# Lecture 4.
Thermodynamics
[Ch. 2]

- Energy, Entropy, and Availability Balances

- Phase Equilibria
  - Fugacities and activity coefficients
  - K-values

- Nonideal Thermodynamic Property Models
  - P-v-T equation-of-state models
  - Activity coefficient models

- Selecting an Appropriate Model

Thermodynamic Properties

- Importance of thermodynamic properties and equations in separation operations
  - Energy requirements (heat and work)
  - Phase equilibria : Separation limit
  - Equipment sizing

- Property estimation
  - Specific volume, enthalpy, entropy, availability, fugacity, activity, etc.
  - Used for design calculations
    - Separator size and layout
    - Auxiliary components : Piping, pumps, valves, etc.

Energy, Entropy and Availability Balances

Heat transfer in and out

Q_{in}, T_s Q_{out}, T_s
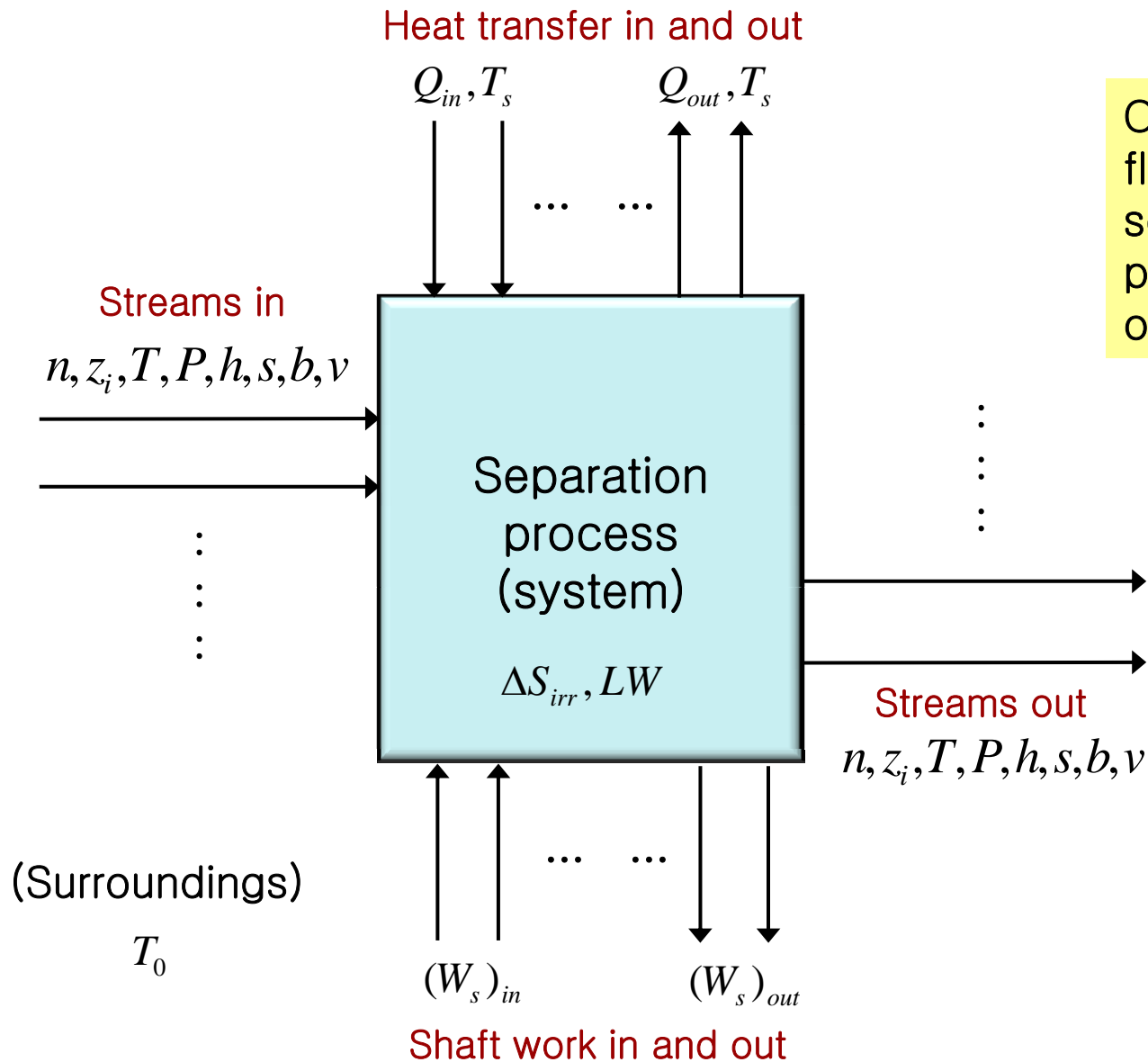
One or more feed streams flowing into the system are separated into two or more product streams that flow out of the system.

