

CHAPTER VI
ESTIMATION OF THERMODYNAMIC PROPERTIES
AND TRANSPORT PROPERTY

6.1 INTRODUCTION

Thermodynamic properties are important for chemical process design and simulation of any processes. In this chapter, we will consider methods for estimating thermodynamic properties which are necessary for calculating phase equilibria. The end of this chapter estimation of transport property (liquid viscosity) is taken into consideration.

6.2 ESTIMATION OF COMPRESSIBILITY FACTOR(Z) ,MOLAR VOLUME (V)

The compressibility factor and molar volume can be calculated from cubic equation equation (5-2). An equivalent form is equation (5-3). We can solve this equation by a numerical method to get values of compressibility factor. Molar volume can be calculated from

$$V = \frac{ZRT}{P} \quad (6-1)$$

Solution of the above equation provides two values of Z and V. For vapor phase, compressibility factor and molar volume are Z^V and V^V respectively, and for liquid phase, compressibility factor and molar volume are Z^L and V^L respectively.

6.3 ESTIMATION OF FUGACITY (f) AND FUGACITY COEFFICIENT (ϕ)

6.3.1 Fugacity of a pure component

Equation of state will be used to identify the state of vapor-liquid equilibrium in pure fluid. At vapor-liquid equilibrium, the equality of molar Gibbs free energy in the coexisting phases are

$$G^L(T, P) = G^V(T, P) \quad (6-2)$$

with
$$dG = -SdT + VdP \quad (6-3)$$

so that
$$\left(\frac{\partial G}{\partial P} \right)_T = -S \quad (6-4)$$

$$\left(\frac{\partial G}{\partial P} \right)_T = V \quad (6-5)$$

From equations of state, we can compute V as a function of P and T , only equation (6-5) will be considered further. Integration of equation (6-5) between any two pressure P_1 and P_2 (at constant temperature) yields

$$G(T_1, P_2) - G(T_1, P_1) = \int_{P_1}^{P_2} V dP \quad (6-6)$$

If the fluid is an ideal gas, $V^{id} = \frac{RT}{P}$, so that

$$G^{id}(T_1, P_2) - G^{id}(T_1, P_1) = \int_{P_1}^{P_2} \frac{RT}{P} dP \quad (6-7)$$

Subtracting equation (6-7) from equation (6-6) gives

$$\left[G(T_1, P_2) - G^{id}(T_1, P_2) \right] - \left[G(T_1, P_1) - G^{id}(T_1, P_1) \right] = \int_{P_1}^{P_2} \left(V - \frac{RT}{P} \right) dP \quad (6-8)$$

Setting P_1 equal to zero, at the pressure equal to zero all fluids are ideal gases so that

$$G(T_1, P=0) = G^{id}(T_1, P=0), \text{ yields}$$

$$G(T, P) - G^{id}(T, P) = \int_0^P \left(V - \frac{RT}{P} \right) dP \quad (6-9)$$

Fugacity is a thermodynamic function which is defined as

$$f = P \exp \left\{ \frac{G(T, P) - G^{id}(T, P)}{RT} \right\} = P \exp \left\{ \frac{1}{RT} \int_0^P \left(V - \frac{RT}{P} \right) dP \right\} \quad (6-10)$$

Fugacity coefficient is defined as

$$\phi = \frac{f}{P} = \exp \left\{ \frac{G(T, P) - G^{id}(T, P)}{RT} \right\} = \exp \left\{ \frac{1}{RT} \int_0^P \left(V - \frac{RT}{P} \right) dP \right\} \quad (6-11)$$

From this definition, the fugacity has units of pressure and that $f \longrightarrow P$ as

$P \longrightarrow 0$; that is, the fugacity becomes equal to the pressure at pressures low enough that the fluid approaches the ideal gas state. Similarly, the fugacity coefficient $\phi = \frac{f}{P} \longrightarrow 1$ as $P \longrightarrow 0$.

