

ESTIMATION OF PHYSICAL PROPERTIES

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1. SCOPE

Knowledge of physical properties is essential for process engineers to simulate a process or to design many kinds of industrial equipment. Reliable experimental data are always to be preferred over values obtained by estimation methods. But all too often reliable data are not available.

In this standard practice, brief introduction to physical-property estimation methods and their usage are described.

2. DEFINITIONS

TYPE of Physical Properties

According to the substances, physical properties are classified as follows:

- Pure Component Properties : Properties of well-defined compounds, or molecules.
- Mixture Properties : Properties of mixtures of well-defined compounds
- Petroleum Properties : Properties of pseudocomponents subdivided from petroleum distillation data.

Physical properties are also classified as follows:

- Physical Constants : Constants characteristic for a compound, such as normal boiling point and critical constants.
- Thermodynamic Properties : Properties based on thermodynamic relationship, such as PVT data and thermal data.
- Transport Properties : Properties related to transportation of fluids, such as viscosity and surface tension.

3. WORK PROCEDURE

3.1 Data Source and Data Search

It is highly desirable to use actual process data obtained from a client or a process owner. If process data are not available, searching for the desired data in handbooks or references becomes necessary.

Nowadays, on-line data search is most convenient, if the data are not found in handbooks to hand.

Representative data sources and on-line data bases are listed in Chapter 9.

3.2 General Principles of Physical Property Estimation

Physical constants are the basis of Physical-property estimation. Normal boiling point and molecular structure are most important, followed by critical constants. Fig. 3.2.1 shows the route of physical-property estimation schematically.

On the other hand, physical-property estimation for petroleum fractions requires a different method. Petroleum fractions are subdivided to pseudocomponents based on the distillation data and bulk or fractional densities. Normal boiling points, densities and molecular weights of the pseudocomponents are estimated at first. All other properties can be estimated using these values. The estimation methods were developed by the American Petroleum Institute (API), and can be applied to pure hydrocarbons successfully. The estimation schemes are shown in Fig. 3.2.2.

4. PROPERTIES OF PURE COMPONENTS**4.1 Physical Constants**

Physical constants essential for process design, and recommendable estimation methods are listed in Table 4.1.1. Among them, accuracy of the estimation of normal boiling point and melting point are poor. —
Detailed information on individual methods is described in reference A-1).

4.2 Thermodynamic Properties

Thermodynamic properties are important for basic design especially calculation of separation processes such as distillation. The recommendable estimation methods are briefly described.

Besides the recommendable methods, simple estimation methods are given below as well.

These simple methods are, however, only suitable for quick rough estimation and accuracy is generally not as good as that of the recommendable methods.

4.2.1 Vapor Pressure: P

Riedel and Lee-Kesler methods are recommended. But these methods are not suitable for highly polar compounds such as alcohols.

[Simple Methods]

Method 1: In the case that vapor pressures at two different temperatures (t_1 , t_2) are available.

Antoine Equation is applied.

$$\log P = A - B / (C + t) \quad (1)$$

C may be estimated by normal boiling point as shown in Table 4.2.1.

B may be calculated from the value of C and two vapor pressure- temperature pairs:

$$B = [(t_2 + C)(t_1 + C) / (t_2 - t_1)] \times \log (P_2 / P_1) \quad (2)$$

A can be obtained by substitution of the values of B, C and any one of two vapor pressure-temperature pairs in Antoine equation.

<Example 4.2.1-1>

The normal boiling point of MMA (methyl methacrylate) is 101.12°C and it shows the vapor pressure of 76.36mmHg at 40°C. Estimate the vapor pressure of MMA at 50, 60, 80 and 100°C.

<Solution>

From Table 4.2.1, C = 221.

$$B = [(101.12 + 221)(40 + 221) / (101.12 - 40)] \times \log (760 / 76.36) \\ = 1372.72$$

$$A = \log P + B / (t + C) \\ = \log 760 + 1372.72 / (101.12 + 221) \\ = 7.14234$$

At 50°C,

$$\log P = 7.14234 - 1372.72 / (50 + 221) \\ = 2.077$$

$$P = 119.4 \text{ mmHg}$$

The calculated vapor pressure from the Antoine constants given in Ref. M-1) is 117.5mmHg. Error is 1.9mmHg (1.6%).

