CHEMICAL ENGINEERING THERMODYNAMICS II (0905322)

12 -Minimization of the Gibbs Energy

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Justification

- Equilibrium constants does not lend itself to standardization so as to allow general programs to be written.
- An alternative criterion of equilibrium is based on the fact that **at equilibrium the total Gibbs free energy of the system has its minimum value**.
  - Applied to multiple reactions, this criterion is the basis for a general scheme of computer solution.

Formulation

- The total Gibbs free energy of the system (considered a single phase here for simplicity)
  - The problem is to find the vector of mole fractions $\{n_i\}$ such that
    - minimizes G for a specified P and T, $G_{T,P} = G(n_1, n_2, \cdots, n_N)$
    - Subject to the constraints of material balances.
  - The solution is based on Langrangian multipliers.

Formulation Steps and Solution Methodology

1. Formulate material balances basing them on **atomic balances** (*w* balances).
2. Introduce **Lagrange multipliers** λ_k (*w* multipliers) and combine with the material balances.
3. Define an **objective function** by adding the sum of material balances combined with the Lagrange multipliers.
4. Take the **partial derivatives** of the objective function with respect to the moles of each chemical species present in the system (*N* equilibrium equations) and set them equal to zero since this is a necessary condition for the minimum.
5. **Solve** the resulting N + *w*, usually nonlinear, equations to obtain the vector of equilibrium mole fractions that minimizes the Gibbs free energy.
6. This is a general procedure unlike the equilibrium constants which requires elaboration and formulation for each problem.

Solution Methodology : Material Balances

1. Formulate the constraining equations, i.e., the material balances
   a. Reacting molecular species are not conserved. However, total number of atoms of each element is constant.
   b. Subscript *k* identifies a particular atom.
   c. A_k is the total number of atomic masses of the k^{th} element in the system determined by the initial constitution in the system.
   d. Let a_{ik} be the number of atoms of the k^{th} element present in each molecule of chemical species *i*.
   e. The material balance on each element *k* is

$$\sum_i n_i a_{ik} = A_k \qquad ,k = 1,\cdots,w$$

$$\sum_i n_i a_{ik} - A_k = 0 \qquad ,k = 1,\cdots,w$$

Solution Methodology : Lagrange Multipliers

- Introduce the Lagrange multipliers λ_k, one for each element balance

$$\lambda_k \left(\sum_i n_i a_{ik} - A_k \right) = 0 \quad , k = 1, \cdots, w$$

- Sum over k to obtain

$$\sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k \right) = 0$$

Solution Methodology : Define your objective function

- Define the objective function by combing the sum of the Lagrange multipliers and the total Gibbs free energy of the system

$$F = G + \sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k \right)$$

- The objective function *F* is identical with the Gibbs free energy of the system (*G*) since the summation term is zero.
- The partial derivatives of *F* and *G* with respect to the $\{n_i\}$ are different, because *F* incorporates the constraints of the material balance.

Solution Methodology : Partial Differentiation

- The minimum value of *F* (and *G*) when all of the partial derivatives are zero

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j \neq i} = 0$$

- Take the required derivatives and set them to zero

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j \neq i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i} + \sum_k \lambda_k a_{ik} = 0 \quad , i = 1, \cdots, N$$

$$\mu_i + \sum_k \lambda_k a_{ik} = 0 \quad , i = 1, \cdots, N$$

$$G_i^{\circ} + RT \ln \frac{f_i}{f_i^{\circ}} + \sum_k \lambda_k a_{ik} = 0 \quad , i = 1, \cdots, N$$

- For gas phase reactions and standard states as the pure ideal gases at 1 bar (or 1 atm)

$$G_i^{\circ} + RT \ln \frac{f_i}{P^{\circ}} + \sum_k \lambda_k a_{ik} = 0 \quad , i = 1, \cdots, N$$

- If G_i^o is arbitrarily set to zero for all elements in their standard states, then for compounds $G_i^o = \Delta G_{fi}^o$

$$\Delta G_{fi}^{\circ} + RT \ln \frac{y_i \phi_i P}{P^{\circ}} + \sum_k \lambda_k a_{ik} = 0 \quad , i = 1, \cdots, N$$

Solution Methodology : Solve the System of Equations

- The final expression for the equilibrium equations constitutes N equations, one for each chemical species and there are w atomic balances resulting in $N + w$ equations that are to be solved simultaneously for the mole fractions and Lagrange multipliers.