The fugacity function has been introduced because its relation to the Gibbs free energy makes it useful in phase equilibrium calculations. Criterion for equilibrium between two phases is $G^L = G^V$, when temperature and pressure are constant and equal in both phases. Using this result in equation (6-10) yields

$$f^L(T, P) = f^V(T, P) \quad (6-12)$$

as the condition for phase equilibrium. Equation (6-12) can be used as the criterion for equilibrium. The fugacity is related to the equation of state, the equality of fugacities provides a direct way of doing phase equilibrium calculation using equation of state.

Equations of state are in a form in which pressure is an explicit function of volume and temperature. Therefore, it is useful to have an equation relating the fugacity to an integral over volume.

An equation is started with equation (6-11) and using equation (6-13) at constant temperature in form

$$dP = \frac{1}{V} d(PV) - \frac{P}{V} dV = \frac{P}{Z} dZ - \frac{P}{V} dV \quad (6-13)$$

Integration of the above equation provides

$$\ln \frac{f(T, P)}{P} = \ln \phi = \frac{1}{RT} \int_{V=\infty}^V \left[\frac{RT}{V} - P \right] dV - \ln Z + (Z - 1) \quad (6-14)$$

where $Z = \frac{PV}{RT}$

6.3.2 Fugacity of a pure gas species

Fugacity of a pure gaseous species can be computed using a volumetric equation of state, that is

$$\ln \frac{f^V(T, P)}{P} = \frac{1}{RT} \int_{V=\infty}^{V=Z^V RT/P} \left(\frac{RT}{V} - P \right) dV - \ln Z^V + (Z^V - 1) \quad (6-15)$$

where superscript V has been used to designate for the fugacity and compressibility of vapor phases. The fugacity of a pure gas can be computed by integration of equation (6-15). At low pressures, where a gas can be described by the ideal gas law.

$$PV = RT \quad \text{or} \quad Z^V = 1 \quad (6-16)$$

that is

that is

$$\ln \frac{f^v(T, P)}{P} = 0 \quad \text{or} \quad f^v(T, P) = P \quad (6-17)$$

Thus, for a low pressure gas, the fugacity of a species is equal to total pressure.

For Cubic equation

Redlich-Kwong equation

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \quad (6-18)$$

$$\ln \frac{f^v}{P} = Z^v - 1 - \ln \left[Z^v \left(1 - \frac{b}{V^v} \right) \right] - \frac{a}{bRT^{1.5}} \ln \left(1 + \frac{b}{V^v} \right) \quad (6-19)$$

where

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} \quad (6-20)$$

$$b = \frac{0.08664RT_c}{P_c} \quad (6-21)$$

Soave equation

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)} \quad (6-22)$$

$$\ln \frac{f^v}{P} = Z^v - 1 - \ln \left[Z^v \left(1 - \frac{b}{V^v} \right) \right] - \frac{a\alpha}{bRT} \ln \left(1 + \frac{b}{V^v} \right) \quad (6-23)$$

where

$$a = \frac{0.42748R^2T_c^2}{P_c} \quad (6-24)$$

$$b = \frac{0.08664RTc}{Pc} \quad (6-25)$$

$$\alpha = \left[1 + (0.48 + 1.57\omega - 0.176\omega^2)(1 - Tr^{0.5})\right]^2 \quad (6-26)$$

Peng-Robinson equation

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2bV - b^2} \quad (6-27)$$

$$\ln \frac{f^V}{P} = (Z^V - 1) - \ln\left(Z^V - \frac{bP}{RT}\right) - \frac{a}{2.8284bRT} \ln\left[\frac{Z^V + 2.4142bP/RT}{Z^V - 0.4142bP/RT}\right] \quad (6-28)$$

where

$$a = \frac{0.45724R^2Tc^2}{Pc} \quad (6-29)$$

$$b = \frac{0.07780RTc}{Pc} \quad (6-30)$$

$$\alpha = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - Tr^{0.5})\right]^2 \quad (6-31)$$

