

# Chemical Equilibrium Composition

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For a fixed  $T$  &  $P$ , the eq<sup>m</sup> cond<sup>n</sup> becomes

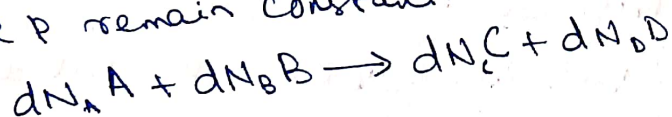
$$dg_{mix} = 0_{T,P}$$

A chemical react<sup>n</sup> at a specified temp &  $P$  can't proceed in the direction of the increasing Gibbs function since this will be a violation of 2nd law of thermodynamics.

However, if the temp & pressure is changed, the reacting system will assume a different eq<sup>m</sup> state, which is the state of minimum Gibbs function at the new temp or pressure.

To obtain a rel<sup>n</sup> for chemical eq<sup>m</sup> in terms of the properties of the individual components, consider a mixture of 4 chemical components, A, B, C & D that exist in eq<sup>m</sup> at a specified  $T$  &  $P$ . Let the number of moles of the respective components be  $N_A$ ,  $N_B$ ,  $N_C$  &  $N_D$ .

→ Now consider a reaction that occurs to an infinitesimal extent during which differential amounts of A & B (reactants) are converted to C & D (products) while  $T$  &  $P$  remain constant.



The eq<sup>m</sup> criterion requires that the change in the Gibbs function of the mixture during this process be equal to zero, i.e.,

$$(dg)_{T,P} = \sum (dg_i)_{T,P} = \sum (\bar{g}_i dN_i) = 0_{T,P}$$

$$\underline{\underline{\sum \bar{g}_C dN_C + \bar{g}_D dN_D + \bar{g}_A dN_A + \bar{g}_B dN_B = 0}} \quad \text{--- (1)}$$

where the  $\bar{g}_i$  are the molar Gibbs functions (also called the chemical potentials) at the specified  $T$  &  $P$  &  $dN_i$ 's are the differential changes in the number of moles of the components.

React <sup>n</sup> Chamber	
$T, P$	
$N_A$ moles of A	
$N_B$ moles of B	
$N_C$ " " C	
$N_D$ " " D	
$dN_A A + dN_B B \rightarrow dN_C C + dN_D D$	

An infinitesimal react<sup>n</sup> in a chamber at const  $T$  &  $P$ .

The chemical expression between  $dN$  & Stoichiometric Coefficient of ~~an elementary~~ react<sup>n</sup> is



$a, b, c, d$  are the stoichiometric coefficients, which are

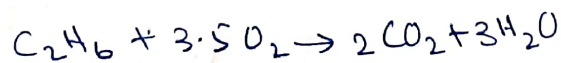
Stoichiometric react<sup>n</sup> plays an important role in the determination of eq<sup>n</sup> composition of the reacting mixtures because the changes in the number of moles of the components are proportional to the stoichiometric coefficients.

$$dN_A = -\epsilon a \quad \text{or} \quad \frac{dN_A}{-a} = \epsilon \quad \left. \begin{array}{l} \frac{dN_B}{-b} = \epsilon \\ \frac{dN_C}{c} = \epsilon \\ \frac{dN_D}{d} = \epsilon \end{array} \right\} \quad \text{or} \quad d\gamma_A = -\epsilon \gamma_A \text{ \& so on} \quad \text{--- (2)}$$

$\epsilon$  is the Proportionality const. & represents the extent of a react<sup>n</sup>.

Minus sign indicates because the number of moles of reactants decrease & as the react<sup>n</sup> progresses.

→ For example, if the reactants are  $C_2H_6$  &  $O_2$  & the products are  $CO_2$  &  $H_2O$ , the react<sup>n</sup> of 1 μmol of  $C_2H_6$  results in a 2 μmol increase in  $CO_2$  & a 3-μmol increase in  $H_2O$  & a 3.5 μmol decrease in  $O_2$  in accordance with the stoichiometric eq<sup>n</sup>.



i.e. the change in the number of moles of a component is one-millionth ( $\epsilon = 10^{-6}$ ) of the stoichiometric coefficient of that compound in this case.