The vapor pressures estimated at other temperatures are given below.

Temperature	°C	50	60	80	100
Estimated Value	mmHg	119.4	180.8	381.1	734.4
Literature Value	mmHg	117.5	176.6	373.7	733.4
Error	mmHg	1.9	4.2	8.1	1.0
Relative Error	%	1.6	2.4	2.2	0.1

Method 2 : In the case where only one vapor pressure is available.

Find the Antoine constants of an analogous compound, having a similar chemical structure.

Set the values of B and C to be equal to those of the analogous compound.

The value of A may be estimated by the temperature-vapor pressure pair.

If the known vapor pressure is normal boiling point, C may be estimated using Table 4.2.1 and only B is set equal to that of the analogous compound.

This method, however, often gives large estimation errors at temperatures largely different from the temperature at which the vapor pressure was measured.

<Example 4.2.1-2>

The normal boiling point of isobutyl acetate is 118.1°C.

Estimate the vapor pressure of isobutyl acetate at 40,60,80, and 100°C.

<Solution>

From Table 4.2.1, C = 221. B is set to 1368.29 from the Antoine constant of butyl acetate given in Ref. M-1)

$A = \log 760 - 1368.29 / (221 + 118.1) = 6.91588$

The estimated vapor pressures are shown below compared with the literature values.

Temperature	°C	50	60	80	100
Estimated Value	mmHg	47.1	111.3	234.5	450.1
Literature Value	mmHg	41.5	100.6	218.9	435.5
Error	mmHg	5.6	10.7	15.6	14.6
Relative Error	%	13.5	10.6	7.1	3.3

4.2.2 Ideal Gas Heat Capacity: C_p^0

Benson method is recommended.

Harrison-Seaton method, Ref. H-7) is much simpler than Benson method and gives only slightly inferior results.

4.2.3 Enthalpy of Vaporization: ΔH_v

Vetere and Riedel methods are recommended.

[Simple method]

Clausius-Clapeyron equation is combined with Antoine equation.

$$dP / dT = \Delta H_v / (T \cdot \Delta V) \quad (3)$$

$$\log P = A - B / (C + t) \quad (4)$$

where ΔV is volume change in vaporization, that is $\Delta V = V_g - V_l = RT (Z_g - Z_l) / P$

$$\text{then, } \Delta H_v = 2.303B \cdot R \cdot T^2 \cdot (Z_g - Z_l) / (t + C)^2 \quad (5)$$

The difference in the compressibility factors can be estimated using the following equation.

$$Z_g - Z_l = \sqrt{1 - (P / P_c) / (T / T_c)^3} \quad (6)$$

If T_c and P_c are not known and cannot be estimated, $(Z_g - Z_l)$ can be obtained from Table 4.2.2. This method cannot be applied to the gas-phase associating compounds, such as carboxylic acids.

<Example 4.2.3>

Estimate the enthalpy of vaporization of methanol at 50°C.

<Solution>

From Ref. M-1) Antoine constants of methanol are

$A = 8.08097$, $B = 1587.271$, and $C = 239.726$

From Ref. E-10) $T_c = 512.64\text{K}$ and $P_c = 79.86\text{atm}$.

The vapor pressure at 50°C is 416.6mmHg (0.548atm) from the Antoine equation.

$$T_r = (50 + 273.15) / 512.64 = 0.630$$

$$P_r = 0.548 / 79.86 = 0.0069$$

Then

$$Z_g - Z_l = \sqrt{1 - 0.0069 / 0.630^3} = 0.986$$

$$R = 1.9872 \text{ cal/mol} \cdot \text{K}$$

$$\begin{aligned} \Delta H_v &= 2.303 \times 1587.271 \times 1.9872 \times (50+273.15)^2 \times 0.986 / (50+239.726)^2 \\ &= 8883 \text{ cal/mol} \end{aligned}$$

Observed value in Ref. E-10) is 8628 cal/mol.

The estimation error is 255cal/mol (3.0%).

4.2.4 Liquid Heat Capacity: C_{p_l}

The Chueh-Swanson method is recommended for estimation of liquid heat capacity at 20°C, and for temperature dependency the Missenard method is recommended.

[Simple Method]

The assumption is made that various groups in a molecule contribute a definite value to the total molar heat capacity.

Chueh and Swanson have proposed the values shown in Table 4.2.3 to estimate C_{p_l} at 20°C.