6.3.3 Fugacity of a pure liquid species

The fugacity of a pure liquid species can be computed by equation of state as follows:

$$\ln \frac{f^L(T, P)}{P} = \frac{1}{RT} \int_{V=\infty}^{V=Z^L RT/P} \left(\frac{RT}{V} - P\right) dV - \ln Z^L + (Z^L - 1) \quad (6-32)$$

where the superscript L is designated for the fugacity and compressibility of the liquid phase. Integration of equation (4-30) will provide the fugacity of liquid phase.

For Cubic equation

Soave equation

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)} \quad (6-33)$$

$$\ln \frac{f^L}{P} = Z^L - 1 - \ln \left[Z^L \left(1 - \frac{b}{V^L} \right) \right] - \frac{a\alpha}{bRT} \ln \left(1 + \frac{b}{V^L} \right) \quad (6-34)$$

where

$$a = \frac{0.42748R^2T_c^2}{P_c} \quad (6-35)$$

$$b = \frac{0.08664RT_c}{P_c} \quad (6-36)$$

$$\alpha = \left[1 + (0.48 + 1.57\omega - 0.176\omega^2)(1 - Tr^{0.5}) \right]^2 \quad (6-37)$$

Peng-Robinson equation

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2bV - b^2} \quad (6-38)$$

$$\ln \frac{f^L}{P} = (Z^L - 1) - \ln \left(Z^L - \frac{bP}{RT} \right) - \frac{a}{2.8284bRT} \ln \left[\frac{Z^L + 2.4142bP/RT}{Z^L - 0.4142bP/RT} \right] \quad (6-39)$$

where

$$a = \frac{0.45724 R^2 T_c^2}{P_c} \quad (6-40)$$

$$b = \frac{0.07780 R T_c}{P_c} \quad (6-41)$$

$$\alpha = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - Tr^{0.5}) \right]^2 \quad (6-42)$$

Fugacity of a pure liquid which is calculated by equation of state is on for saturation line only and the numerical values of the liquid phase fugacity and vapor phase fugacity are identical along the saturation line.

6.3.4 The fugacity of species in gaseous and liquid mixtures

The fugacity of species in gaseous mixtures is calculated by equation (6-43).

$$\ln \frac{\bar{f}_i^V(T, P, y_i)}{y_i P} = \frac{1}{RT} \int_{V=\infty}^{V=Z^V RT/P} \left[\frac{RT}{V} - N \left(\frac{\partial P}{\partial N_i} \right)_{T, V, N_j \neq i} \right] dV - \ln Z^V \quad (6-43)$$

The fugacity of liquid mixtures is calculated by equation (6-44).

$$\ln \frac{\bar{f}_i^L(T, P, x_i)}{x_i} = \frac{1}{RT} \int_{V=\infty}^{V=Z^L RT/P} \left[\frac{RT}{V} - N \left(\frac{\partial P}{\partial N_i} \right)_{T, V, N_j \neq i} \right] dV - \ln Z^L \quad (6-44)$$

For Cubic equation

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2} \quad (6-45)$$

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B^*) + \frac{A^*}{B^*(u^2 - 4w)^{0.5}} \left(\frac{b_i}{b} - \delta_i \right) \ln \frac{2Z + B^*(u + (u^2 - 4w)^{0.5})}{2Z + B^*(u - (u^2 - 4w)^{0.5})} \quad (6-46)$$

$$\text{where } \phi_i = \frac{\bar{f}_i}{y_i P} \quad (6-47)$$

$$\frac{b_i}{b} = \frac{Tc_i / Pc_i}{\sum_j y_j Tc_j / Pc_j} \quad (6-48)$$

$$\sigma_i = \frac{2a_i^{0.5}}{a} \sum_j y_j a_j^{0.5} (1 - k_{ij}) \quad (6-49)$$

