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:

$$\boxed{|v_1|A_1 + |v_2|A_2 + \ldots \rightarrow |v_3|A_3 + |v_4|A_4 + \ldots}$$

Where $\boxed{|v_i|}$ are stoichiometric numbers and A_i stands for chemical formulas

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

Reaction coordinate

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

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:

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

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

$$\boxed{n = \sum_i n_i = n_0 + v\varepsilon}$$

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

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

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

assume there are present initially 2 mol CH_4, 1 mol H_2O, 1 mol CO and 4 mol H_2. Determine expressions for the mole fractions y_i as functions of ε.

Solution:

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

$$\boxed{\nu = \sum_i \nu_i = -1 - 1 + 1 + 3 = 2}$$

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

$$\boxed{y_{CH_4} = \frac{2 - \varepsilon}{8 + 2\varepsilon}} \quad \boxed{y_{CO} = \frac{1 + \varepsilon}{8 + 2\varepsilon}}$$

$$\boxed{y_{H_2O} = \frac{1 - \varepsilon}{8 + 2\varepsilon}} \quad \boxed{y_{H_2} = \frac{4 + 3\varepsilon}{8 + 2\varepsilon}}$$

Multireaction

- Two or more independent reactions proceed simultaneously
  - $\nu_{i,j}$: the stoichiometric number of species *i* in reaction *j*.
  - the change of the moles of a species n_i: $\boxed{dn_i = \sum_j \nu_{i,j} d\varepsilon_j}$

integration

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

summation

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

total stoichiometric number:

$$\boxed{\nu_j \equiv \sum_i \nu_{i,j}}$$

$$\boxed{n = n_0 + \sum_j \nu_j\, \varepsilon_j}$$

$$\boxed{y_i = \frac{n_{i0} + \sum_j \nu_{i,j}\, \varepsilon_j}{n_0 + \sum_j \nu_j\, \varepsilon_j}}$$