<Example 4.2.4>

Estimate the liquid heat capacity of 1,4-pentadiene at 20°C.

<Solution>

From Table 4.2.3

$$C_{p_l} = 2 (\text{CH}_2=) + 2 (-\text{CH}=) + (-\text{CH}_2-) + \text{corrections noted in Table 4.2.3}$$

$$= 2 (5.20) + 2 (5.10) + 7.26 + 4.5 + 2.5$$

$$= 34.9 \text{ cal/mol} \cdot \text{K}$$

The observed value is 35.1cal/mol·K.

4.2.5 Vapor Heat Capacity : C_{pv}

The heat capacity of a real gas is related to the value in the ideal-gas state at the same temperature.

$$C_{pv} = C_p^0 + \Delta C_{pv} \quad (7)$$

ΔC_{pv} , a residual heat capacity, is calculated by equations of state, such as SRK or PR.

For Lee-Kesler method, a residual heat capacity is represented as below.

$$\Delta C_{pv} = C_{pv} - C_p^0 = (\Delta C_p)^{(0)} + \omega(\Delta C_p)^{(1)} \quad (8)$$

where ω is an acentric factor.

$(\Delta C_p)^{(0)}$ and $(\Delta C_p)^{(1)}$ are shown in tabular forms in ref. A-1).

The heat capacity of a real gas can be approximated to be that of ideal gas at low pressures and high temperatures.

4.2.6 Liquid and Vapor Enthalpies: H_l and H_v

Enthalpies of real substances are calculated by either of the following two methods:

Method A: Both liquid and vapor enthalpies are calculated by the addition of ideal gas enthalpy and enthalpy departure, that is the difference of enthalpy from ideal gas enthalpy.

$$H_l = (H-H^0)_l + H^0 \quad (9)$$

$$H_v = (H-H^0)_v + H^0 \quad (10)$$

Enthalpy departure, $(H-H^0)_l$ or $(H-H^0)_v$, can be calculated by an equation of state, or estimated from generalized thermodynamic chart, e.g. Fig. 4.2.1.

Method B: Liquid enthalpy is obtained by integration of liquid heat capacity.

Addition of enthalpy of vaporization to liquid enthalpy gives vapor enthalpy.

$$H_l = \int C_{p,l} dt \quad (11)$$

$$H_v = H_l + \Delta H_v \quad (12)$$

Method B is suitable for hand calculation.

4.2.7 Liquid Density: ρ

Gunn-Yamada and Le Bas methods are recommended. For nonpolar compounds, e.g. hydrocarbons, API and Lee-kesler methods can be used as well.

[Simple Methods]

Method 1:

The model by Elbro et al. for predicting the molar volume of a liquid, V_m , is simply stated as follows:

$$V_m = \sum n_i \cdot \Delta V_i \quad (13)$$

where n_i is the number of group i , and the temperature dependency of the molar group volume ΔV_i , is given by the following polynomial function:

$$\Delta V_i = A_i + B_i \times T + C_i \times T^2 \quad (14)$$

where temperature (K) can vary between the melting and normal boiling point. Parameters A, B, and C are given in Table 4.2.4 for 36 groups.

<Example 4.2.7-1>

Estimate the liquid density of isopropyl acetate at 20°C.

<Solution>

$$V_m = V(\text{CH}_3\text{COO}) + V(\text{CH}) + 2V(\text{CH}_3)$$

At 20°C, or 293.15K

$$V(\text{CH}_3\text{COO}) = 42.820 - 20.50 \times 10^{-3}(293.15) + 16.42 \times 10^{-5}(293.15)^2 = 50.92$$

$$V(\text{CH}) = 6.297 - 21.92 \times 10^{-3}(293.15) = -0.13$$

$$V(\text{CH}_3) = 18.960 + 45.58 \times 10^{-3}(293.15) = 32.32$$

$$V_m = 50.92 - 0.13 + 2(32.32) = 115.44 \text{ cm}^3/\text{mol}$$

The molecular weight is 102.133, then

$$\rho = 102.133/115.44 = 0.885 \text{ g/cm}^3$$

The observed value from Ref. E-12) is 0.877 g/cm³. The estimation error is 0.008 g/cm³ (0.9%).