For gaseous mixtures, Z in equation (6-46) is replaced by Z^V and \bar{f}_i in equation (6-47) by \bar{f}_i^V . Constants in equation (6-46), (6-47), (6-48) for cubic equation (RK, SRK, PR) are already mentioned in chapter III. For liquid mixtures, we do not have the information to calculate ϕ_i from basic PVT data (Pradeep B. Deshpande, 1985). For liquid phase, estimation of fugacity will use activity coefficient model which can be write as

$$\bar{f}_i = \gamma_i x_i f_i^L$$

where γ_i is called the activity coefficient (in the liquid phase) of component i . Data for γ_i are calculated from experimental-phase equilibrium data. In this work we use especially equation of state to predict fugacity and fugacity coefficient therefore it can not estimate fugacity and fugacity coefficient for liquid mixtures.

6.4 ESTIMATION OF ENTHALPY, ENTROPY, ENTHALPY DEPARTURE AND ENTROPY DEPARTURE

Enthalpy, entropy are useful thermodynamic properties. In analyzing process equipment, a variation in these properties can be related to operating variable, for example, the temperature rise a fluid in a heat exchanger. Therefore, it is important to estimate such property variations as the temperature and pressure.

Evaluation of enthalpy

Enthalpy is a function of temperature and pressure. Thus

$$H = f(P, T) \quad (6-50)$$

$$dH = \left(\frac{\partial H}{\partial P} \right)_T dP + \left(\frac{\partial H}{\partial T} \right)_P dT \quad (6-51)$$

$$\Delta H = H_2 - H_1 = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P} \right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T} \right)_{P_2} dT \quad (6-52)$$

$$\Delta H = H_2 - H_1 = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P} \right)_{T_2} dP + \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T} \right)_{P_1} dT \quad (6-53)$$

Enthalpy is a state function, we can compute its change between two states by the integration along any convenient path. In first method, path ADC, is a process consisting of an isothermal path and an isobaric path. The isothermal change of H takes place from P₁ to P₂, while the isobaric change occurs from T₁ to T₂. The second method, path ABC, the variation in H is determined at P₁ from T₁ to T₂ and then the variation of H from P₁ to P₂ is determined at T₂. These paths are shown in Figure 6-1.