Substituting the rel<sup>s</sup> in eq<sup>n</sup> (2) into eq<sup>n</sup> (1) & cancelling  $\epsilon$

$$\gamma_C \bar{g}_C + \gamma_D \bar{g}_D - \gamma_A \bar{g}_A - \gamma_B \bar{g}_B = 0 \quad \text{--- (3)}$$

This eq<sup>n</sup> involves the stoichiometric coefficients & the molar Gibbs f<sup>s</sup> of the reactants & products & it is known as



the criterion for chemical eq<sup>m</sup>

→ It is valid for any chemical react<sup>n</sup> regardless of the Phases involved.

Eq<sup>n</sup> (3) is developed for a chemical react<sup>n</sup> that involves 2 reactants & 2 Products for simplicity but can be easily modified to handle chemical react<sup>n</sup>s with any number of reactants & Products.

Equilibrium Const for ideal gas mixtures

Consider a mixture of ideal gases that exist in eq<sup>m</sup> at a specified T & P. Like entropy, the Gibbs f<sup>n</sup> of an ideal gas depends on both T & P.

→ Gibbs f<sup>n</sup> values are usually listed vs temp at a fixed reference pressure of 1 atm.

→ Variation of Gibbs f<sup>n</sup> of an ideal gas with P at a fixed T is determined by  $\bar{g} = \bar{h} - T\bar{s}$  & the entropy change ( $\Delta\bar{s}$ ) rel<sup>n</sup> for isothermal processes ( $\Delta\bar{s} = -R_u \ln(P_2/P_1)$ ) \* (Details in page 5)

$$\Rightarrow (\Delta\bar{g})_T = \Delta\bar{h} - T(\Delta\bar{s})$$
  
0 (since T = const)  $\Rightarrow$  Their ~~abs~~ enthalpies of formation & sensible enthalpies are the same

$$= + T R_u \ln \frac{P_2}{P_1}$$

The Gibbs f<sup>n</sup> of component i of an ideal gas mixture at its Partial Pressure  $P_i$  & mixture temp T can be expressed as

$$\bar{g}_i(T, P_i) = \bar{g}_i^0(T) + R_u T \ln \left( \frac{P_i}{P^0} \right)$$

$\bar{g}_i^0(T, P^0)$  is the Gibbs f<sup>n</sup> of component i at 1 atm pressure & temp T. This is also known as Gibbs f<sup>n</sup> (or energy) of formation.

$P_i \rightarrow$  Partial Pressure of component i.

~~$\bar{g}_i^0$  at 298 K is known as standard Gibbs ~~energy~~ of formation.~~

Substituting Gibbs free expression for each component into eqn (3) we get

$$c \left[ \bar{g}_c^0(T) + R_u T \ln \left( \frac{p_c}{p^0} \right) \right] + d \left[ \bar{g}_d^0(T) + R_u T \ln \left( \frac{p_d}{p^0} \right) \right] - a \left[ \bar{g}_a^0(T) + R_u T \ln \left( \frac{p_a}{p^0} \right) \right] - b \left[ \bar{g}_b^0(T) + R_u T \ln \left( \frac{p_b}{p^0} \right) \right] = 0$$