Method 2:

If the critical constants of a compound are known, or estimated, liquid density can be estimated by the generalized correlation shown in Fig. 4.2.2.

Where the reduced density, ρ_r , is defined as

$$\rho_r = \rho/\rho_c = V_c/V \quad (15)$$

<Example 4.2.7-2>

Estimate the density of liquid ammonia at 310K (36.85°C) and 100bar (98.7atm).

<Solution >

From Ref. B-1) $T_c = 405.6\text{K}$, $P_c = 112.8\text{bar}$ and $V_c = 72.5\text{cm}^3/\text{mol}$.

$$T_r = 310/405.6 = 0.764$$

$$P_r = 100/112.8 = 0.887$$

From Fig. 4.2.2 $\rho_r = 2.38$.

$$V = V_c/\rho_r = 72.5/2.38 = 30.5\text{cm}^3/\text{mol}$$

In comparison with the experimental value of 28.6 cm³/mol, this result is in error by 6.6%.

4.2.8 Vapor Density: ρ_v

Vapor density is usually calculated by an equation of state, such as Soave-Redlich-Kwong (SRK) and Peng-Robinson(PR).

[Simple Methods]

The ideal-gas equation of state is available for estimating vapor density, or molar volume at low pressures.

$$PV_m = RT \quad (16)$$

At high pressures, generalized thermodynamic chart shown from Fig. 4.2.3 to Fig. 4.2.7 are used to estimate the compressibility factor, Z ,

where $Z = Z^0 + \omega Z^1$

The value of Z is applied into $PV_m = ZRT$ to give molar volume V_m .

The compressibility factor Z was also correlated by generalized virial-coefficient method resulting in the following equations.

$$Z^0 = 1 + (0.083 - \frac{0.042}{T_r^{1.6}}) \times \frac{P_r}{T_r} \quad (17)$$

$$Z^1 = (0.139 - \frac{0.172}{T_r^{4.2}}) \times \frac{P_r}{T_r} \quad (18)$$

<Example 4.2.8>

Estimate the molar volume of butane at 510K and 25bar by each of the following:

- (a) The ideal-gas equation.
- (b) The generalized compressibility-factor correlation.
- (c) The generalized virial-coefficient correlation

<Solution>

- (a) By the ideal-gas equation,

$$V = RT/P = 83.14 \cdot 510/25 = 1696 \text{ cm}^3/\text{mol}$$

- (b) Taking the value of T_c and P_c from Ref.B-1),

$$T_r = 510/425.2 = 1.198 \text{ and } P_r = 25/38.0 = 0.658$$

Figures 4.2.3 and 4.2.5 provide:

$$Z^0 = 0.865, Z^1 = 0.038$$

$\omega = 0.193$, then

$$Z = Z^0 + \omega Z^1 = 0.872$$

$$V = ZRT/P = 0.872 \cdot 83.14 \cdot 510/25 = 1479 \text{ cm}^3/\text{mol}$$

If we take $Z = Z^0$, neglecting the term ωZ^1 , then $V = 1467 \text{ cm}^3/\text{mol}$, which is less than 1 percent lower than the value obtained above.

- (c) Z^0 and Z^1 are given by Eqs. (17) and (18) as follows:

$$Z^0 = 0.872$$

$$Z^1 = 0.032$$

$$Z = 0.879$$

$$V = 1490 \text{ cm}^3/\text{mol}$$

The experimental value is $1481 \text{ cm}^3/\text{mol}$.

4.3 Transport Properties

Transport properties are related to transportation of fluids and used for sizing of various kinds of equipment and hydraulic calculation for pumps, compressors, piping, etc.

4.3.1 Liquid Viscosity: μ_l

The Orrick-Erbar and Letsou-Stiel methods are recommended for estimating the liquid viscosity.

[Simple Methods]

Method 1: If only one viscosity datum is available, viscosity at other temperatures can be approximately extrapolated by the equation:

$$\mu^{-0.2661} = \mu_0^{-0.2261} + (t - t_0) / 233 \quad (19)$$

or estimated from Fig. 4.3.1.

Method 2: If two pairs of temperature-viscosity data are available, it is often a good approximation to assume μ_1 is linear, reciprocal to absolute temperature:

$$\log \mu_1 = A + B/T \quad (20)$$

General viscosity chart can be also used.

4.3.2 Vapor Viscosity: μ_v

The Reichenberg method is recommended.