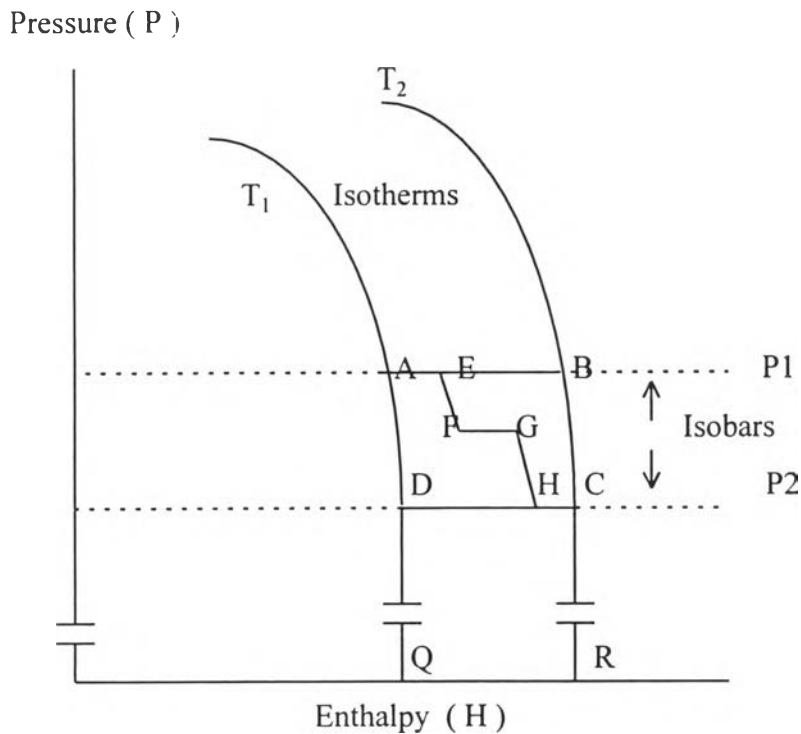


Figure 6.1 Isotherms and isobars for changes in enthalpy

In Figure 6.1, equation (6-52) is illustrated by path ADC, whereas equation (6-53) refers to path ABC. The net enthalpy change (ΔH) is represented the change from A to C. The other path is AEFBHC. Calculation ΔH by this path, values of $\left(\frac{\partial H}{\partial P}\right)_T$ and $\left(\frac{\partial H}{\partial P}\right)_P$ must be available for the various isotherms and isobars. The path for determining ΔH in Figure 6-1 with values of heat capacity at ideal gas state is (C_p^0) AQRC, that is

$$\Delta H = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_{T_1} dP + \int_{T_1}^{T_2} C_p^0 dT + \int_{P_2}^{P_1} \left(\frac{\partial H}{\partial P}\right) dP \quad (6-54)$$

or

$$\Delta H = (H^0 - H_{P_1})_{T_1} + \int_{T_1}^{T_2} C_p^0 dT - (H^0 - H_{P_2})_{T_2} \quad (6-55)$$

$(H^0 - H_{P_1})_{T_1}$ and $(H^0 - H_{P_2})_{T_2}$ are called departure function. C_p^0 is heat capacity at ideal gas state and $\int_{T_1}^{T_2} C_p^0 dT$ is enthalpy change at ideal gas state.

Evaluation of entropy

Entropy is a function of temperature and pressure. That is

$$S = f(P, T) \quad (6-56)$$

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT \quad (6-57)$$

For path ADC

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial P} \right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T} \right)_{P_2} dT \quad (6-58)$$

For path ABC

$$\Delta S = S_2 - S_1 = \int_{P_1}^{P_2} \left(\frac{\partial S}{\partial P} \right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T} \right)_{P_1} dT \quad (6-59)$$

For path AQRC

$$\Delta S = \int_{P_1}^{P^o} \left(\frac{\partial S}{\partial P} \right)_{T_1} dP + \int_{P_1}^{P_2} \left(\frac{R}{P} \right) dP + \int_{T_1}^{T_2} C_p^o \frac{dT}{T} + \int_{P^o}^{P_2} \left(\frac{\partial S}{\partial P} \right)_{T_2} dP \quad (6-60)$$

$$\Delta S = (S^o - S_{P_1})_{T_1} + R \left(\ln \frac{P_1}{P_2} \right) + \int_{T_1}^{T_2} C_p^o \frac{dT}{T} - (S^o - S_{P_2})_{T_2} \quad (6-61)$$

The term $R \left(\ln \frac{P_1}{P_2} \right) + \int_{T_1}^{T_2} C_p^o \frac{dT}{T}$ is an ideal gas entropy.

Departure functions

Let L be the value of some thermodynamic property of pure component (or a mixture with a fixed composition) at some P, T . If L^o is defined to be the value of L at the same temperature and composition but at an ideal gas state and at a reference pressure P^o then a departure function is defined as $L - L^o$ or $L^o - L$. In the reference state at T, P^o , the molal volume V^o would be given by $V^o = RT/P^o$. Departure function can be expressed in a term of Helmholtz energy (A) at constant temperature and composition, the variation in the Helmholtz energy with molar volume is

$$dA = -PdV \quad (6-62)$$

Integrating at constant temperature and composition from reference volume (V^o) to the system volume (V) gives

$$A - A^o = - \int_{V^o}^V PdV \quad (6-63)$$

We break the integral into two parts:

$$A - A^o = - \int_{\infty}^V PdV - \int_{V^o}^{\infty} PdV \quad (6-64)$$

The first integral requires real gas properties, that is, $P=f(V)$ at constant temperature T . The second is an ideal gas properties. Rearrange equation (6-64) gives

$$A - A^o = - \int_{\infty}^V \left(P - \frac{RT}{V} \right) dV - RT \left(\ln \frac{V}{V^o} \right) \quad (6-65)$$

