

Chemical reaction equilibrium

- Reaction Co-ordinate,
- Application of equilibrium criteria to chemical reactions,
- Standard Gibb's Energy change and Equilibrium constant,
- Relation of equilibrium constant,
- Effect of Temperature on Equilibrium constants,
- Equilibrium conversions for single reactions

Chemical reaction

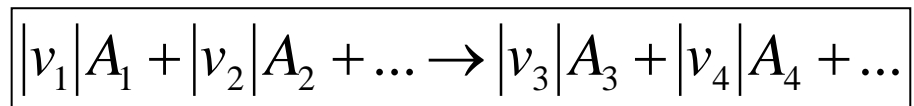
- Both the rate and equilibrium conversion of a chemical reaction depend on the temperature, pressure, and composition of reactants.
 - Although reaction rates are not susceptible to thermodynamic treatment, equilibrium conversions are.

Why we have to study Chemical reaction equilibrium ?....

- to determine the effect of temperature, pressure, and initial composition on the equilibrium conversions of chemical reactions.

Reaction coordinate

- A general chemical reaction:



Where $|v_i|$ are stoichiometric numbers and A_i stands for chemical formulas

- Sign conversion (v) – positive for products and negative for reactants

Reaction coordinate

$$\frac{dn_1}{v_1} = \frac{dn_2}{v_2} = \frac{dn_3}{v_3} = \frac{dn_4}{v_4} = \dots \equiv d\varepsilon$$

Reaction coordinate, which characterizes the extent or degree to which a reaction has taken place.

- A differential change in the number of moles of a reacting species:

$$dn_i = v_i d\varepsilon \quad (i = 1, 2, \dots, N)$$

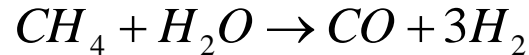
$$\int_{n_{i0}}^{n_i} dn_i = v_i \int_0^\varepsilon d\varepsilon \quad (i = 1, 2, \dots, N)$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \varepsilon}{n_0 + v \varepsilon}$$

$$n = \sum_i n_i = n_0 + v \varepsilon$$

$$n_i = n_{i0} + v_i \varepsilon \quad (i = 1, 2, \dots, N)$$

[Example] For a system in which the following reaction occurs,



assume there are present initially **2 mol CH₄**, **1 mol H₂O**, **1 mol CO** and **4 mol H₂**. Determine expressions for the mole fractions y_i as functions of ε .

Solution:

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \nu \varepsilon}$$

$$\nu = \sum_i \nu_i = -1 - 1 + 1 + 3 = 2$$

$$n_0 = \sum_i n_{i0} = 2 + 1 + 1 + 4 = 8$$

$$y_{\text{CH}_4} = \frac{2 - \varepsilon}{8 + 2\varepsilon}$$

$$y_{\text{CO}} = \frac{1 + \varepsilon}{8 + 2\varepsilon}$$

$$y_{\text{H}_2\text{O}} = \frac{1 - \varepsilon}{8 + 2\varepsilon}$$

$$y_{\text{H}_2} = \frac{4 + 3\varepsilon}{8 + 2\varepsilon}$$

Multireaction

- Two or more independent reactions proceed simultaneously
 - $v_{i,j}$: the stoichiometric number of species i in reaction j .
 - the change of the moles of a species n_i :

$$dn_i = \sum_j v_{i,j} d\varepsilon_j$$

integration

$$n_i = n_{i0} + \sum_j v_{i,j} \varepsilon_j$$

summation

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

$$v_j \equiv \sum_i v_{i,j}$$

$$n = n_0 + \sum_j v_j \varepsilon_j$$

total stoichiometric number:

$$y_i = \frac{n_{i0} + \sum_j v_{i,j} \varepsilon_j}{n_0 + \sum_j v_j \varepsilon_j}$$