamma_i x_i$$

### (B) Equilibrium Constant ( $K$ ) for Liquid-Phase Reactions:

$$\left. \begin{aligned} K &= \prod_i (\gamma_i x_i)^{\nu_i} = \prod_i (\gamma_i)^{\nu_i} \prod_i (x_i)^{\nu_i} = K_\gamma \cdot K_x \\ K &= \prod_i (\gamma_i x_i)^{\nu_i} = \prod_i (\gamma_i C_i / C_T)^{\nu_i} \\ K &= \prod_i (\gamma_i)^{\nu_i} \prod_i (C_i)^{\nu_i} \prod_i (C_T)^{-\nu_i} \\ K &= K_\gamma \cdot K_c \cdot (C_T)^{-\delta} \end{aligned} \right| \begin{aligned} &\text{where,} \\ K_\gamma &\equiv \prod_i (\gamma_i)^{\nu_i} \\ K_c &\equiv \prod_i (C_i)^{\nu_i} \\ K_x &\equiv \prod_i (x_i)^{\nu_i} \end{aligned}$$

For ideal solutions (molecular species are similar in size & chemical nature):

$$\gamma_i = 1$$

$$\therefore K_\gamma = 1$$

$$K = K_c \cdot (C_T)^{-\delta}$$

$$\text{where } C_T \text{ (total conc. at equil.)} = N_T / V = (N_{T0} + \delta N_{A0} X_e) / V_0 = (C_{T0} + C_{A0} \delta X_e)$$

For reactions occurring in ideal solution with no change in the total number of moles ( $\delta=0$ ):  $K = K_c$

$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^\circ$$

## In Summary:

1. For Gas Phase RXNs:  $K = K_\phi \cdot K_p \cdot (P^\circ)^{-\delta}$

For ideal gases:

$$K = K_p \cdot (P^\circ)^{-\delta}$$

$$K = K_c \cdot (RT / P^\circ)^\delta$$

where,

$$K_\phi = \prod_i (\hat{\phi}_i)^{\nu_i}$$

$$K_p = \prod_i (P_i)^{\nu_i}$$

$$K_c = \prod_i (C_i)^{\nu_i}$$

$$\delta = \sum_i \nu_i$$

2. For Liquid Phase RXNs:  $K = K_\gamma \cdot K_c \cdot (C_T)^{-\delta}$

For ideal solutions:

$$K = K_c \cdot (C_T)^{-\delta}$$