The departure function for A depends on V° . $A - A^\circ$ does not vanish even for an ideal gas unless V° is chosen to equal V . Other departure functions are obtained from equation (6-35):

$$S - S^\circ = - \frac{\partial}{\partial T} (A - A^\circ)_v \quad (6-66)$$

$$S - S^\circ = \int_{\infty}^V \left[\left(\frac{\partial P}{\partial T} \right)_v - \frac{R}{V} \right] dV + R \left(\ln \frac{V}{V^\circ} \right) \quad (6-67)$$

$$H - H^\circ = (A - A^\circ) + T(S - S^\circ) + RT(Z - 1) \quad (6-68)$$

Evaluation of departure functions

Redlich-Kwong equation

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2}$$

$$A - A^\circ = -RT \left(\ln \frac{V - b}{V} \right) - \frac{a}{b} \left(\ln \frac{V + b}{V} \right) - RT \left(\ln \frac{V}{V^\circ} \right) \quad (6-69)$$

$$S - S^\circ = R \left(\ln \frac{V - b}{V} \right) - \frac{a}{2bT} \left(\ln \frac{V + b}{V} \right) + R \left(\ln \frac{V}{V^\circ} \right) \quad (6-70)$$

Soave and Peng-Robinson equations

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2}$$

The departure function for A depends on V^0 . $A - A^0$ does not vanish even for an ideal gas unless V^0 is chosen to equal V . Other departure functions are obtained from equation (6-35):

$$S - S^0 = -\frac{\partial}{\partial T}(A - A^0)_v \quad (6-66)$$

$$S - S^0 = \int_{\infty}^V \left[\left(\frac{\partial P}{\partial T} \right)_v - \frac{R}{V} \right] dV + R \left(\ln \frac{V}{V^0} \right) \quad (6-67)$$

$$H - H^0 = (A - A^0) + T(S - S^0) + RT(Z - 1) \quad (6-68)$$

Evaluation of departure functions

Redlich-Kwong equation

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2}$$

$$A - A^0 = -RT \left(\ln \frac{V - b}{V} \right) - \frac{a}{b} \left(\ln \frac{V + b}{V} \right) - RT \left(\ln \frac{V}{V^0} \right) \quad (6-69)$$

$$S - S^0 = R \left(\ln \frac{V - b}{V} \right) - \frac{a}{2bT} \left(\ln \frac{V + b}{V} \right) + R \left(\ln \frac{V}{V^0} \right) \quad (6-70)$$

Soave and Peng-Robinson equations

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2}$$

$$A - A^o = \frac{a}{b(u^2 - 4w)^{1/2}} \left[\ln \left(\frac{2Z + B^*(u - (u^2 - 4w)^{1/2})}{2Z + B^*(u + (u^2 - 4w)^{1/2})} \right) \right] - RT \left(\ln \frac{Z - B^*}{Z} \right) - RT \left(\ln \frac{V}{V^o} \right) \quad (6-71)$$

$$S - S^o = R \left(\ln \frac{Z - B^*}{Z} \right) + R \left(\ln \frac{V}{V^o} \right) - \frac{1}{b(u^2 - 4w)^{1/2}} \left(\frac{\partial a}{\partial T} \right) \ln \left(\frac{2Z + B^*(u - (u^2 - 4w)^{1/2})}{2Z + B^*(u + (u^2 - 4w)^{1/2})} \right) \quad (6-72)$$

where

$$\frac{\partial a}{\partial T} = -\frac{R}{2} \left(\frac{\Omega_a}{T} \right)^{1/2} \sum_i \sum_j y_i y_j (1 - k_{ij}) \left[f w_i \left(\frac{a_i T c_i}{P c_j} \right)^{1/2} + f w_i \left(\frac{a_j T c_i}{P c_i} \right)^{1/2} \right] \quad (6-73)$$

