CHEMICAL ENGINEERING THERMODYNAMICS II (0905322)

10 -Notation for Chemical Reactions

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Outline

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NOTATION FOR CHEMICAL REACTIONS

- General equation for a single chemical reaction,

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \quad \Longrightarrow \quad \nu_C C + \nu_D D - \nu_A A - \nu_B B = 0$$

- Generalized mathematical notation,

$$\sum_J \nu_J J = 0$$

- where ν is stoichiometric number,
  - Positive for products,
  - Negative for reactants.
  - **Zero for inert species**

EXAMPLE

$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$$

$$CO_2 - CO - \frac{1}{2}O_2 = 0$$

$$\nu_1 = \nu_{CO} = -1$$

$$\nu_2 = \nu_{O_2} = -\frac{1}{2}$$

$$\nu_3 = \nu_{CO_2} = 1$$

$$\nu_J = \begin{bmatrix} -1 & -\frac{1}{2} & 1 \end{bmatrix}$$

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$$

$$H_2O - H_2 - \frac{1}{2}O_2 = 0$$

$$\nu_1 = \nu_{H_2} = -1$$

$$\nu_2 = \nu_{O_2} = -\frac{1}{2}$$

$$\nu_3 = \nu_{H_2O} = 1$$

$$\nu_J = \begin{bmatrix} -1 & -\frac{1}{2} & 1 \end{bmatrix}$$

SIMULTANEOUS CHEMICAL REACTIONS

- A general notation for *R* simultaneous reactions. The index for reactions is *i* and for components is *j*.

$$\sum_{J} \nu_{ij} J_{i} = 0, \quad i = 1, 2, \cdots, R$$

CHEMICAL REACTIONS and INDEPENDENCE

- Independent chemical reactions is a term used to designate the smallest collection of reactions that, on forming various linear combinations, includes all possible chemical reactions among the species present.
  - No reaction in the set can itself be a linear combination of the others.
- Matrix methods are used to obtain the minimum set of reactions.
  - The **rank** of the matrix is very important term!

EXAMPLE

- Determine the number of independent reactions for the hydro-isomerization of benzene.

$$-C_6H_6 - 3H_2 + C_6H_{12} = 0$$
$$-C_6H_6 - 3H_2 + C_5H_9CH_3 = 0$$
$$-C_6H_{12} + C_5H_9CH_3 = 0$$

$$\begin{bmatrix} C_6H_6 & H_2 & C_6H_{12} & C_5H_9CH_3 & \\ -1 & -3 & 1 & 0 & \text{Rxn 1} \\ -1 & -3 & 0 & 1 & \text{Rxn 2} \\ 0 & 0 & -1 & 1 & \text{Rxn 3} \end{bmatrix}$$

$$\begin{bmatrix} C_6H_6 & H_2 & C_6H_{12} & C_5H_9CH_3 \\ -1 & -3 & 1 & 0 \\ -1 & -3 & 0 & 1 \\ 0 & 0 & -1 & 1 \end{bmatrix} \xrightarrow[\text{from the second}]{\text{subtract first row}} \begin{bmatrix} C_6H_6 & H_2 & C_6H_{12} & C_5H_9CH_3 \\ -1 & -3 & 1 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & -1 & 1 \end{bmatrix}$$

$$\begin{bmatrix} C_6H_6 & H_2 & C_6H_{12} & C_5H_9CH_3 \\ -1 & -3 & 1 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & -1 & 1 \end{bmatrix} \xrightarrow[\text{from the third}]{\text{subtract second row}} \begin{bmatrix} C_6H_6 & H_2 & C_6H_{12} & C_5H_9CH_3 \\ -1 & -3 & 1 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

Since the third row is zeros and further reduction does not yield any rows with zeros, the **rank** of this matrix is two, and only two reactions are independent.

Use Matlab's `rank` function to find the rank of this matrix

```
nui = [-1 -3 1 0;-1 -3 0 1; 0 0 -1 1]
indeprxns = rank(nui)
whichrxn = rref(nui)
```

```
nui =

    -1    -3     1     0
    -1    -3     0     1
     0     0    -1     1

indeprxns =
     2
```

```
whichrxn =

     1     3     0    -1
     0     0     1    -1
     0     0     0     0
```

MOLAR EXTENT OF REACTION

- Define n_j to represent the number of moles of species *j* in the system at any time *t*, and $n_{j,0}$ to represent the initial numbers of moles of species *j*.
- Define the **molar extent of reaction** (ξ) or **reaction coordinate** as:

$$\xi = \frac{n_j - n_{j,0}}{\nu_j}$$

- The extent of reaction relates the moles at any time to the initial number of moles, and the stoichiometric coefficient.
  - Set to zero for the initial state of the system prior to reaction
- The important characteristic of ξ is that it has the same value for each molecular species involved in a reaction.
  - We can calculate all other mole numbers in a system given ξ and initial mole numbers.
- The molar extent of reaction is not a fractional conversion variable. **Its value is not restricted to be between 0 and 1**.