4.3.3 Liquid Thermal Conductivity: κ_l

The Sato-Riedel and Missenard methods are recommended.

4.3.4 Vapor Thermal Conductivity: κ_v

The Stiel-Thodos method is recommended.

4.3.5 Surface Tension: σ

The Macleod-Sugden and Brock-Bird methods are recommended.

[Simple Method]

Imoto's Method

$$\sigma = 0.25 \times \alpha \times \frac{\Delta U_v}{V_m^{2/3} \times N_a^{1/3}} \times 10^7 \quad (21)$$

Where σ : Surface tension dyne/cm
 ΔU_v : Internal energy of vaporization J/mol
 V_m : Molar volume cm³/mol
 N_a : Avogadro number 6.022×10^{23} /mol

Ideal gas rule is assumed:

$$\Delta U_v = \Delta H_v - RT \quad (R = 8.314 \text{ J/mol} \cdot \text{K}) \quad (22)$$

ΔH_v may be estimated from vapor pressure or Antoine constants as shown in 4.2.3. The value of α is listed in Table 4.3.1.

<Example 4.3.5>

Estimate the surface tension of decane at 25°C.

<Solution>

Enthalpy of vaporization of decane may be estimated as shown in Section 4.2.3.

From Ref. C-5) Antoine equation of decane is

$$\log P = 6.94365 - 1495.17 / (193.86 + t)$$

At 25°C $P = 1.29 \text{ mmHg}$, then $Z_g - Z_l$ can be assumed to be unity.

$$\begin{aligned} \Delta H_v &= 2.303 \times 1495.17 \times 8.314 \times (25 + 273.15)^2 \times (1 / (193.86 + 25)^2) \\ &= 53110 \text{ J/mol (Measured value is 50700 J/mol from Ref.E-3)} \end{aligned}$$

$$\begin{aligned} \Delta U_v &= 53110 - 8.314 \times 298.15 \\ &= 50630 \text{ J/mol} \end{aligned}$$

Molar volume may be estimated by the method described at Section 4.2.6.

From Table 4.2.4

$$V(\text{CH}_3) = 18.96 + 45.58 \times 10^{-3} T$$

$$V(\text{CH}_2) = 12.52 + 12.94 \times 10^{-3} T$$

$$V_m = 2V(\text{CH}_3) + 8V(\text{CH}_2) = 196.1 \text{ cm}^3/\text{mol (Measured value is 195.5 cm}^3/\text{mol)}$$

From Table 4.3.1 $\alpha = 0.6$

$$\begin{aligned} \sigma &= 0.25 \times 0.6 \times \frac{50630}{(196.1)^{2/3} \times (6.022 \times 10^{23})^{1/3}} \times 10^7 \\ &= 26.6 \text{ dyne/cm} \end{aligned}$$

Ref. C-5) gives the following equation for the surface tension of decane.

$$\sigma = 25.67 - 0.09197 \times t$$

According to this equation, at $t = 25^\circ\text{C}$

$$\sigma = 23.4 \text{ dyne/cm}$$

The estimation error is 3.2 dyne/cm (13.7%).

5. PROPERTIES OF MIXTURES

Properties of mixtures are usually estimated by application of appropriate mixing rules using the properties of components comprising the mixtures.

The representative mixing rules for individual properties are shown below.

Notice that the mixing rules sometimes give large errors for the mixtures containing highly polar compounds, e.g. aqueous solutions. Therefore it is highly recommendable to use experimental data for aqueous mixtures.

5.1 Liquid Density

COSTALD and Racket equations, which are widely used correlation models for liquid densities of pure components, have their own mixing rules.

When the densities of mixtures is estimated by those of their components, the following simple molar additivity is used.

$$\rho = \frac{1}{\sum \frac{\omega_i}{\rho_i}} \quad (23)$$

Where

ρ	:	Density of the mixture [kg/m ³]
ρ_i	:	Density of component i
ω_i	:	Weight fraction of component i

5.2 Vapor Density

To estimate the densities or molar volumes of vapor mixtures, equation of state, such as SRK, PR, and Lee-Kesler is the most recommendable method.

In most cases, binary interaction parameters are required for high accuracy. Values of the parameters determined from vapor-liquid equilibrium data can be used in volume calculations.

At low pressures, ideal gas equation of state may be used.

