CHE 415 Chemical Engineering Thermodynamics II

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Chemical Reaction Equilibria

Learning Objectives for today's lecture

- At the end of this week's lecture, you should be able to:

  – Describe the concept of reaction coordinates as it applies to chemical reactions.

  – Describe and determine the expression between mole fractions of the components in a chemical reaction and the extent of reactions for both single and multiple reactions.

  – Explain and derive the criteria for chemical reaction equilibrium.

INTRODUCTION TO CHEMICAL REACTION EQUILIBRIA

- The design and operation of reaction equipment requires the versatility of Chemical Engineers with the thermodynamics and kinetics of chemical reactions.
- Thermodynamics predicts the equilibrium conversion that would be achieved in a chemical reaction and also the effect of operating conditions on it,
- whereas the kinetics deals with the rate or speed with which the desired conversion is attained in practice.
- Thermodynamic analysis can also give information about the feasibility of chemical reactions.
- The progress and extent of a chemical reaction are affected by changes in the reaction conditions like temperature, pressure, composition of the reactants, etc.
- The influence of these controllable variables on the thermodynamics of reaction, or on the equilibrium conversion, in some situation may be in conflict with the influence of these variables on the kinetics of the reaction.

INTRODUCTION TO CHEMICAL REACTION EQUILIBRIA

- Thus, both kinetics (the rate) and thermodynamics (the equilibrium) of the reaction must be considered in the choice of reaction conditions in the commercial process for any chemical reaction.
- Equilibrium conversion of a reaction sets a limit and provides a goal by which we measure improvement in the process.

REACTION COORDINATE

- The generalized representation of a chemical reaction is given by

$$0 = \sum_i \nu_i A_i$$

  8-1
  - where A is the chemical symbol for the various species taking part in the reaction and n is the stoichiometric number.
- Consider the reaction
- $$2A + 3B \longrightarrow L + 2M$$
- This is a special case of the general form of Eq. (8-1), with $n_L = 1$, $n_M = 2$, $n_A = -2$, and $n_B = -3$.
- The stoichiometric numbers are positive for products, negative for reactants and zero for inert species.
- In the general form, this reaction may be represented as
- $$0 = L + 2M - 2A - 3B$$
- The changes in the number of moles of various species taking part in the reaction are in direct proportion to their stoichiometric numbers.
- Let Δn_i denote the change in the number of moles of component i due to the reaction.
- For one mole of A disappearing in the reaction
- $\Delta n_A = -1$, $\Delta n_B = -1.5$, $\Delta n_L = 0.5$ and $\Delta n_M = 1$.

REACTION COORDINATE

- We see that

$$\frac{\Delta n_A}{v_A} = \frac{\Delta n_B}{v_B} = \frac{\Delta n_L}{v_L} = \frac{\Delta n_M}{v_M}$$

- For differential amounts of the species, the above result can be written as

$$\frac{dn_A}{v_A} = \frac{dn_B}{v_B} = \frac{dn_L}{v_L} = \frac{dn_M}{v_M}$$

- For the thermodynamic analysis of chemical reactions the concept of 'extent of reaction,' also called 'reaction coordinate' is useful.
- It is denoted by ε.
- The reaction coordinate measures the progress of a reaction and is defined as the degree to which a reaction has advanced.
- It has the advantage that the change in the extent of reaction $d\varepsilon$ is the same for each component, whereas the changes in the number of moles are different for different species taking part in the reaction.
- The extent of reaction and the number of moles taking part in the reaction are related as $\frac{dn_i}{v_i} = d\varepsilon$ or $dn_i = v_i \, d\varepsilon$ 8-2
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REACTION COORDINATES

❑ For the initial state of the system, that is, before the reaction, the value of ε is zero.

❑ To derive the relationship between the mole fraction of the components taking part in the reaction and the extent of the reaction.

❑ Let n_{i0} be the number of moles of the species initially present in the system and n_i the number of moles present after the reaction.

❑ Then $\qquad n_i = n_{i0} + \Delta n_i$

    ❑ where Δn_i is the change in the number of moles of i due to the reaction.