For Soave equation

$$f w_i = 0.4800 + 1.5740 w_i - 0.1760 w_i^2$$

$$\Omega_a = 0.42748$$

For Peng-Robinson equation

$$f w_i = 0.37464 + 1.54226 w_i - 0.26992 w_i^2$$

$$\Omega_a = 0.45724$$

The departure functions of $H-H^o$ does not depend upon the value of the reference state pressure P^o . In contrast $S-S^o$ does depend upon P^o . Either of two reference state is chosen. First, P^o is set equal to a unit pressure, for instance, 1 bar if that is the pressure unit chosen. Then $V^o=RT$ but it is essential to express R in the same units of pressure. In the second reference state, $P^o=P$, the system pressure. Then $V/V^o=Z$, the compressibility factor. In this work, the second reference is chosen because it can be compared with other program.

6.5 ESTIMATION OF VAPOR PRESSURE AND HEAT OF VAPORIZATION

6.5.1 Vapor pressure

Theory and corresponding states correlations

When the vapor phase of pure fluid is in equilibrium with the liquid phase, the equality of chemical potential, temperature, and pressure in both phase leads to the Clausius-Clapeyron equation which is expressed as follows:

$$\frac{dP_{vp}}{dT} = \frac{\Delta H_v}{T\Delta V_v} = \frac{\Delta H_v}{(RT^2 / P_{vp})\Delta Z_v} \quad (6-74)$$

$$\frac{d \ln P_{vp}}{d(1/T)} = - \frac{\Delta H_v}{R\Delta Z_v} \quad (6-75)$$

In equation (6-74), (6-75), ΔH_v and ΔZ_v refer to difference in the enthalpy and compressibility factor of saturated vapor and saturated liquid. Vapor pressure estimation and correlation equations can be derived from an integration of equation (6-75). An assumption for integration is constant $\Delta H_v / R\Delta Z_v$ and isothermal condition. The integration of equation (6-75) provides

$$\ln P_{vp} = A - \frac{B}{T} \quad (6-76)$$

where $B = \Delta H_v / R\Delta Z_v$

A, B = Constants from reference data

Equation (6-76) is sometimes called the Clapeyron equations. It is a fairly good equation for approximating vapor pressure over small temperature intervals but near the critical point, because both ΔH_v and ΔZ_v are weak function of temperature and decrease with rising temperature.

Antoine vapor pressure correlation

Antoine proposed a simple modification of equation (6-76) which has been widely used over limited ranges of temperature.

$$\ln P_{vp} = A - \frac{B}{T+C} \quad (6-77)$$

When $C=0$ equation (6-77) becomes to the Clapeyron equation. A, B, C are constants of Antoine equation which derived from experimental data. P_{vp} is a vapor pressure in bars and T is a temperature in kelvin. The applicable temperature range for Antoine equation is not large and in most instances corresponds to a pressure range of about 0.01 to 2 bar. The Antoine equation should not be used outside the stated temperature limits. Extrapolation beyond these limits may lead to absurd results.

Wagner vapor pressure correlation

Wagner proposed an equation to predict vapor pressure over wide range of temperature in the form of

$$\ln\left(\frac{P_{vp}}{P_c}\right) = \frac{a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6}{Tr} \quad (6-78)$$

where $\tau = 1 - Tr$

$$Tr = \frac{T}{T_c}$$

A, B, C are constants of Wagner equation which are derived from experimental data. The Wagner equation can be used at condition of a reduced temperature of 0.5 up to critical point. Extrapolations outside these range may lead to unacceptable.