Mole Fractions from Extent of Reaction

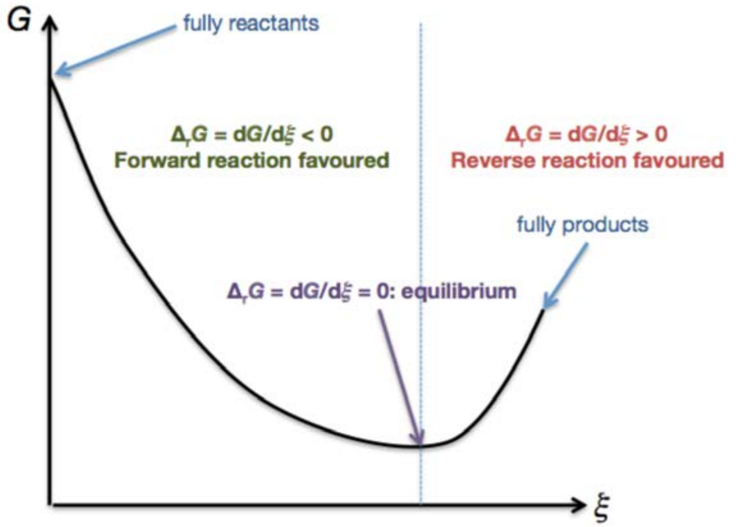
- Use definition of mole fractions and extent of reaction to obtain:

$$y_j = \frac{n_j}{n} = \frac{n_{j,0} + \nu_j \xi}{\sum_j n_{j,0} + \sum_j \nu_j \xi} = \frac{n_{j,0} + \nu_j \xi}{n_0 + \nu \xi}$$

For a system in which the following reaction occurs:

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

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 as a function of ξ.



For a system in which the following reaction occurs: $CH_4 + H_2O \rightleftharpoons CO + 3H_2$

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 as a function of ξ.

$$\nu = \sum_j \nu_j = -1 - 1 + 1 + 3 = 2$$

$$n_0 = \sum_j n_{j,0} = 2 + 1 + 1 + 4 = 8$$

$$y_j = \frac{n_j}{n} = \frac{n_{j,0} + \nu_j \xi}{\sum_j n_{j,0} + \sum_j \nu_j \xi} = \frac{n_{j,0} + \nu_j \xi}{n_0 + \nu \xi}$$

$$y_{CH_4} = \frac{2 - \xi}{8 + 2\xi}$$

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

$$y_{H_2O} = \frac{1 - \xi}{8 + 2\xi}$$

$$y_{H_2} = \frac{4 + 3\xi}{8 + 2\xi}$$

EXTENT OF REACTION FOR MULTIPLE REACTIONS

- For *R* independent reactions occurring simultaneously, define an extent of reaction for each reaction

$$n_j = n_{j,0} + \sum_{i=1}^{R} \nu_{ij} \xi_i$$

- Sum over all species

$$n = \sum_j \left(n_{j,0} + \sum_{i=1}^{R} \nu_{ij} \xi_i \right) = n_0 + \sum_j \sum_{i=1}^{R} \nu_{ij} \xi_i$$

$$y_j = \frac{n_{j,0} + \sum_{i=1}^{R} \nu_{ij} \xi_i}{n_0 + \sum_j \sum_{i=1}^{R} \nu_{ij} \xi_i} = \frac{n_{j,0} + \sum_{i=1}^{R} \nu_{ij} \xi_i}{n_0 + \sum_i \nu_i \xi_i}$$

For a system in which the following reaction occurs

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

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$

If there are present initially 2 mol CH_4, and 3 mol H_2O. Determine expressions for the mole fractions as a function of ξ_1 and ξ_2.

	j					
i	CH_4	H_2O	CO	CO_2	H_2	ν_i
1	-1	-1	1	0	3	2
2	-1	-2	0	1	4	2

$$y_j = \frac{n_{j,0} + \sum_{i=1}^{R} \nu_{ij}\xi_i}{n_0 + \sum_i \nu_i \xi_i}$$

$$y_{CH_4} = \frac{2 - \xi_1 - \xi_2}{5 + 2\xi_1 + 2\xi_2}$$

$$y_{H_2O} = \frac{3 - \xi_1 - 2\xi_2}{5 + 2\xi_1 + 2\xi_2}$$

$$y_{CO} = \frac{\xi_1}{5 + 2\xi_1 + 2\xi_2}$$

$$y_{H_2} = \frac{3\xi_1 + 4\xi_2}{5 + 2\xi_1 + 2\xi_2}$$

$$y_{CO_2} = \frac{\xi_2}{5 + 2\xi_1 + 2\xi_2}$$

RATE OF REACTION IN BALANCE EQUATIONS

- The instantaneous rate of change of the number of moles of species *j* due to chemical reaction only is given in terms of exten of reaction as:

$$\left(\frac{\partial n_j}{\partial t}\right)_{\text{rxn}} = \sum_{i=1}^{R} \nu_{ij}\,\xi_i$$

- Divide the molar extent of reaction by the system volume to obtain the molar extent of reaction per unit volume $\hat{\xi}$.
  - This will yield the rate of reaction per unit volume term most frequently used in chemical engineering.

$$\left(\frac{dn_j}{dt}\right)_{\text{rxn}} = \sum_{i=1}^{R} \nu_{ij}\frac{d(V\,\hat{\xi}_i)}{dt} = \frac{dV}{dt}\sum_{i=1}^{R} \nu_{ij}\,\hat{\xi}_i + V\sum_{i=1}^{R} \nu_{ij}\frac{d\,\hat{\xi}_i}{dt}$$

$$= \frac{dV}{dt}\sum_{i=1}^{R} \nu_{ij}\,\hat{\xi}_i + V\sum_{i=1}^{R} \nu_{ij}\,r_i$$