5.3 Liquid Viscosity

$$\mu = \left[\sum \left(x_i \mu_i^{\frac{1}{3}} \right) \right]^3 \quad (24)$$

refs. A-4), 5).

5.4 Vapor Viscosity

$$\mu = \frac{\sum (y_i \mu_i \sqrt{M_i})}{\sum (y_i \sqrt{M_i})} \quad (25)$$

refs. A-5), 6).

5.5 Liquid Thermal Conductivity

$$\frac{1}{\kappa^2} = \frac{\sum x_i M_i \frac{1}{\kappa_i^2}}{\sum x_i M_i} \quad \text{or} \quad \frac{1}{\kappa^2} = \sum \omega_i \frac{1}{\kappa_i^2} \quad (26)$$

refs. A-6).

Where

x_i	:	Mole fraction of component i
w_i	:	Weight fraction of component i
M_i	:	Molecular weight of component i

5.6 Vapor Thermal Conductivity

$$\kappa = \frac{\sum \left[y_i \kappa_i (M_i)^{\frac{1}{3}} \right]}{\sum \left[y_i (M_i)^{\frac{1}{3}} \right]} \quad (27)$$

refs. A-5), 6).

5.7 Surface Tension

$$\frac{1}{\sigma} = \sum \left(x_i \frac{1}{\sigma_i} \right) \quad (28)$$

refs. A-1).

Where x_i : Mole fraction of component i in liquid
 ω_i : Weight fraction of component i in liquid
 y_i : Mole fraction of component i in vapor
 M_i : Molecular weight of component i

6. PROPERTIES OF PETROLEUM FRACTIONS

The references for properties of petroleum fractions are given in Chapter 9 with symbol R.

7. PHASE EQUILIBRIUM

Knowledge of phase equilibria is important for designing separation processes.

Usage of phase-equilibrium calculation models is described below. Further details of individual methods are shown in Refs. A-6), A-7) and B.

7.1 Vapor-Liquid Equilibrium**7.1.1 Ideal Solution Model**

The ideal solution model, or ideal K-value method is only applicable to systems which exhibit behavior close to ideality in the liquid phase.

Mixtures consisting of the components having similar chemical structures, such as BTX (benzene-toluene-xylene) and mixed xylenes show nearly ideal behavior.

7.1.2 Activity Coefficient Methods

Activity coefficient models are suitable for VLE calculation for strongly nonideal systems at low pressures.

A number of activity coefficient models were published. The classic Margules and van Laar methods are rarely used now. The regular solution model is also scarcely used, but this model is used as part of the Chao-Seader (CS) and Grayson-Streed (GS) methods described later.

Wilson, NRTL (Non-Random Two Liquid) and UNIQUAC (Universal Quasi-Chemical) are most recommendable for nonideal systems. There are no significant differences in accuracy among these three methods.

7.1.3 Activity Coefficient with Group Contribution Method

The group contribution methods for the calculation of activity coefficients are particularly attractive because they make it possible to predict phase equilibria for which no experimental data exist.

Two group contribution methods have gained widespread popularity: ASOG (analytical solution of groups) and UNIFAC (UNiquac FACtor). The UNIFAC model is more elaborate than ASOG.

The errors of UNIFAC method are about twice as large as those of the usual activity coefficient methods, Wilson, NRTL, UNIQUAC, with well optimized binary parameters.

Modification of UNIFAC has been proposed by two groups of researchers, UNIFAC-Dortmund and UNIFAC-Lyngby, to improve the accuracy.

A drawback of these methods is the necessity to use a special parameter table.

7.1.4 Gas-Phase Association

In systems containing carboxylic acids, such as acetic acid and acrylic acid, two or three acid molecules tend to form a dimer or trimer, resulting in large deviation from vapor ideality even at very low pressures.

To account for this gas-phase association, two methods are used.

Method A: Consideration of gas-phase association constants.

Association constants are defined in terms of partial pressures of monomer, dimer and trimer.

JAPETS uses this method, but only the Wilson method with gas-phase association is available.

Method B: Hayden-O'Connell method.

This method is a modification of virial coefficient based on the association.

Hayden-O'Connell method is widely used in commercial simulators combined with any kind of activity coefficient models.

7.1.5 Equation of State Methods

Equations of state are now widely used for calculating the phase equilibria of mixtures of nonpolar and slightly polar substances at high pressures.