Rearranging, we'll get

$$\begin{aligned} & - \left( c \bar{g}_c^0(T) + d \bar{g}_d^0(T) - a \bar{g}_a^0(T) - b \bar{g}_b^0(T) \right) \\ & = c R_u T \ln \left( \frac{p_c}{p^0} \right) + d R_u T \ln \left( \frac{p_d}{p^0} \right) - a R_u T \ln \left( \frac{p_a}{p^0} \right) - b R_u T \ln \left( \frac{p_b}{p^0} \right) \\ & = R_u T \left[ \ln \left( \frac{p_c}{p^0} \right)^c + \ln \left( \frac{p_d}{p^0} \right)^d \right] - R_u T \left[ \ln \left( \frac{p_a}{p^0} \right)^a + \ln \left( \frac{p_b}{p^0} \right)^b \right] \\ & = R_u T \left[ \ln \left( \frac{p_c}{p^0} \right)^c \times \left( \frac{p_d}{p^0} \right)^d \right] - R_u T \left[ \ln \left( \frac{p_a}{p^0} \right)^a \times \left( \frac{p_b}{p^0} \right)^b \right] \\ & - \left( c \bar{g}_c^0(T) + d \bar{g}_d^0(T) - a \bar{g}_a^0(T) - b \bar{g}_b^0(T) \right) = R_u T \left[ \ln \frac{\left( \frac{p_c}{p^0} \right)^c \times \left( \frac{p_d}{p^0} \right)^d}{\left( \frac{p_a}{p^0} \right)^a \times \left( \frac{p_b}{p^0} \right)^b} \right] \quad \text{--- (4)} \end{aligned}$$

For our convenience, we define standard state Gibbs free energy as

$$\Delta G^0(T) = c \bar{g}_c^0(T) + d \bar{g}_d^0(T) - a \bar{g}_a^0(T) - b \bar{g}_b^0(T)$$

or alternatively,  $\Delta G^0(T) = c \bar{g}_{f,c}^0(T) + d \bar{g}_{f,d}^0(T) - a \bar{g}_{f,a}^0(T) - b \bar{g}_{f,b}^0(T)$

From eqn (4), the argument of natural logarithm can be defined as,  $K_p$  (Equilibrium constant)

$$K_p = \frac{\left( \frac{p_c}{p^0} \right)^c \times \left( \frac{p_d}{p^0} \right)^d}{\left( \frac{p_a}{p^0} \right)^a \times \left( \frac{p_b}{p^0} \right)^b} \quad \text{--- (5)}$$

From Eqn (4), we can be rewritten as

$$\Delta G^0(T) = - R_u T \ln K_p \quad \text{--- (6)}$$

$$\Rightarrow K_p = \exp \left( \frac{-\Delta G^\circ(T)}{R_u T} \right) \text{--- (7)}$$

$$m K_p = \exp \left( \frac{a \bar{g}_A^\circ(T) + b \bar{g}_B^\circ(T) - c \bar{g}_C^\circ(T) - d \bar{g}_O^\circ(T)}{R_u T} \right) \text{--- (8)}$$

From eq<sup>n</sup> (5), we can write

$$K_p = \frac{N_C^c N_O^d}{N_A^a N_B^b} \left( \frac{p_{\text{mixture}}}{p^\circ N_{\text{Total}}} \right)^{c+d-a-b} \text{--- (9)}$$

$$p_C = \frac{N_C}{N_T} \times p_{\text{mixture}}$$

& so on

a, b, c & d are the stoichiometric coefficients.

Where  $N_{\text{Total}}$  is the total number of moles present in the react<sup>n</sup> chamber, including any inert gases.

$p_{\text{mixture}}$  is the total pressure of the mixture.

$K_p$  of an ideal gas mixture at a specified temp. can be determined from a knowledge of the standard state Gibbs function change at the same temp.

Once the eq<sup>m</sup> const,  $K_p$  is available, it can be used to determine the eq<sup>m</sup> composition of reacting ideal gas mixture, as given by eq<sup>n</sup> (9).

$K_p$  is dimensionless & depends on temp. only. This is because

$K_p$  depends on  $\Delta G^\circ(T)$ , which depends on temperature only.

$$\bar{S}_2 = -R_u \ln(p_2/p^\circ) \quad \bar{S}_1 = -R_u \ln(p_1/p^\circ)$$

$$S_2 - S_1 = -R_u [\ln(p_2/p^\circ) - \ln(p_1/p^\circ)]$$

$$= -R_u \ln \left( \frac{p_2/p^\circ}{p_1/p^\circ} \right) = -R_u \ln(p_2/p_1)$$