6.5.2 Heat of vaporization

Estimation heat of vaporization (ΔH_v) from the law of corresponding states.

From Clausius-Clapeyron equation (equation 6-74), in reduced form, becomes

$$d \ln P_v p_r = \frac{-\Delta H_v}{RT_c \Delta Z_v} d \frac{1}{T_r} \quad (6-79)$$

The reduced enthalpy of vaporization $\frac{-\Delta H_v}{RT_c}$ is a function of $\frac{d \ln P_v p_r}{d(1/T_r)}$. Both these parameters are assumed to be functions of T_r or $P_v p_r$.

Pitzer acentric factor correlation

Pitzer et al. have shown that ΔH_v can be related to temperature (T), reduced temperature (T_r) and acentric factor (ω). For a close approximation, an analytical representation of this correlation for $0.6 < T_r < 1.0$ is

$$\frac{\Delta H_v}{RT_c} = 7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456} \quad (6-80)$$

Heat of vaporization at normal boiling point ($\Delta H_{v,b}$)

$$\Delta H_{v,b} = RT_c \Delta Z_{v,b} \left(T_{b,r} \frac{\ln(P_c / 1.01325)}{1 - T_{b,r}} \right) \quad (6-81)$$

Equation (6-81) has been widely employed to make estimation of $\Delta H_{v,b}$. This form has been called Giacalone equation.

Riedel method

Riedel modified equation (6-81) is proposed as follows,

$$\Delta H_{v,b} = 1.093RT_c \left[Tb_r \frac{\ln Pc - 1.013}{0.930 - Tb_r} \right] \quad (6-82)$$

Chen method

Chen proposed a relation between ΔH_v , PvP_r and Tr as follows

$$\Delta H_{v,b} = RT_c Tb_r \frac{3.978Tb_r - 3.958 + 1.555 \ln Pc}{1.07 - Tb_r} \quad (6-83)$$

Vetere method

Vetere proposed a relation similar to Chen as follow

$$\Delta H_{v,b} = RT_c Tb_r \frac{0.4343 \ln Pc - 0.69431 + 0.89584 Tb_r}{0.37691 - 0.37306 Tb_r + 0.15075 Pc^{-1} Tb_r^{-2}} \quad (6-84)$$

Variation of heat of vaporization with temperature

The latent heat of vaporization decrease steadily with temperature and is zero at the critical point. A widely used correlation between ΔH_v and T is the Watson's correlation

$$\Delta H_{v2} = \Delta H_{v1} \left(\frac{1 - Tr_2}{1 - Tr_1} \right)^{0.38} \quad (6-84)$$

When heat of vaporization is predicted by heat of vaporization at normal boiling point, ΔH_{v1} in equation (6-84) is replaced by $\Delta H_{v,b}$ and Tr_1 is reduced temperature at boiling point ($Tr_1 = Tb/Tc$). ΔH_{v2} is heat of vaporization at reduced temperature Tr_2 ($Tr_2 = T2/Tc$).

6.6 ESTIMATION OF LIQUID VISCOSITY

Effect of temperature on liquid viscosity

The viscosities of liquids decrease with increasing temperature either under isobaric conditions or as saturated liquids. Van Velzen et al., Yaws et al. and Duhne have published constants to allow an estimation of liquid viscosities for most liquids whose experimental data exist. Correlation of experimental liquid viscosity data are shown below this paragraph. The correlation for estimate liquid viscosity have three equations as follows:

$$\text{Equation 1:} \quad \eta = AT^B$$

$$\text{Equation 2:} \quad \ln \eta = A + B/T$$

$$\text{Equation 3:} \quad \ln \eta = A + B/T + CT + DT^2$$

η = Liquid viscosity, centipoises (cp).

T = Temperature, kelvins (K).

A, B, C, D = Constants to calculate liquid viscosity.