Streams in

n, z_i, T, P, h, s, b, v

Separation process (system)

$\Delta S_{irr}, LW$

Streams out

n, z_i, T, P, h, s, b, v

(Surroundings)

T_0

$(W_s)_{in}$ $(W_s)_{out}$

Shaft work in and out

n	Molar flow rate
z	Mole fraction
T	Temperature
P	Pressure
h	Molar enthalpy
s	Molar entropy
b	Molar availability
v	Specific volume

Energy Balance

- Continuous and steady-state flow system

- Kinetic, potential, and surface energy changes are neglected

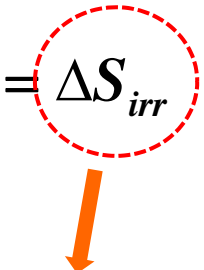- First law of thermodynamics (conservation of energy)

(stream enthalpy flows + heat transfer + shaft work)$_{\text{leaving system}}$

− (stream enthalpy flows + heat transfer + shaft work)$_{\text{entering system}}$

= 0

$$\sum_{\substack{\text{out of} \\ \text{system}}} (nh + Q + W_s) - \sum_{\substack{\text{in to} \\ \text{system}}} (nh + Q + W_s) = 0$$

Entropy Balance

- The first law provides no information on energy efficiency

- Second law of thermodynamics

(stream entropy flows + entropy flows by heat transfer)$_{\text{leaving system}}$

− (stream entropy flows + entropy flows by heat transfer)$_{\text{entering system}}$

= production of entropy by the process

$$\sum_{\substack{\text{out of}\\\text{system}}} \left(ns + \frac{Q}{T_s} \right) - \sum_{\substack{\text{in to}\\\text{system}}} \left(ns + \frac{Q}{T_s} \right) = \Delta S_{irr}$$

– Production of entropy

– Irreversible increase in the entropy of the universe

– Quantitative measure of the thermodynamic inefficiency of a process

Availability (Exergy) Balance

- The entropy balance contains no terms related to shaft work
- The entropy is difficult to relate with power consumption
- Availability (exergy)：Available energy for complete conversion to shaft work
- Stream availability function： $b = h - T_0 s$

  a measure of the maximum amount of stream energy that can be converted into shaft work if the stream is taken to the reference state

(Entropy balance) × T$_0$ − (Energy balance)

$$\sum_{\substack{\text{in to} \\ \text{system}}} \left[nb + Q\left(1 - \frac{T_0}{T_s}\right) + W_s \right] - \sum_{\substack{\text{out of} \\ \text{system}}} \left[nb + Q\left(1 - \frac{T_0}{T_s}\right) + W_s \right] = LW$$

(stream availability flows + availability of heat + shaft work)$_{\text{entering system}}$

− (stream availability flows + availability of heat + shaft work)$_{\text{leaving system}}$

= loss of availability (lost work)

Lost Work, Minimum Work, and Second Law Efficiency

- Lost work, $LW = T_0 \Delta S_{irr}$

  - The greater its value, the greater is the energy inefficiency
  - Its magnitude depends on the extent of process irreversibilities
  - Reversible process : $LW = 0$

- Minimum work of separation, $W_{\min}$

  - Minimum shaft work required to conduct the separation
  - Equivalent to the difference
    in the heat transfer and shaft work
    $$W_{\min} = \sum_{\substack{\text{out of} \\ \text{system}}} nb - \sum_{\substack{\text{in to} \\ \text{system}}} nb$$

- The second-law efficiency

$$\eta = \frac{W_{\min}}{LW + W_{\min}} = \frac{(\text{minimum work of separation})}{(\text{equivalent actual work of separation})}$$

Phase Equilibria

- The phase equilibria of the given system provide possible equilibrium compositions (separation limit)

- Equilibrium : Gibbs free energy for all phases is a minimum

$$G = G(T, P, N_1, N_2, ..., N_C)$$

$$dG = -SdT + VdP + \sum_{components} \mu_i dN_i$$

$$dG_{system} = \sum_{phases} \left[\sum_{components} \mu_i^{(p)} dN_i^{(p)} \right]_{P,T} \quad \text{(at constant T \& P)}$$

$$dN_i^{(1)} = -\sum_{p=2}^{N} dN_i^{(p)} \quad \text{(conservation of moles of each species, no reaction)}$$

$$\mu_i^{(1)} = \mu_i^{(2)} = ... = \mu_i^{(N)}$$

The chemical potential of a particular species in a multicomponent system is identical in all phases at physical equilibrium.