For the mixtures of light hydrocarbons and inorganic gases e.g. N_2 , CO, CO_2 , O_2 , H_2S , H_2 , simple cubic equations of SRK (Soave-Redlich-Kwong) and PR (Peng-Robinson) with classic quadratic mixing rules are recommendable.

Nowadays, modifications of mixing rules of equations of state to improve the ability to represent the phase behavior of strongly nonideal mixtures, especially for polar compounds, have been developed.

In many models SRKMHV2 (SRK with Huron-Vidal 2nd order mixing rule) and PRMHV2 are recommendable for the mixtures containing polar compounds at high pressures. The modified UNIFAC-Lyngby model is used as the mixing rule in these methods.

7.1.6 Binary Parameters

Binary interaction parameters are necessary for high accuracy of calculation of phase equilibria using both activity coefficient methods and equations of state.

Binary parameters can be determined from phase equilibrium data in literature or measured on site by using ASPEN Data Regression System or JAPETS VLE-D and VLE-P.

The simulators such as PRO II and ASPEN incorporate a large number of parameters. It is, however, important to check if all the necessary parameters are stored. It is also desired to check the source of the parameters in order to evaluate whether the parameters were determined in similar conditions to the system to be calculated.

In Table 7.1.1 and 7.1.2, standard interaction parameters k_{ij} for SRK and PR equations of state are shown. It should be noted that these values are obtained from VLE data measured in wide range of temperature and pressure.

7.1.7 Treatment of Noncondensable Components

In the case that noncondensable components such as inorganic gases are included in the systems which are to be calculated by an activity coefficient model, Henry's constants are used to estimate the solubilities: see section 7.4.

7.1.8 Semiempirical Methods

There are several semiempirical methods mainly used for VLE of the systems containing petroleum pseudocomponents.

The BK10 (Braun K-10) is a classical convergence pressure method and is used for low-pressure VLE of petroleum fractions.

The CS (Chao-Seader) method was originally developed for the vapor-liquid equilibrium in light hydrocarbon systems. The CS method uses the regular-solution model, the Redlich-Kwong equation of state and Pitzer's corresponding-state principle for calculations of the activity coefficients, vapor fugacity coefficients and liquid fugacities, respectively.

The GS (Grayson-Streed) method is a modification of the CS method to improve the accuracy of the systems containing hydrogen and/or methane and to extend the application range of temperature and pressure.

7.1.9 Recommendable Methods for Process Simulation

Table 6.1.3 lists the available VLE calculation methods in the representative process simulators.

Guidelines for choosing appropriate methods for special applications are shown in Table 7.1.4.

7.2 Liquid-Liquid Equilibrium or Liquid Mutual Solubility

Liquid-liquid equilibrium is described by the following equation:

$$\gamma_1^1 x_1^1 = \gamma_1^2 x_1^2 \quad (29)$$

The superscripts 1 and 2 mean two liquid phases.

Activity coefficients in the equation are determined from LLE data using NRTL or UNIQUAC equation.

The LLE can be estimated by the UNIFAC-LL group contribution method.

7.3 Freezing Point and Solubilities of Solids in Liquids

Solubility of the solid 2 in the solvent 1 is given by the equation:

$$\ln \gamma_2 x_2 = -\frac{\Delta H_m}{RT} \left(1 - \frac{T}{T_m}\right) - \frac{\Delta C_p}{R} \left(\frac{T_m - T}{T}\right) - \frac{\Delta C_p}{R} \ln \frac{T_m}{T} \quad (30)$$

Where	γ_2	:	Activity coefficient of component 2 (solute)
	x_2	:	Mole fraction of component 2 in liquid
	ΔH_m	:	Enthalpy of fusion of component 2
	T	:	Temperature [K]
	T_m	:	Melting point of component 2 [K]

$$\Delta C_p = C_{pl} - C_{pls}$$

Difference of heat capacity of component 2

Activity coefficient γ_2 may be calculated by Wilson, NRTL, UNIQUAC, or UNIFAC equation.

[Simple Method]

Neglecting the difference in heat capacities of solid and liquid, ΔC_p the following equation is obtained:

$$\ln \gamma_2 x_2 = -\frac{\Delta H_m}{RT} \left(1 - \frac{T}{T_m}\right) \quad (31)$$