❑ Integration of Eq. (8-2) yields

$$\Delta n_i = \nu_i \int_0^\varepsilon d\varepsilon = \nu_i \varepsilon$$

❑ Therefore,

❑ $\qquad\qquad\qquad n_i = n_{i0} + \nu_i \varepsilon$ 8-3

❑ The mole fraction of component i in the reaction mixture is y_i
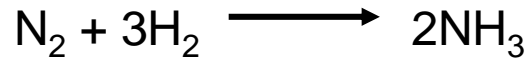
❑ $\qquad\qquad y_i = \dfrac{n_i}{\sum n_i} = \dfrac{n_{i0} + \nu_i \varepsilon}{\sum n_{i0} + \varepsilon \sum \nu_i} = \dfrac{n_{i0} + \nu_i \varepsilon}{n_0 + \varepsilon \nu}$ 8-4

    ❑ where $n_0 = \sum n_{i0}$ and $\nu = \sum \nu_i$

EXAMPLE

A gas mixture containing 2 moles nitrogen, 7 moles hydrogen and 1 mole ammonia initially, is undergoing the following reaction:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Derive expressions for the mole fractions of various components in the reaction mixture in terms of the extent of reaction.

Solution

Equations (8-3) and (8-4) relate the mole fraction of various constituents in the system to the extent of reaction.

So,

$$n_0 = \Sigma \ n_{i0} = 2 + 7 + 1 = 10$$

and

$$v = \Sigma \ v_i = 2 - 1 - 3 = - 2$$

(a) For mole fraction of N_2

$$y_{N_2} = \frac{n_{N_2,\,0} + v_{N_2} \varepsilon}{n_0 + \varepsilon v} = \frac{2 - \varepsilon}{10 - 2\varepsilon}$$

(b) For mole fraction of H_2

$$y_{H_2} = \frac{n_{H_2,\,0} + v_{H_2} \varepsilon}{n_0 + \varepsilon v} = \frac{7 - 3\varepsilon}{10 - 2\varepsilon}$$

EXAMPLE

(c) For mole fraction of NH_3

$$y_{NH_3} = \frac{n_{NH_3,0} + v_{NH_3}\varepsilon}{n_0 + \varepsilon v} = \frac{1 + 2\varepsilon}{10 - 2\varepsilon}$$

❑ MULTIPLE REACTION

❑ Also relationship between mole fraction of species and the extent of reactions can be develop for species in multiple reactions.

❑ When two or more reactions occur simultaneously, the number of moles of each component changes because of several reactions.

❑ Equation (8-2) can be modified as

❑
$$dn_i = \sum_j v_{i,j}\, d\varepsilon_j \qquad \text{8-5}$$

❑ where $v_{i,j}$ is the stoichiometric number for species i in the jth reaction and ε_j is the extent of this reaction.

❑ Eq.8-3 is also modified to account for the multiple reactions, and the number of moles of I after the reaction is

❑
$$n_i = n_{i0} + \sum_j v_{i,j}\, \varepsilon_j \qquad \text{8-6}$$

REACTION COORDINATES IN MULTIPLE REACTIONS

❑ The total number of moles is obtained by summing the number of moles of individual species.

$$n = \sum_i n_{i0} + \sum_i \sum_j \nu_{i,j} \varepsilon_j = n_0 + \sum_j \left(\sum_i \nu_{i,j} \right) \varepsilon_j$$

❑ Let $\sum_i \nu_{i,j} = \nu_j$, the sum of the stoichiometric numbers in the jth reaction.

❑ Then the above equation can be written as

❑
$$n = n_0 + \sum_j \nu_j \varepsilon_j \qquad \text{8-7}$$
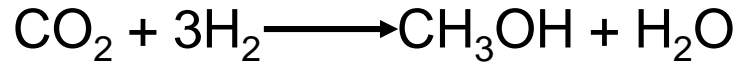
❑ The mole fraction of component I in the mixture is

❑
$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j \nu_{i,j} \varepsilon_j}{n_0 + \sum_j \nu_j \varepsilon_j} \qquad \text{8-8}$$

EXAMPLE

A gas mixture containing 3 mol CO_2, 5 mol H_2 and 1 mol water is undergoing the following reactions:

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$
$$CO_2 + H_2 \longrightarrow CO + H_2O$$

Develop expressions for the mole fraction of the species in terms of the extent of reaction.