Fugacities and Activity Coefficients

- Chemical potential
  - Units of energy
  - Not easy to understand physical meaning

- More convenient quantities
  - Fugacity : pseudo-pressure $\bar{f}_i = C \exp(\mu_i / RT)$
  - Equality of chemical potentials → equality of fugacities
  - Fugacity coefficient $\phi_i = f_i / P$ $\bar{\phi}_i = \bar{f}_i / y_i P$
    - Ratio of fugacity and pressure
    - Reference : ideal gas
  - Activity $a_i = \bar{f}_i / f_i^0$
    - Ratio of fugacities
    - Reference : ideal solution
  - Activity coefficients $\gamma_i = a_i / x_i = \bar{f}_i / x_i f_i^0$
    - Ratio of activity and composition
    - Departure from ideal solution behavior

At equilibrium,

$$\bar{f}_i^{(1)} = \bar{f}_i^{(2)} = \cdots = \bar{f}_i^{(N)}$$

$$a_i^{(1)} = a_i^{(2)} = \cdots = a_i^{(N)}$$

$$T^{(1)} = T^{(2)} = \cdots = T^{(N)}$$

$$P^{(1)} = P^{(2)} = \cdots = P^{(N)}$$

K-Values

- Phase equilibrium ratio : ratio of mole fractions of a species present in two phases at equilibrium

- K-value (vapor-liquid equilibrium ratio; K-factor)
  : for the vapor-liquid case
  $$K_i \equiv y_i / x_i$$

- Distribution coefficient (liquid-liquid equilibrium ratio)
  : for the liquid-liquid case
  $$K_{Di} \equiv x_i^{(1)} / x_i^{(2)}$$

- Relative volatility : for the vapor-liquid case
  $$\alpha_{ij} \equiv K_i / K_j$$

- Relative selectivity : for the liquid-liquid case
  $$\beta_{ij} \equiv K_{Di} / K_{Dj}$$

Phase Equilibrium Calculations (VLE)

$$\overline{f}_{iV} = \overline{f}_{iL}$$ For vapor-liquid equilibrium

- Ideal gas + Ideal solution

$$y_i P = x_i P_i^{sat}$$ $$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P}$$

- Phi-Phi approach : equation-of-state form of K-value

$$\overline{\phi}_{iV} y_i P = \overline{\phi}_{iL} x_i P$$ $$K_i = \frac{\overline{\phi}_{iL}}{\overline{\phi}_{iV}}$$

- Gamma-Phi approach : activity coefficient form of K-value

$$\overline{\phi}_{iV} y_i P = \gamma_{iL} x_i f_{iL}^o$$ $$K_i = \frac{\gamma_{iL} f_{iL}^o}{\overline{\phi}_{iV} P} = \frac{\gamma_{iL} \phi_{iL}}{\overline{\phi}_{iV}}$$

Nonideal Thermodynamic Property Models

- <u>No universal equations</u> are available for computing, for <u>nonideal mixtures</u>, values of thermodynamic properties such as density, enthalpy, entropy, fugacities, and activity coefficients as functions of T, P, and phase composition.

  ⇒ (1) P−v−T equation−of−state models

  (2) Activity coefficient or free−energy models

- P−v−T equation−of−state models

  Nonideality is due to (1) the volume occupied by the molecules and (2) intermolecular forces among the molecules

    e.g. the van der Waals equation

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Useful Equations of State

Name	Equation	Equation Constants and Functions
(1) Ideal gas law	$P = \dfrac{RT}{v}$	None
(2) Generalized	$P = \dfrac{ZRT}{v}$	$Z = Z\{P_r, T_r, Z_c \text{ or } \omega\}$ as derived from data
(3) Redlich–Kwong (R–K)	$P = \dfrac{RT}{v-b} - \dfrac{a}{v^2+bv}$	$b = 0.08664 R T_c / P_c$ $a = 0.42748 R^2 T_c^{2.5} / P_c T^{0.5}$
(4) Soave Redlich Kwong (S R K or R K S)	$P = \dfrac{RT}{v-b} - \dfrac{a}{v^2+bv}$	$b = 0.08664 R T_c / P_c$ $a = 0.42748 R^2 T_c^2 \left[1 + f_\omega \left(1 - T_r^{0.5}\right)\right]^2 / P_c$ $f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$
(5) Peng–Robinson (P–R)	$P = \dfrac{RT}{v-b} - \dfrac{a}{v^2+2bv-b^2}$	$b = 0.07780 R T_c / P_c$ $a = 0.45724 R^2 T_c^2 \left[1 + f_\omega \left(1 - T_r^{0.5}\right)\right]^2 / P_c$ $f_\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$