Solution The total moles initially present,

$$n_0 = 3 + 5 + 1 = 9$$

For the first reaction,

$$n_1 = -1 - 3 + 1 + 1 = -2$$

For the second reaction,

$$n_2 = -1 - 1 + 1 + 1 = 0$$

The mole fractions are calculated using Eq. (8-8)
For CO_2

$$y_{CO_2} = \frac{3 + (-1) \times \varepsilon_1 + (-1) \times \varepsilon_2}{9 + (-2) \times \varepsilon_1 + (0) \times \varepsilon_2} = \frac{3 - \varepsilon_1 - \varepsilon_2}{9 - 2\varepsilon_1}$$

Lets do for the remaining.

Solution

Similarly, for H_2:

$$y_{H_2} = \frac{5 - 3\varepsilon_1 - \varepsilon_2}{9 - 2\varepsilon_1},$$

For CH_3OH:

$$y_{CH_3OH} = \frac{\varepsilon_1}{9 - 2\varepsilon_1}$$

For H_2O:

$$y_{H_2O} = \frac{1 + \varepsilon_1 + \varepsilon_2}{9 - 2\varepsilon_1},$$

For CO:

$$y_{CO} = \frac{\varepsilon_2}{9 - 2\varepsilon_1}$$

CRITERIA OF CHEMICAL REACTION EQUILIBRIUM

❑ At constant temperature and pressure, the transfer of materials from one phase to another under equilibrium is found to occur with no change in the free energy.

❑ Stated mathematically,

❑ $$dG^t_{T,P} = 0$$ 8-9

❑ This criterion is quite general and not restricted to physical transformations alone.

❑ Similarly, when a chemical reaction occurs at equilibrium there is no change in the Gibbs free energy of the system, provided the change is taking place at constant temperature and pressure.

❑ Consider a closed system in which a chemical reaction represented by the following general equation has been allowed to reach a state of equilibrium at a given temperature and pressure.

❑ aA + bB ⟶ lL + mM   8-10
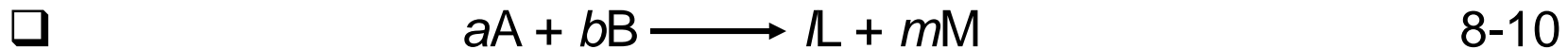
❑ An infinitesimal change is allowed to occur in the system whereby the number of moles of various species change.

❑ The increments in the number of moles are dnA, dnB, dnL and dnM for components A, B, L and M respectively.

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CRITERIA OF CHEMICAL REACTION EQUILIBRIUM

❑ The free energy change for the process occurring at constant temperature and pressure is given by

❑
$$dG^t_{T,P} = \Sigma \mu_i \, dn_i \qquad\qquad 8.11$$

❑ where mi is the chemical potential of component i.

❑ For the reaction under consideration, Eq. 8-11 takes the form

$$dG^t_{T,P} = \mu_L \, dn_L + \mu_M \, dn_M + \mu_A \, dn_A + \mu_B \, dn_B$$

❑ By Eq.8-2, $dn_i = v_i d\varepsilon$ so that the above equation becomes

❑
$$dG^t_{T,P} = (v_L\mu_L + v_M\mu_M + v_A\mu_A + v_B\mu_B) \, d\varepsilon \qquad 8\text{-}12$$

$$= (l\mu_L + m\mu_M - a\mu_A - b\mu_B) \, d\varepsilon$$

❑ where $- a, - b, l$ and m are the stoichiometric numbers which are positive for products and negative for the reactants and e is the extent of reaction.

❑ In general, for an infinitesimal change in a reacting system, we can write Eq. 8-12 as
$$dG^t_{T,P} = \Sigma \, \mu_i v_i \, d\varepsilon$$

❑ Since the process is occurring at equilibrium conditions, Eq.8-9 should be satisfied so that
$$dG^t_{T,P} = \Sigma \, \mu_i v_i \, d\varepsilon = 0$$

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CRITERIA OF CHEMICAL REACTION EQUILIBRIUM

$$\sum \mu_i \nu_i = 0$$

❑ This is the criterion of equilibrium for chemical reactions.
❑ For the present reaction given by 8-10, this criterion means that

$$(l\mu_L + m\mu_M) - (a\mu_A + b\mu_B) = 0$$

❑ The left-hand side of Eq. 8-15 is the free energy change dG accompanying the complete reaction under equilibrium conditions.
❑ Hence, dG = 0 under equilibrium.