- Mixing rules

$$a = \sum_{i=1}^{C} \left[\sum_{j=1}^{C} y_i y_j (a_i a_j)^{0.5} \right] \qquad b = \sum_{i=1}^{C} y_i b_i$$

Models for Activity Coefficients

$$\gamma_i = \gamma_i(T, x_1, x_2, ..., x_C)$$

Table 2.9 Empirical and Semitheoretical Equations for Correlating Liquid-Phase Activity Coefficients of Binary Pairs

Name	Equation for Species 1	Equation for Species 2
(1) Margules	$\log \gamma_1 = Ax_2^2$	$\log \gamma_2 = Ax_1^2$
(2) Margules (two-constant)	$\log \gamma_1 = x_2^2[\bar{A}_{12} + 2x_1(\bar{A}_{21} - \bar{A}_{12})]$	$\log \gamma_2 = x_1^2[\bar{A}_{21} + 2x_2(\bar{A}_{12} - \bar{A}_{21})]$
(3) van Laar (two-constant)	$\ln \gamma_1 = \dfrac{A_{12}}{[1 + (x_1 A_{12})/(x_2 A_{21})]^2}$	$\ln \gamma_2 = \dfrac{A_{21}}{[1 + (x_2 A_{21})/(x_1 A_{12})]^2}$
(4) Wilson (two-constant)	$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2)$ $+ x_2\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \dfrac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$	$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1)$ $- x_1\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \dfrac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$
(5) NRTL (three-constant)	$\ln \gamma_1 = \dfrac{x_2^2 \tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \dfrac{x_1^2 \tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2}$ $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$	$\ln \gamma_2 = \dfrac{x_1^2 \tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} + \dfrac{x_2^2 \tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2}$ $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$
(6) UNIQUAC (two-constant)	$\ln \gamma_1 = \ln \dfrac{\Psi_1}{x_1} + \dfrac{\bar{Z}}{2} q_1 \ln \dfrac{\theta_1}{\Psi_1}$ $+ \Psi_2\left(l_1 - \dfrac{r_1}{r_2}l_2\right) - q_1 \ln(\theta_1 + \theta_2 T_{21})$ $+ \theta_2 q_1\left(\dfrac{T_{21}}{\theta_1 + \theta_2 T_{21}} - \dfrac{T_{12}}{\theta_2 + \theta_1 T_{12}}\right)$	$\ln \gamma_2 = \ln \dfrac{\Psi_2}{x_2} + \dfrac{\bar{Z}}{2} q_2 \ln \dfrac{\theta_2}{\Psi_2}$ $+ \Psi_1\left(l_2 - \dfrac{r_2}{r_1}l_1\right) - q_2 \ln(\theta_2 + \theta_1 T_{12})$ $+ \theta_1 q_2\left(\dfrac{T_{12}}{\theta_2 + \theta_1 T_{12}} - \dfrac{T_{21}}{\theta_1 + \theta_2 T_{21}}\right)$

Notes on Using Phase Equilibrium Models

- Low pressure VLE
  - Gamma–Phi approach recommended
  - Poynting correction (modified Raoult's law) required for medium pressure
  - Cannot be applied when T or P condition exceeds critical T, P

- High pressure VLE
  - Phi–Phi approach recommended
  - Special care should be taken for polar components (alcohols, water, acids, amines, etc.)

- Check binary interaction parameters matrix
  - If parameters exist, use them
  - If parameters do not exist,
    - Try to obtain by regression of experimental data
    - Use group contribution method (e.g. UNIFAC)

- Special applications → Specialized models required
  - Polymer solution
  - Electrolyte solution
  - Biomolecular applications

Selecting an Appropriate Model

(LG): light gases   (HC): hydrocarbons
(PC): polar organic compounds   (A): aqueous solutions
(E): electrolytes

- If the mixture is (A) with no (PC)
  - If (E) are present → modified NRTL equation
  - If (E) are not present → a special model

- If the mixture contains (HC), covering a wide boiling rage
  → The corresponding-states method of Lee-Kesler-Plöcker

- If the boiling range of a mixture of (HC) is not wide
  - For all T and P → the P-R equation
  - For all P and noncryogenic T → the S-R-K equation
  - For all T, but not P in the critical region → the Benedict-Webb-
    Rubin-Starling method

- If the mixture contains (PC)
  - If (LG) are present → the PSRK method
  - If (LG) are not present → a suitable liquid-phase γ method